Handbook of Food Process Modeling *and* Statistical Quality Control

with Extensive MATLAB® Applications

SECOND EDITION

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Mustafa Özilgen

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Preface

It has been more than a decade since the first edition of this book appeared on shelves. Paperback, hardbound, and e-book versions of the first edition were available in the market. More than 130 Internet booksellers included the first book on their lists; I was more than happy with the welcome of the scientific community. Students who used the first edition in their classes are now directors of major food establishments and, I am proud of them all.

The second edition developed by way of an opportunity that presented itself. I taught classes at the Massey University in New Zealand; we established our own company in Ankara, Turkey. I chaired the Chemical Engineering Department, Yeditepe University in Istanbul, where the most notable contributors were starting a PhD program and a food engineering department. Teaching bioengineering classes to the genetic engineering students was one of my most exciting experiences.

Turkey has the 18th largest economy in the world and the food industry makes up a big part of it. There are about 45 food engineering departments in Turkish Universities. I was honored to be among the founders of the first and 39th departments. The 39th department was the first food engineering department in a foundation (private) Turkish university.

I appreciate the contributions of Seda Genc, Fatih Uzun, and all of my undergraduate and graduate students, who helped to write the MATLAB® codes through their projects or homework. I appreciate the help provided by Dr. Esra Sorguven of the Mechanical Engineering Department of Yeditepe University, in the solutions of the examples involving the partial differential equation toolbox. I also appreciate the author's license from MATLAB® (MathWorks Book Program, A#: 1-577025751).

The second edition of the book is substantially different from the first edition in the sense that

i. The title of the book is modified following the recommendations of experts from academia and the industry. It is intended to present the book as a compendium of applications within its scope.
ii. The new edition covers extensive MATLAB applications. The model equations are solved with MATLAB and the resulting figures are generated by the code. The models are compared mostly with real data from the literature. Some errors occurred while reading the data; therefore, the model parameters sometimes had different values than those of the references.
iii. Tabular values and plots of mathematical functions are produced through MATLAB codes.
iv. All of the MATLAB codes are given on the CD accompanying the book. A summary of the important features and functions of the MATLAB codes used in the book are given in Table 1.1. The readers may refer to this table to locate the functions or syntax they need. They may copy lines from the examples and write their own code with them. I wrote my own codes by following this procedure. I would recommend achieving each task in the code in a stepwise manner and then going on to the next task. Each task is usually defined in the examples with phrases such as

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% enter the data, % plot the data, % modeling, % plot the model, etc. I tried to maintain this order in the codes when possible.

v. A few food processing methods (i.e., *pulsed electric field* and *high pressure processing*) gained importance after the first edition. Some examples are included to cover the development.

vi. Feedback to the first edition indicated that simple models were welcomed, while the sophisticated ones were avoided. The *80%–20% rule; that is*, *obtaining 80% of the total possible benefits within the 20% of the highest difficulty level of the models* continued to be the motto. Examples to comprehensive and easy mathematical models with sound theoretical background and a larger scope of application are given priority. Using MATLAB helped to achieve this goal.

vii. It should be noted that this book was authored for educational purposes only. The models were compared with real experimental data to make them as realistic as possible. Some commercial applications, design, or research may need more accuracy, which is beyond the scope of this book.

viii. The statistical toolbox of MATLAB was used extensively in Chapter 5. In some examples, relatively longer solutions were preferred to the shortcut alternatives because of their educational value. Sampling methods with new acceptance were published during the last decade. They are included in the book, while the older practices were removed.

ix. I have gone through the files of classes that I have been teaching over the years and added selected exam questions to the end of each chapter. The comprehension questions were designed to test the students' understanding of the topics. Correct answers to these questions are prerequisite for understanding the rest of the material.

I will be more than happy to hear recommendations. I will evaluate them carefully to make future editions of the book more useful.

Summary

The *Handbook of Food Process Modeling and Statistical Quality Control* is written along the guidelines of the "80%–20% rule," which means obtaining 80% of the total possible benefits within the 20% of the highest attainable modeling difficulty level. Fundamental techniques of mathematical modeling of processes essential to the food industry are explained in this text. Instead of concentrating on detailed theoretical analysis and mathematical derivations, important mathematical prerequisites are presented in summary tables. Readers' attention is focused on understanding modeling techniques, rather than the finer mathematical points. Examples of comprehensive and easy mathematical models with sound theoretical background and a larger scope of application are given priority. MATLAB has been used extensively to achieve this goal.

Topics covered include modeling of transport phenomena, kinetics, and unit operations involved in food processing and preservation. Statistical process analysis and quality control as applied to the food industry are also discussed. The book's main feature is the large

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number of fully worked examples presented throughout. Included are examples from almost every conceivable food process, most of which are based on real data provided from numerous references. Each example is followed by a clear, step-by-step worked solution, and the associated MATLAB code.

Tabular values and plots of mathematical functions are also produced with MATLAB. All of the codes are given in the CD accompanying the book. A summary of the MATLAB functions and syntax used in the book are given in a table, so the readers will be able to locate them easily. Most of the codes are written in the same sequential order and the readers are informed about them in the code with remarks like *% enter the data*, *% plot the data*, *% modeling*, *% plot the model*, and so on. There are also in-depth explanations in the codes to help readers understand them easily. Comprehension questions were added to each chapter to test the students' understanding of the topics.

This book contains 163 fully solved examples, 217 MATLAB codes (provided in full detail), 273 figures (most of which are printouts of the codes), and 52 tables.

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Author

Mustafa Özilgen is a chemical engineer. He has a BS and MS from the Middle East Technical University in Turkey and a PhD from the University of California–Davis. He is author or coauthor of numerous refereed publications and the author of two books. The first edition of this book was published with the title *Food Process Modeling and Control, Chemical Engineering Applications* (Gordon & Breach; Amsterdam, 1998). A recent book authored by Professor Özilgen is *Information Build-up During the Progression of Industrialization* (in Turkish, Arkadas Publishing Co., Turkey, 2009).

Mustafa Özilgen has taught numerous classes at the University of California–Davis, Middle East Technical University, Ankara, Turkey, and the Massey University in New Zealand. He was a member of the organizing committee and co-editor of the proceedings of CHEMECA 1998, the annual Australian and New Zealander Chemical Engineering conference. He also worked for the Marmara Research Center of Turkish Scientific and Technical Research Center, Gebze. He was a recipient of one of the major research awards offered by the Turkish Scientific and Technical Research Center in 1993. He is currently working as a professor and chairperson of the Food Engineering Department at Yeditepe University, Istanbul, Turkey.

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1

Introduction to Process Modeling

1.1 The Property Balance

Most of the mathematical models, which appear in the engineering literature, are based on the balance of one or more conserved properties. The property balance starts after choosing an abstract or conceptual system. The universe, which remains outside of the system, is referred to as the surroundings. The property balance around the system described in Figure 1.1 may be stated as

$$\left\{\begin{array}{l}\text{input}\\ \text{rate of the}\\ \text{property}\\ \text{to the}\\ \text{system}\end{array}\right\} - \left\{\begin{array}{l}\text{output}\\ \text{rate of the}\\ \text{property}\\ \text{from the}\\ \text{system}\end{array}\right\} + \left\{\begin{array}{l}\text{generation}\\ \text{rate of the}\\ \text{property}\\ \text{within the}\\ \text{system}\end{array}\right\} - \left\{\begin{array}{l}\text{consumption}\\ \text{rate of the}\\ \text{property}\\ \text{within the}\\ \text{system}\end{array}\right\} = \left\{\begin{array}{l}\text{accumulation}\\ \text{rate of the}\\ \text{property}\\ \text{within the}\\ \text{system}\end{array}\right\}$$

or

$$\psi^{\bullet}_{in} - \psi^{\bullet}_{out} + \psi^{\bullet}_{gen} - \psi^{\bullet}_{con} = \psi^{\bullet}_{acc}, \tag{1.1}$$

where:

$\psi^{\bullet}_{in}$ = rate at which an extensive property enters the system
$\psi^{\bullet}_{out}$ = rate at which an extensive property leaves the system
$\psi^{\bullet}_{gen}$ = rate at which an extensive property generated in the system
$\psi^{\bullet}_{con}$ = rate at which an extensive property consumed in the system
$\psi^{\bullet}_{acc}$ = rate at which an extensive property accumulates in the system.

In this formulation the *input* includes all extensive property that is added to the system across the system boundary and the output describes the amount of extensive property that leaves the system across the system boundary. Properties, like heat, may be transferred to or from the system without any material crossing the system boundary. The generation and the consumption terms describe the quantity of an extensive property that is created or destroyed in the system, respectively.

In Equation 1.1 the "*conserved property*" Ψ may be total mass, an atom, a molecule, linear or angular momentum, total energy, mechanical energy, or charge. Property balances

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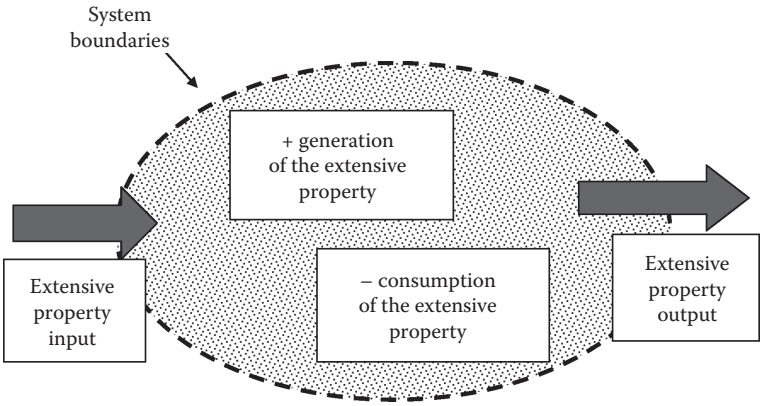


FIGURE 1.1
Description of the system for the application of the conservation laws.

were performed for many centuries without recognizing their common nature. Newton's second law of motion, developed in 1687 to relate the net force on an object to its mass and acceleration, is indeed an application of the conservation law to linear momentum. It was one of the earliest examples to the conservation laws. The first law of thermodynamics is actually an energy balance, engineering Bernoulli equation that is used to calculate energy dissipation by a liquid while flowing through a pipe and Kirchhoff's voltage law, which was formulated in 1845, are indeed different expressions for the first law of thermodynamics. Kirchhoff's current law, which states that the total charge flowing into a node must equal the total charge flowing out of the node, is developed on the concept of conservation of charge, and based on the same concept with the mass balance.

We will use MATLAB® extensively to solve the equations resulting from the property balances. The word MATLAB stands for *matrix laboratory*. The "Command Window" consists of a sequence of executable statements. It calls the built-in functions or the M-files and executes them (*MATLAB, Getting Started Guide* 2008). Table 1.1 gives a list of the selected examples where you may see the application of some skills, syntax, and functions in a working code. You may refer to MATLAB help for further information.

MATLAB skills, syntax, and functions described in Table 1.1 are also used in numerous other examples, which are not listed here. Tables 5.1, 5.2 and 5.3 provide more information about statistical MATLAB tools. Tables 2.10 through 2.17 provide more information about MATLAB functions related with Bessel functions and error functions. Table 2.20 describes how to obtain the Laplace transforms by using the symbolic toolbox. In order to get additional information about any topic covered in Table 1.1 (e.g., *plotyy*) type *lookfor plotyy* or *help plotyy* or doc plotyy and enter while you are in the command window. You may also search for *MATLAB plotyy* on the Internet; in addition to the large number of documents provided by MATLAB and its users, you may join the forums where users share information.

You may experience problems with the apostrophe '. Although most of the computers support the ASCII code apostrophes, there are some computers that do not. If you have one of these computers, the apostrophe may appear on the screen, but the software may not recognize it. If your code should not work because of this reason, get a working apostrophe from a running example and replace the nonworking ones by the copy and paste method.

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TABLE 1.1

MATLAB® Skills, Syntax, and Functions Guide

Skills, Syntax, and Functions	Explanation and Examples to Refer
1. Plotting skills, syntax, and functions guide	
plot	plot(B(1:4,3),D(1:4),'--*') % plots first to fourth row, third column elements of matrix B versus, from first to fourth elements of D vector. Notation '--*' makes a dashed line with legend * at the data or computation points. Example 1.1 plot(tData1,a,'x',tData2,b,'o'); hold on, % plots a versus tData1 with legend 'x' and b versus tData2with legend ,'o'. Remark hold on makes the plot wait for the execution of the next lines, so they are plotted together. Example 1.4 f = ['ro', 'bd', 'gv', 'ks', 'm*']; % defines the color and the legends (ro is red o, bd is blue diamond, gv is green triangle, ks is black square, m* is magenta *) hold on; plot(time, C, f((2*(6-i)-1):(2*(6-i)))); % makes the plot by using the colors and the legends described by f. Example 3.11
plotyy	[AX,H1,H2] = plotyy(time, T(2,:), time, F(2,:)); hold on % prepare a plot with y axis on both left- and right-hand sides. Example 4.10
semilogy semilogx	semilogy(tau,Lethalithy,'--') % makes a semi log plot with y axis in log scale, x axis in linear scale, Example 4.6. Other option semilogx. Figure 3.5.
loglog	loglog(tData2,fData2, 'x'); hold on % makes a plot with both x and y axis are in log scale. Example 5.51
legend	legend('T fluid','T particle surface','T particle center','Location','West') % inserts a legend to the graph 'Location','West' describes the location where you want to place the legend. Location options: East, West, South, North, SouthEast, SouthWest, NorthEast, NorthWest, Best. Example 4.10 legend(H2,'F particle surface','F particle center','Location','East') % insert a legend to the figure for the parameters in association with the right-hand side y axis. Example 4.10
figure	% if you should type figure in your code it will start a new figure. figure Example 2.1
xlim, ylim	ylim([0 5]); % limit of the range of the y axis xlim([0 1000]); % limit of the range of the x axis Example 4.11 ylim(AX(1), [80 140]) % limit of the range of the left-hand side y axis in plotyy ylim(AX(2), [0 40]) % limit of the range of the right-hand side y axis in plotyy Example 4.10 % REMARKS: Among other uses, xlim and ylim are needed when you plot a few figures on top of each other (do not forget to use hold on, after each plot). If you should not use xlim or ylim, each figure may set different limits and you may not be able to compare the model with the data.
xlabel ylabel	xlabel('Time (s)') % label for x axis ylabel('Temperature \circ C') % label for y axis set(get(AX(2),'ylabel'), 'string', 'F (min)') % label for right-hand side y axis in plotyy Example 4.10 zlabel('cratio') % z axis in a 3-D plot Example 3.30

(*Continued*)

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TABLE 1.1 (CONTINUED)

MATLAB® Skills, Syntax, and Functions Guide

Skills, Syntax, and Functions	Explanation and Examples to Refer
line style	plot(t,log(c(:,1)),'-',t,log(c(:,2)),':'); hold on % line style is described with '-' (solid line) and ':' (dashed line made of point). Other options are '--' (dashed solid line) and '.-' (dashed line with point and dash characters). Example 3.1. set(H1,'LineStyle','- -') % line style of a property, which is related with the left-hand side y axis in plotyy. set(H2,'LineStyle','-') % line style of a property, which is related with the left-hand side y axis in plotyy. Example 4.10
legend style	plot(tData,log(cData1),'s',tData,log(cData2),'o'); hold on % 'v'legends: 's' square, 'o' o, other options are 'v' , '^', ' < ' , ' > ' triangles, ,'d' diamond, 'p' pentagene, 'h' hexagone, 'x', ' + ' and '*'. Example 3.1
title	title('bar chart of the log cell areas') % inserts a title to a plot. Example 5.2
surface	surf(c11,c21,r21total); hold on % plots a surface in a 3-D plot. Example 3.15
colormap	colormap gray % sets the color of the surface, other options for gray are jet, HSV, hot, cool, spring, summer, autumn, winter, bone, copper pink, lines. Example 3.15
grid	% inserts grids to a figure. Example 4.41
meshgrid	[e,t] = meshgrid(e,t); % [X,Y] = meshgrid(x,y) transforms the x and y vectors into X and Y arrays, which can be used to evaluate functions of two variables and three-dimensional mesh/surface plots. Example 3.30
set(line…)	set(line([0 1],[0 1]),'Color',[0 0 0]); % draws a line between points defined by ([0 1],[0 1]). Color of the line is defined by 'Color',[0 0 0] (black). Other alternatives are [1 1 0] yellow, [1 0 1] magenta, [0 1 1] cyan, [1 0 0] red, [0 1 0] green, [0 0 1] blue, [1 1 1] white. Example 4.41
2. Printing skills, syntax, and functions guide	
fprintf	% fprintf writes formated data. fprintf('Waxy rice starch contains 100 %% Amylopectin and 0 %% Amylose') % prints the characters between ' '. fprintf('\nTotal bond energy of the waxy rice starch is %.2g kJ/mol',Energy) % prints the characters between ' ' and value of variable Energy to the location marked as %.2g (number before . describes the field length, number after . describes the precision alternatives to g are c character, f fixed point, e exponential notation). Example 1.1 % tabulate the data: fprintf('\nAge and fraction of the liquid pockets\n\n') fprintf(' t(s) Fraction\n') fprintf('---------- ----------\n') for i = 1:11 fprintf('%-15g %7g\n',a(i,1), a(i,4)) end % \n means skipping a line the number of \'s defines the number of the lines to be skipped. Example 3.11
display	% display(X) prints the value of a variable or expression, X. display(z1); Example 5.5

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TABLE 1.1 (CONTINUED)

MATLAB® Skills, Syntax, and Functions Guide

Skills, Syntax, and Functions	Explanation and Examples to Refer
3. Line and curve fitting skills, syntax, and functions guide	
polyfit	c = polyfit(tData,xDataFreeMoisture,N) % fits a Nth order polynomial to the data. Example 4.12
nlinfit	beta = nlinfit(x,y,fun,beta0) % returns a coefficients vector beta for nonlinear regression, y is the dependent variables vector, x is dependent variables vector, beta0 is the vector of the initial estimates of beta. Notice: beta may depend on beta0. Examples 2.7, 4.7
lsline	% after plotting a linear data if you should write lsline least squares line will be plotted. Example 1.3
polyval	xModel = polyval(c,tModel); % returns the value of a polynomial of degree n evaluated at tModel. The input argument c is a vector of length $n + 1$ whose elements are the coefficients in descending powers of the polynomial to be evaluated. $xModel = c(1)tModel^n + c(2)tModel^{n-1} + \ldots + c(n + 1)$ Example 4.12
4. Mathematical functions and operations skills, syntax, and functions guide	
sum	sum_xi = sum(xi); % sum all xi values Example 1.2
mean	DeffAvg50 = mean(Deff50); % mean of Deff50 values Example 4.34
factorial	Pa2 = (factorial(n)/(factorial(x)*factorial(n-x)))*(p^x)*(1-p)^(n-x); % factorial(n) is the product of all the integers from 1 to n, i.e. prod(1:n). The answer is accurate for n < = 21. Example 5.35
square root	Se = sqrt(mean(d2)); % square root of mean of d2 values Example 2.15
range	% y = range(x) returns the range of the values in x. Example 5.16
error function	c(j,k) = c1 + (c0-c1)*erf(z) ; % erf(z) error function of z. Example 2.13
complementary error function	error_func(i) = erfc(L/(2*sqrt(a*times(i)))); % complementary error function of (L/(2*sqrt(a*times(i))). Example 4.5
Bessel function	s(n) = exp(-(alpha* time(j)/(Radius^2))*(Bn(n)^2))*besselj(0,z)/ ((Bn(n)^2)*besselj(1,Bn(n))); % besselj(0,z) zero order Bessel function evaluated at z, besselj(1,Bn(n)) first order Bessel function evaluated at Bn(n). Example 2.10
complementary Bessel function	K14_besselfunction(i) = besselk(0.25,(R^2)/(8*a*times(i))); % K1/4 is the modified Bessel function of the second kind of order ¼. Example 4.5
integral	NTU = quad(@calculateNTU,yB,yA) % quad computes the integral described by function 'calculate' between the limits yB and yA with fourth order Runge-Kutta method. Example 4.39
fminsearch	Lmin = fminsearch(y,5); % starts at 5 and attempts to find a minimizer Lmin of y. Example 5.54
ceil round floor fix	B = ceil(A); % rounds the number A toward plus infinity (the other alternatives are B = round(A), which rounds A to the nearest integer or B = floor(A), which rounds A to the nearest integers less than or equal to A, B = fix(A) rounds the elements of A toward zero). Example 5.54

(*Continued*)

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TABLE 1.1 (CONTINUED)

MATLAB® Skills, Syntax, and Functions Guide

Skills, Syntax, and Functions	Explanation and Examples to Refer
5. Statistical functions skills, syntax, and functions guide	
correlation coefficient	rmatrix = corrcoef(lnXdata1,tData1); % find the correlation coefficient matrix of the data given in vectors lnXdata and tData1 r = rmatrix(1,2); % convert the correlation coefficient matrix into a single number. Example 2.15

standard error	% determine the standard error
	for j = 1:1:size(tData1);
	lnXmodel = lnX0-K*tData1;
	d1 = (lnXdata1-lnXmodel);
	d2 = d1*d1';
	end;
	Se = sqrt(mean(d2));
	Example 2.15

hypothesis testing concerning one mean	H = ztest(xBarExp,mu,sigma) % where xBar is the sample mean and sigma is the population standard deviation. The outcome H = 0 indicates that the hypothesis cannot be rejected, the outcome H = 1 indicates that the null hypothesis can be rejected. Example 5.14
hypothesis testing concerning two means when the population standard deviations are known	% refer to Example 5.15
binocdf	% y = binocdf(x,n,p) returns the binomial cumulative distribution function with parameters n and p at the values in x. ATI2 = n + (N-n)*(1-binocdf(c,n,p)); Example 5.54
normcdf	% p = normcdf(x,mu,sigma) returns the cumulative distribution function of the normal distribution with mean mu and standard deviation sigma, evaluated at the values in x. fModel2 = normcdf(log(t),lnMuTemp2,sigma); Example 5.51
anova1	% (anova one means one way of analysis of variance) p = 100*anova1(x,[ ], 'off'); % p = probability of having the rows of matrix x be the same. Example 5.25
anova2	% [p,table] = anova2(...) returns two items where p is a vector of p-values for testing column, row, and if possible interaction effects, table is a cell array containing the contents of the anova table. [p Table] = anova2(x,1, 'off') Example 5.26
vartest2	H = vartest2(X,Y) performs an F test of the hypothesis that two independent samples, in the vectors X and Y, come from normal distributions with the same variance H = vartest2(Vjuice,Vbeverage,alpha) Example 5.24
normspec	normspec(specs,mu,sigma,*region*) % shades the region either 'inside' or 'outside' the specification limits. Figure 5.2.
6. Solution of algebraic, ordinary, and partial differential equations	
division of matrices, solution of set of linear algebraic equations	H = D./MM; Example 1.1
fzero	xe(i) = fzero('EthanolEquilibrium',0.5); % finds the value of the independent variable xe, which makes the value of the function 'EthanolEquilibrium',zero. around xe = 0.5. Example 4.41

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TABLE 1.1 (CONTINUED)

MATLAB® Skills, Syntax, and Functions Guide

Skills, Syntax, and Functions	Explanation and Examples to Refer
ode45	% ode45 solves the ordinary differential equations. [t,c] = ode45(@ascorbicacid1,tspan,c0); solves the ordinary differential equation described in the m-function 'ascorbicacid1' tspan is the time span (time from beginning to end, you may also enter a time matrix) of the solution, c0 is the initial condition. The solution returns t and c values, which are given on the left-hand side of the syntax. Example 3.1. % we may also use ode45 to solve a set of simultaneous ordinary differential equations. Example 3.4
pdepe	sol = pdepe(m,@pdex1pde,@pdex1ic,@pdex1bc,r,t); % solves initial-boundary value problem defined in m-function 'pdex1pde' with the initial condition defined in function 'pdex1ic' with the boundary conditions defined in function 'pdex1bc'. m = 2 for the given problem, r = computation points along the radius, t = time matrix. Example 4.20
pdetoolbox	% The Partial Differential Equation Toolbox contains tools for solution of partial differential equations in 2-D space and time. A set of command-line functions and a graphical user interface let you preprocess, solve, and postprocess generic 2-D PDEs. Example 4.16

Example 1.1: Application of the First Law of Thermodynamics to Nutrition

Equation E.1.1.1 may be used to describe the conservation of energy around the system boundaries (Figure E.1.1.1) after substituting

$$\psi^{\bullet}_{m} = m^{\bullet}_{in}(u + e_p + k + P\nu)_{in} + Q, \tag{E.1.1.1}$$

$$\psi^{\bullet}_{out} = m^{\bullet}_{out}(u + e_p + k + P\nu)_{out}, \tag{E.1.1.2}$$

and

$$\psi^{\bullet}_{acc} = \frac{d}{dt}\left[m_{syst}(u + e_p + k)_{syst}\right], \tag{E.1.1.3}$$

where $m^{\bullet}$ is the mass flow rate, u is the *internal energy* per unit mass, e_p is the *potential energy* per unit mass, and k is the kinetic energy per unit mass. The term Q represents the heat entering into the system without being associated with the incoming mass.

Internal energy is associated with the energy stored in the atomic and the molecular structure. Potential energy is associated with the position of an object with respect to a reference position. The term $P\nu$ is the pressure–volume work describing the work done by the molecules behind a specific molecule that pushes it into or out of the system, where P is the pressure and ν is the volume per unit mass of the fluid. Heat transfer with conduction, convection, or radiation may be achieved independent of the mass influx or out flux from the system. Therefore the term Q appears as a separate entity in Equation E.1.1.1. If the system consumes energy by performing work, the term $\psi^{\bullet}_{con}$ of the general property balance equation E.1.1.1 may be described as

$$\psi^{\bullet}_{con} = W. \tag{E.1.1.4}$$

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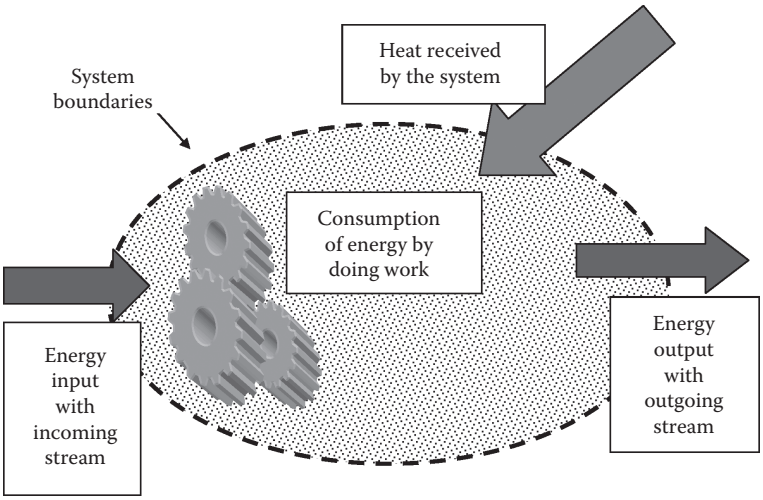


FIGURE E.1.1.1
Description of the system for conservation of energy.

After substituting Equations E.1.1.1 through E.1.1.4 in Equation 1.1 we will obtain the *first law of thermodynamics* as

$$\left[m^{\bullet}(u+e_p+k+Pv)\right]_{\text{in}}-\left[m^{\bullet}(u+e_p+k+Pv)\right]_{\text{out}}+Q-W=\frac{d}{dt}\left[m_{\text{acc}}(u+e_p+k)_{\text{acc}}\right] \quad \text{(E.1.1.5)}$$

Organisms store internal energy, u, within their structures. High energy bonds of the fat and starch molecules are the most common energy reserves of the animal and the plant cells, respectively. These bonds are broken to release their energy to achieve the biological processes. Energy and the number of the interatomic bonds of some common fatty acids are given in Table E.1.1.

a. Starch is produced as granules in the plants cells. All granules consist of amylose and amylopectin in percentages that change with the source. About 1000–4000 glucose units are linked with α-(1→4) bonds to make amylose. There are about 2000–20,000 α-(1→4) linked glucose units in amylopectin. There is also one residue in about every 20 glucose units linked with α-(1→6) bonds and form the branch points in amylopectin. Amylose is made up of between 1000 and 4400 and amylopectin is formed of 2000–200,000 glucose units. MATLAB® code E.1.1.a computes the total bond energy of starch molecules originating from waxy rice (code 1), rice (code 2), cassava (code 3), corn (code 4), wheat (code 5), and sweet potato (code 6). In order to run this m-function, after saving it in your computer, go to the command window, type starch, enter it. You will be asked to enter the code of the starch of interest. Enter it. The total bond energy of the specified starch with 10,000 glucose monomers will appear on the screen.
b. Calculate the total bond energy of each fatty acid.
   We may describe the total bond energy of the fatty acids in matrix form as

$$|D|=|B||C|^{T}. \quad \text{(E.1.1.6)}$$

   Where corresponding elements of $|B|$ and $|C|$ give the number and the energy of the bonds in one mole of a fatty acid. Matrix $|D|$ gives the total bond energy of each fatty acid stated in $|A|$. MATLAB® code E.1.1.b is employed to print out the total bond energy of the fatty acids. The total bond energy of the fatty acids is also plotted as a function of their C–H bonds. The bond energy of 17 C containing fatty acids are also plotted as a number of the C = C bonds in their structure.
c. When a 70 kg person runs at a speed of 10 km/hour, he burns 50 kJ in a minute. Determine how many grams of each fatty acid he consumes in 1 h.

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TABLE E.1.1

Molar Mass, Number of the Interatomic Bonds/Molecule, and Energy/Bond of the Glucose Units of Starch and Fatty Acids

BOND and its Energy (kJ/mol) →	**C = C (cdc) 606**	**C–C (cc) 334**	**C–H (ch) 410**	**C = O (cdo) 723**	**O–H (oh) 456**	**C–O (co) 330**
Molar mass ↓	**Number/ Molecule ↓**	**Number/ Molecule ↓**	**Number/ Molecule ↓**	**Number/ Molecule ↓**	**Number/ Molecule ↓**	**Number/ Molecule ↓**
Glucose in amylose 180 (g/mole)	0	6	5	0	2	4
Glucose in amylopectin 180 (g/mole)	0	7	7	0	4	5
Lauric acid 200 (g/mole)	0	11	23	1	1	1
Myristic acid 228 (g/mole)	0	13	27	1	1	1
Palmitic acid 257 (g/mole)	0	15	31	1	1	1
Stearic acid 285 (g/mole)	0	17	35	1	1	1
Palmitoleic acid 299 (g/mole)	1	14	29	1	1	1
Oleic acid 283 (g/mole)	1	16	33	1	1	1
Linoleic acid 281 (g/mole)	2	15	31	1	1	1
Linolenic acid 278 (g/mole)	3	14	29	1	1	1

MATLAB® CODE E.1.1.a

M-File:

```
function starch
disp({'1. Waxy Rice';'2. Rice';'3. Corn';'4. Cassava';'5. Wheat';'6.
Sweet Potato';});
EN = [410 334 330 456];
BRAMILO = [5 6 4 2];
AMILO = [7 7 5 4];
choice = input('Please enter the code of the source of the starch:
','s');
switch choice

case '1'
n = 10000/25;
Energy = n*sum(EN*BRAMILO')+ (10000-n)*sum(EN*AMILO');
fprintf('Waxy rice starch contains 100 %% Amylopectin and 0 %%
Amylose')
fprintf('\nTotal bond energy of the waxy rice starch is %.2g kJ/
mol',Energy)

case '2'
n = 8000/25;
Energy = n*sum(EN*BRAMILO') + (8000-n)*sum(EN*AMILO') +
2000*sum(EN*AMILO');
```

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```
fprintf('Rice starch contains 80 %% Amylopectin and 20 %% Amylose')
fprintf('\nTotal bond energy of the rice starch is %.2g kJ/
mol',Energy)

case '3'
n = 7200/25;
Energy = n*sum(EN*BRAMILO') + (7200-n)*sum(EN*AMILO') +
2800*sum(EN*AMILO');
fprintf('Corn starch contains 72 %% Amylopectin and 28 %% Amylose')
fprintf('\nTotal bond energy of the corn starch is %.2g kJ/
mol',Energy)

case '4'
n = 8300/25;
Energy = n*sum(EN*BRAMILO') + (8300-n)*sum(EN*AMILO') +
1700*sum(EN*AMILO');
fprintf('Cassava starch contains 83 %% Amylopectin and 17 %% Amylose')
fprintf('\nTotal bond energy of the cassava starch is %.2g kJ/
mol',Energy)

case '5'
n = 7400/25;
Energy = n*sum(EN*BRAMILO') + (7400-n)*sum(EN*AMILO') +
2600*sum(EN*AMILO');
fprintf('Wheat starch contains 74 %% Amylopectin and 26 %% Amylose')
fprintf('\nTotal bond energy of the wheat starch is %.2g kJ/
mol',Energy)

case '6'
n = 8200/25;
Energy = n*sum(EN*BRAMILO') + (8200-n)*sum(EN*AMILO') +
1800*sum(EN*AMILO');
fprintf('Sweat potato starch contains 82 %% Amylopectin and 18 %%
Amylose')
fprintf('\nTotal bond energy of the sweat potato starch is %.2g kJ/
mol',Energy)

otherwise
disp({'Unknown Starch!!! Please retry!!';})
end
```

A sample run of the code is given here:

```
'1. Waxy Rice'
    '2. Rice'
    '3. Corn'
    '4. Cassava'
    '5. Wheat'
    '6. Sweet Potato'

Please enter the code of the source of the starch: 5
Wheat starch contains 74 % Amylopectin and 26 % Amylose
Total bond energy of the wheat starch is 8.6e+007 kJ/mol
```

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MATLAB® CODE E.1.1.b

Command Window:

```
clear all
close all

% enter the fatty acid names as characters
A = char('Lauric Acid', 'Myristic Acid', 'Palmitic Acid', 'Stearic
Acid', 'Palmioletic Acid', 'Oleic Acid', 'Linoleic Acid', 'Linolenic
Acid');

% enter the number of the C=C bonds, C-C bonds, C-H bonds, C=O
bonds, O-H bonds, and C-O bonds as the rows of a matrix

B = [ 0 11 23 1 1 1; 0 13 27 1 1 1; 0 15 31 1 1 1; 0 17 35 1 1 1; 1
14 29 1 1 1; 1 16 33 1 1 1; 2 15 31 1 1 1; 3 14 29 1 1 1];

C = [606 334 410 723 456 330]; % bond energies of the C=C, C-C, C-H,
C=O, O-H and C-O bonds

% compute the molar bond energy of each fatty acid
D = B*C';

% tabulate the results:
fprintf('\nBond energy of the fatty acids\n\n')
fprintf('Fatty acid Bond energy (J/mole)\n')
for i = 1:8
fprintf('%-15s %8d\n',A(i,:), D(i))
end

plot(B(1:4,3),D(1:4),'--*') % plot the molar bond energy of a fatty
acid as a function of the number of the C-H bonds in the saturated
fatty acids ('Lauric Acid', 'Myristic Acid', 'Palmitic Acid',
'Stearic Acid')
xlabel('number of the C-H bonds in a saturated fatty acid')
ylabel('Molar bond energy (J/mol)')

j = 1;
for i = 1:8
k = B(i,1) + B(i,2);
if k == 17
E(j,1) = j-1;
E(j,2) = D(i);
j = j + 1;
end
end

figure
plot(E(1:4,1),E(1:4,2),'--*')
xlabel('number of the C=C bonds in a 17 C fatty acid')
ylabel('Molar bond energy (J/mol)')
```

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The following Table and the Figures E.1.1.2 and E.1.1.3 will appear on the screen when we run the code:

```
Bond energy of the fatty acids

Fatty acid          Bond energy   (J/mole)
Lauric Acid            14613
Myristic Acid          16921
Palmitic Acid          19229
Stearic Acid           21537
Palmioletic Acid       18681
Oleic Acid             20989
Linoleic Acid          20441
Linolenic Acid         19893
```

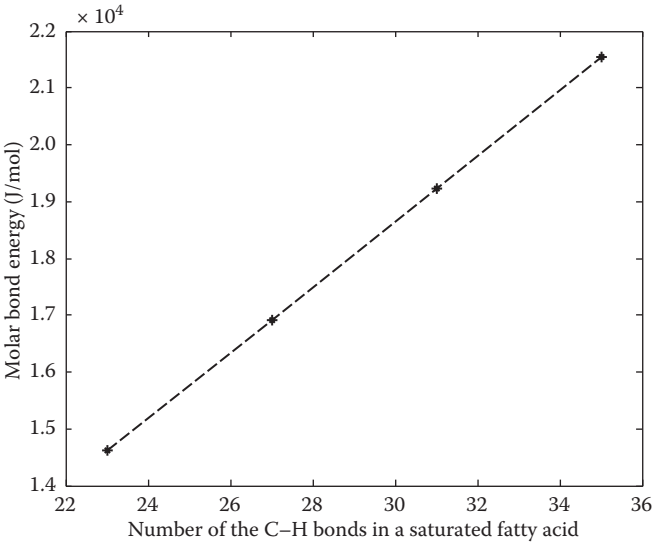


FIGURE E.1.1.2
Variation of the molar bond energy of the saturated fatty acids with a number of the C–H bonds.

There is no energy input or output or heat input, kinetic energy, or potential energy change is involved. Therefore Equation E.1.1.5 is referred to as the *first law of thermodynamics;* Equation E.1.1.5 is simplified as:

$$-W = \frac{d}{dt}\left[m_{acc}(u)_{acc}\right]. \tag{E.1.1.7}$$

Equation E.1.1.7 may be rearranged as:

$$W\Delta t = -\Delta U. \tag{E.1.1.8}$$

It is given in the problem statement that when Δt = 1h, $W\Delta t = -\Delta U$ = 50 kJ, implying that the work is done by extracting 50 kJ from the bonds of the fatty acids. MATLAB code E.1.1.c computes the fatty acid consumption requirement for producing 50 kJ of work.

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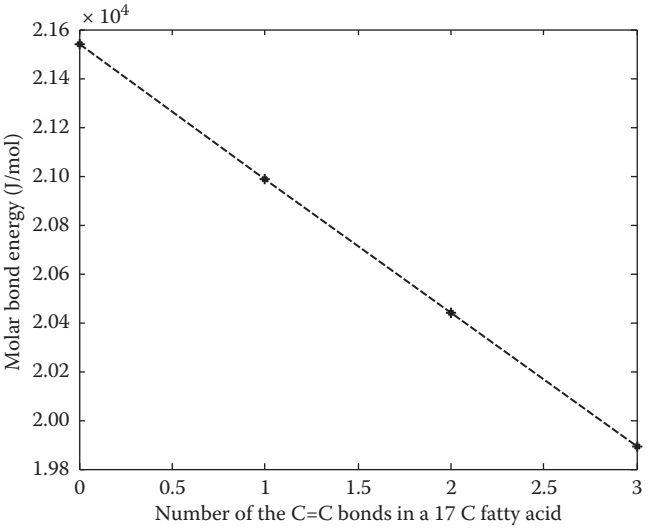


FIGURE E.1.1.3
Variation of the molar bond energy of the 17 carbon fatty acids with a number of the C = C bonds.

MATLAB® CODE E.1.1.c

Command Window:

```
clear all
close all
format short g

% enter the fatty acid names as characters
A = char('Lauric Acid', 'Myristic Acid', 'Palmitic Acid', 'Stearic
Acid', 'Palmioletic Acid', 'Oleic Acid', 'Linoleic Acid', 'Linolenic
Acid');

% enter the molar mass of the fatty acids
MM = [200 228 257 285 299 283 281 278];

% enter the molar bond energies of the fatty acids
D = [14613 16921 19229 21537 18681 20989 20441 19893];

% calculate the molar bond energy/molar mass for each fatty acid
H = D./MM;

% enter the energy requirement for one hour of running
DeltaU = 50000;

% calculate the grams of fatty acid requirement to meet DeltaU
mFattyAcd = DeltaU./MM;

% tabulate the results:
fprintf('\Fatty acid consumption in one hour\n\n')
fprintf('Fatty acid consumption (g)\n')
```

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```
for i=1:8
fprintf('%-15s %7g\n',A(i,:), mFattyAcd(i))
end
```

The following Table will appear on the screen when we run the code:

```
Fatty acid          consumption   (g)
Lauric Acid           250
Myristic Acid         219.298
Palmitic Acid         194.553
Stearic Acid          175.439
Palmioletic Acid      167.224
Oleic Acid            176.678
Linoleic Acid         177.936
Linolenic Acid        179.856
```

1.2 What Is Process Modeling?

A process transforms sets of inputs into sets of desired outputs (Oakland and Followell 1995). Within the context of this book the inputs will mostly be the ingredients and energy, the outputs will be foods, and the process units will be the equipment, which are designed to achieve the purpose. A *mathematical model* is an approximate representation of a process in mathematical terms. A mathematical model can never be an actual representation of a process, since it would be very difficult, confusing, or impossible to describe the whole system with mathematical formulations. The way that people describe real life in mathematical terms is highly subjective and depends on their previous experience and education.

In typical process inputs x_1, x_2 ... x_N may generate the outputs y_1, y_2 ... y_M (Figure 1.2). With a model, the cause-and-result relation between the major process inputs (x_1, x_2 ... x_n) and outputs (y_1, y_2 ... y_m) may be formulated in mathematical terms after simplification. Negligible inputs x_{n+1} ... x_N and outputs y_{m+1} ... y_M are not included with the model. The decision about designation of the negligible and nonnegligible inputs or outputs involves personal preferences. That is the point where modeling becomes a subjective operation, not an objective work. One of the common mistakes made by engineers inexperienced in modeling is to get lost in the complexity of the process. One of the best working guides in process modeling is the *80%–20% rule*, which means *"you get 80% of the benefit with the first 20% of the model complexity"* (Glasscock and Hale 1994). The 80%–20% rule is followed in this book. Fundamental principles of mathematical modeling have been reviewed in numerous studies (Rand 1983; Meyer 1985; Riggs 1988; Teixeira and Shoemaker 1989; Luyben 1990).

Mathematical modeling is usually done after obtaining the data in tabular and graphical forms. The model is a shorthand description of the data and estimates the values of the outputs (y_1, y_2 ... y_m) when the values of the inputs (x_1, x_2 ... x_m) are entered. The model may help to understand the details of the relation between the inputs and the outputs, which may not be understood by plotting the data only, and may explain the mechanism of the events. In the following pages, we will frequently have the sentence *comparison of the experimental data and the model is shown in Figure ....* This sentence actually means that two of the boxes given in the figure are compared. Usually experimental data will be presented with symbols and will represent the process; the mathematical model will be obtained after the

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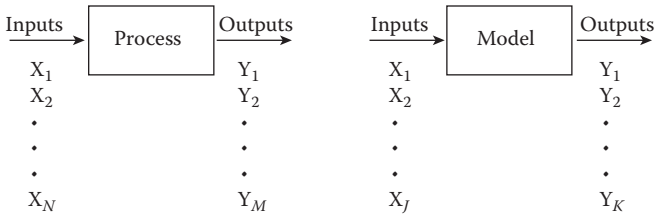


FIGURE 1.2
Comparison of input/output for a process and its model.

pertinent steps, will consist of the other box, and will be presented with solid, dashed, or dotted lines.

A good mathematical model should be general (apply to a wide variety of situations), realistic (based on correct assumptions), precise (its estimates should be finite numbers, or definite mathematical entities), accurate (its estimates should be correct or very near to correct), and there should be no trend in the deviations of the model from the experimental data. A good model should be robust (relatively immune to errors in the input data) and fruitful (its conclusions are useful or points the way to other good models).

Mathematical models may be categorized as *empirical*, *analog*, or *phenomenological* models depending on the basis that the functional relation is suggested. An empirical model assumes the form of the functional relation between the input and the output variables. There is usually no theoretical background sought while suggesting this relation. Empirical models are best when used within the range of the experimental data they are based on. An analogy model may be suggested for a relatively less known process by considering its similarity to a well-known process; that is, electrical circuit analogs may be used for modeling heat transfer or stress/strain relations. The phenomenological models use theoretical approach based on conservation of mass, energy, momentum, and so on to suggest the form of the mathematical model. They may include many different types including microscopic (distributed parameter) or macroscopic (lumped parameter) models.

The first step to building a mathematical model is a definition of the system. The answer to the question "What is going to be predicted by the model by what input data?" should be given while defining the system. Controlling factors of the system should be identified and the data should show the effects of the individual controlling factors. The system may be simplified after neglecting the effects of the marginal inputs (i.e., x_{n+1} ... x_N and outputs y_{m+1} .... y_M). The form of the mathematical model may be suggested by an empirical, analog, or phenomenological approach. The availability of information in the literature about the system, skills, and education of the modeler and purpose of modeling usually determines the form of the model suggested. In Chapters 2 through 4, fundamental principles of phenomenological model building with an application of kinetics, transport phenomena, and unit operations to food engineering processes will be discussed in detail with a theoretical background and examples. We usually end up with a single or a set of mathematical equations after using these fundamental principles. Techniques for a solution to these equations will be discussed in Chapter 2. Empirical model building will be discussed in Chapter 3. An application of mathematical modeling to process control will be discussed in Chapter 5. A comparison of the mathematical model (i.e., solution of the equations) with the experimental data is the final stage of modeling. The model is validated if it agrees with the data. If such an agreement should not be obtained, all the steps of modeling, starting with the definition of the system, is repeated until obtaining satisfactory representation (Figure 1.3).

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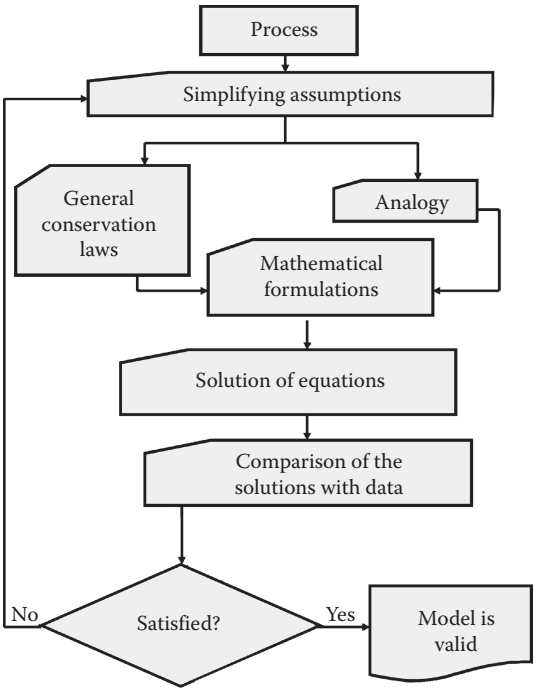


FIGURE 1.3
Schematic description of modeling.

1.3 Empirical Models and Linear Regression

Representation of large amounts of experimental data by means of empirical equations is a practical necessity in science and engineering. The empirical models are easy to use in mathematical operations over a continuous range. The form of the empirical models may be suggested by theoretical or dimensional analysis or by intuition. The simplest empirical model is a line:

$$y = ax + b, \tag{1.2}$$

where y is the dependent variable and x is the independent variable. In a plot of y versus x, parameter a is slope and b is the intercept with $x = 0$ axis. If it is possible to linearize an equation, parameters a and b may be evaluated with linear regression. Procedures of linearization to evaluate the slope and the intercept of some common simple models may be summarized as

Model	Linearization Procedure
$y = a/x + b$	Plot y vs. $1/x$, slope = a, intercept = b
$y = \dfrac{x}{a + bx}$	Rewrite the equation as $1/y = a/x + b$, plot $1/y$ vs. $1/x$, slope = a, intercept = b
$y = be^{ax}$	Rewrite the equation as $\ln y = \ln b + ax$, plot $\ln y$ vs. x, slope = a, intercept = $\ln b$

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In a plot of y vs. x if almost all the data points fall on the line, values of parameters a and b may be easily determined from the slope and the intercept of the graph. When the data points are scattered, it may be possible to draw many lines passing through them. The *best line* is the one with the smallest sum of squares of difference defined as $\sum d_i^2 = \sum_{i=1}^{n}\left[y_i - \left(ax_i + b\right)\right]^2$, where $ax_i + b$ is the value of parameter y predicted by Equation 1.2 and y_i is the experimentally determined value of y corresponding to x_i. The term $d_i = y_i - (ax_i + b)$ is the difference between the experimentally determined and predicted values of y at the point x_i. This difference might be either negative or positive. Regardless of the sign, the magnitude of the difference describes the deviation of the line from the data. When the differences are added up over the entire data set, the negative and positive differences may cancel each other and cause an erroneous conclusion. Working with the squares of the differences eliminates the cause of the erroneous conclusion. The minimum value of the sum of the squares difference is obtained with the following best line parameters:

$$a = \frac{n\sum_{i=1}^{n} x_i y_i - \left(\sum_{i=1}^{n} x_i\right)\left(\sum_{i=1}^{n} y_i\right)}{n\left(\sum_{i=1}^{n} x_i^2\right) - \left(\sum_{i=1}^{n} (x_i)^2\right)}, \tag{1.3}$$

$$b = \frac{\left(\sum_{i=1}^{n} x_i^2\right)\left(\sum_{i=1}^{n} y_i\right) - \left(\sum_{i=1}^{n} x_i y_i\right)\left(\sum_{i=1}^{n} x_i y_i\right)\left(\sum_{i=1}^{n} x_i\right)}{n\left(\sum_{i=1}^{n} x_i^2\right) - \left(\sum_{i=1}^{n} (x_i)^2\right)}. \tag{1.4}$$

Although Equations 1.3 and 1.4 give the values of a and b of the best fitting line, it does not mean that the best fitting line will always describe the correct relation between variables y and x. It is always possible that the relation between y and x may not be actually described with Equation 1.2. The goodness of the best fitting line to describe n sets of data points may be evaluated with a standard error of estimate:

$$s_e = \sqrt{\frac{\sum d^2}{n}}. \tag{1.5}$$

The standard error of estimate is a measure of the degree of association between the data points and the regression line. The larger the standard error of estimate, the larger the scatter of the data points around the fitted line. If all the data points are scattered by approximately normal distribution around the regression line, 99.73% of all the data points are scattered within the range of $\pm 3s_e$.

The correlation coefficient of the data and the best line is

$$r = \sqrt{1 - \frac{s_e^2}{s_y^2}}, \tag{1.6}$$

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where s_y is the standard deviation of values of y around its mean value:

$$s_y = \sqrt{\frac{\sum y^2}{n} - \left(\frac{\sum y}{n}\right)^2}. \tag{1.7}$$

The term S_e^2/S_y^2 is actually a ratio of the variance of the data points around the fitted line to their variance around the mean value of y. Having s_e is much smaller than s_y implies that the scatter of the data points around the fitted line is almost negligible when compared to the scatter around the average value of y. At the limiting condition of this case the ratio $S_e^2/S_y^2 = 0$, thus $r = 1$ implying a perfect fit. Having s_e the same as s_y implies that the scatter of the data points around the fitted line is almost the same as the scatter around the average value of y, implying that the fitted line does not represent the data. At the limiting condition of this case the ratio $S_e^2/S_y^2 = 1$, thus $r = 0$ implying no fit. Values of the correlation coefficient r vary between the limits 0 and 1. The correlation coefficient may also be defined as

$$r = \frac{s_{xy}}{s_x s_y}, \tag{1.8}$$

where s_x is the standard deviation of values of x around their mean value:

$$s_x = \sqrt{\frac{\sum x^2}{n} - \left(\frac{\sum x}{n}\right)^2}, \tag{1.9}$$

and s_{xy} is defined as

$$s_{xy} = \frac{\sum xy}{n} - \left(\frac{\sum x}{n}\right)\left(\frac{\sum y}{n}\right). \tag{1.10}$$

Equation 1.8 also gives the sign of the correlation, whereas Equation 1.6 gives its absolute value only. Having $r = -1$ implies that there is perfect correlation between the two parameters, but while one of them is increasing the other one is decreasing. The square of the correlation coefficient, r^2, may be preferred to describe the correlation between the variables, since it magnifies the deviation from the perfect correlation when r is close to 1.

Parameters a, b, and r as described by Equations 1.3, 1.4, and 1.8, respectively, may be easily calculated with simple scientific calculators containing the related built-in functions by entering the data only. Common spreadsheet computer software also serves the same purpose. Nonlinear regression is more sophisticated, but may be easily done with the common commercially available statistics and mathematics software.

Example 1.2: Survival Kinetics of the Freeze-Dried Lactic Acid Bacteria

The number of the viable microorganisms per gram of a freeze-dried preparation is the major quality factor of the freeze-dried cultures. Variation of the number of the freeze-dried viable microorganisms with time in storage may be expressed as

$$\frac{dx}{dt} = -k_d x. \tag{E.1.2.1}$$

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Equation E.1.2.1 may be integrated as

$$\log x = \log x_0 - \frac{k_d}{2.303} t, \tag{E.1.2.2}$$

where x_0 is the number of the viable microorganisms at $t = 0$. The following counts (number of viable microorganisms/ml) of the freeze-dried lactic acid starter culture microorganisms were reported by Alaeddinoglu, Guven, and Özilgen (1988):

***t*(days)**	**0**	**15**	**30**	**45**	**60**	**90**
log*x*	7.8	7.0	6.2	5.4	4.8	4.4

a. Calculate values of the constants $\log x_0$ and k_d and the correlation coefficient.

Solution: We may change the notation as $y = \log x$, $b = \log x_0$, $a = -k_d/2.303$, then the above equation may be expressed as $y = ax + b$. It may also be shown that $\Sigma x_i = 240$, $\Sigma y_i = 35.6$, $\Sigma x_i\, y_i = 1218$, $\Sigma x_i^2 = 14850$, $(\Sigma x_i^2) = 57{,}600$, and also $n = 6$. After filling them into Equations 1.3 and 1.4, $a = -0.039$, $b = 7.5$. Since $a = -k_d/2.303$ and $b = \log x_0$, we may calculate $k_d = 0.09$ day^{-1} and $\log x_0 = 7.5$.

The fitted equation is $\log x_{reg} = 7.5 - 0.039t$. The squares of the difference between log*x* and $\log x_{reg}$ may be calculated as

***t*(days)**	**log*x***	**$\log x_{reg}$**	**d^2**
0	7.8	7.5	0.09
15	7.0	6.9	0.01
30	6.2	6.3	0.01
45	5.4	5.7	0.09
60	4.8	5.1	0.09
90	4.4	4.0	0.16
			$\Sigma d^2 = 0.4$

$$s_e = \sqrt{\frac{\sum d^2}{n}} = 0.27,\ s_y = \sqrt{\frac{\sum y^2}{n} - \left(\frac{\sum y}{n}\right)^2} = 1.2, \quad \text{and} \quad r = \sqrt{1 - \frac{s_e^2}{s_y^2}} = 0.95,$$

Equation 1.6 is used here and implied an almost perfect fit. Equation 1.8 may also be used to calculate the correlation coefficient as

$$r = \frac{s_{xy}}{s_x s_y} = -0.97,$$

where

$$s_x = \sqrt{\frac{\sum x^2}{n} - \left(\frac{\sum x}{n}\right)^2} = 29.6 \quad \text{and} \quad s_{xy} = \frac{\sum xy}{n} - \left(\frac{\sum x}{n}\right)\left(\frac{\sum y}{n}\right) = -34.3.$$

Equation 1.8 implies a perfect agreement with the previous result. It gives additional information that there is negative correlation between log*x* and *t*; that is, the log number of the viable

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freeze-dried microorganisms decreases as time passes by. Comparison of the best line with the experimental data (symbols) is shown in Figure E.1.2.

b. How many microorganisms/ml will remain viable on the 75th day of storage? State with 99.73% probability.

Solution: When $t = 75$ we may calculate $\log x_{reg} = 7.5 - 0.39t$. Since with $p = 0.9973$ experimental data are scattered within $\pm 3s_e$ range of the best line, the confidence limits are $\log x_{reg} - 3s_e \le \log x \le \log x_{reg} + 3s_e$ after substituting the numbers $3.75 \le \log x \le 5.37$.

MATLAB® code E.1.2 carries out the same computations.

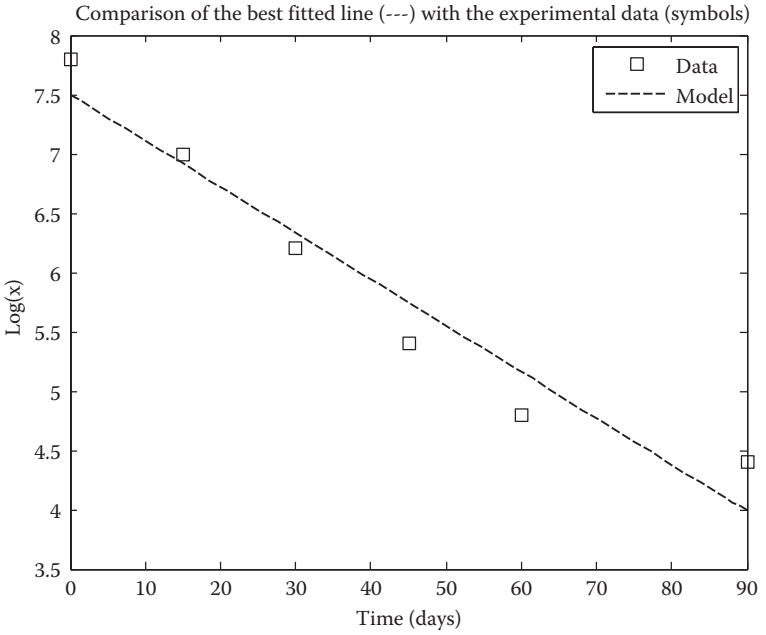


FIGURE E.1.2
Comparison of the model with the experimental data. There is a perfect agreement between the model and the data, with $r = 0.9687$ and $s_e = 0.2973$.

MATLAB® CODE E.1.2

Command Window:

```
clear all
close all
format compact
global kDeath

kDeath = 0.039; % death rate constant
xi = [0 15 30 45 60 90];% times the data collected (day)
yi = [7.8 7.0 6.2 5.4 4.8 4.4]; % log(x)
plot(xi,yi,'s');
sum_xi = sum(xi);
sum_yi = sum(yi);
n = length(xi);
xi_times_yi = 0;
```

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```
xi_square = 0;
yi_square = 0;
for i = 1:n
    xi_times_yi = xi_times_yi + (xi(i)*yi(i));
    xi_square = xi_square + (xi(i)^2);
    yi_square = yi_square + (yi(i)^2);
end
sum_of_Xi_square = (sum(xi))^2;
a = ((n * (xi_times_yi)) - (sum_xi * sum_yi)) / ((n * xi_square)
- (sum_of_Xi_square))
b = ((xi_square * sum_yi) - (xi_times_yi * sum_xi)) / ((n * xi_
square) - (sum_of_Xi_square))
kd = -a * 2.303
logx0 = b
logxreg = (b + a.*xi)
d_square = ((yi - logxreg).^2)
sum_d_square = sum(d_square)
s_e = sqrt(sum_d_square/n)                % standard error of estimate
s_y = sqrt((yi_square/n)-((sum_yi/n)^2)) %standard deviation of
values of y
r = sqrt(1-((s_e^2)/(s_y^2)))             % correlation coefficient
hold all;
box on;
[xi,x] = ode45('microbialdeath',90,exp(7.5));
plot(xi,log(x),'--');
xlabel('Time(days)')
ylabel('log(x)')
title('comparison of the best fitted line (---) with the
experimental data (symbols)')
legend('data','model')
```

M-File:

```
function y = microbialdeath(t,x)
global kDeath
y = -kDeath*x;
```

When we run the code the following lines and Figure E.1.2 will appear on the screen:

```
a =
   -0.0392
b =
    7.5029
kd =
    0.0904
logx0 =
    7.5029
logxreg =
    7.5029   6.9143   6.3257   5.7371   5.1486   3.9714
d_square =
    0.0883   0.0073   0.0158   0.1137   0.1215   0.1837
sum_d_square =
    0.5303
s_e =
    0.2973
```

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```
s_y =
    1.1981
r =
    0.9687
```

Example 1.3: Comparison Between Two Models: Death Kinetics of Microorganisms in Dough

The colony counts of *Saccharomyces cerevisiae* after 60 minutes of leavening for sour dough with an inoculum initially containing 80% *S. cerevisiae* and 20% *Lactobacillus plantarum* were (Yöndem, Özilgen, and Bozoglu 1992)

***t*(min)**	**60**	**90**	**120**	**150**	**180**	**210**
x(cfu/g)	4.5×10^6	3.85×10^6	3.45×10^6	3.3×10^6	3.1×10^6	3.2×10^6

Suggest a mathematical model to describe the death of the yeast.

Solution: The process is the death of the microorganisms during constant temperature pasteurization. The model is expected to predict (output) the colony counts of the surviving microorganisms with time input. It might be assumed that constant fractions of the viable microorganisms die at a constant time interval with the mathematical formulation:

$$\frac{dx}{dt} = -kx. \tag{E.1.3.1}$$

The model assumes that the microorganisms are equally labile when subject to heat treatment and do not affect each other. This is the most common microbial death rate expression in the literature (Chapter 3). The form of the model has been based on assumptions; therefore, it is an empirical model. The solution of the equation is

$$x = x_0 e^{-k} \tag{E.1.3.2}$$

and may be linearized as

$$\ln(x) = \ln(x_0) - kt. \tag{E.1.3.3}$$

MATLAB® code E.1.3.a compares Equation E.1.3.3 with the data.

Disagreement of the model with the data requires us to repeat all the steps of modeling starting from the definition of the system. The process seems like it is defined properly, but the simplifying assumptions may not be correct; that is, microbial death may slow down as microbial concentration approaches a highly resistant small fraction. Such an observation may be caused by nonuniform resistance of the microbial population to death, or dead microorganisms (or their constituents) may protect or increase the resistance of the surviving microorganisms. The model may be revised as

$$\frac{dx}{dt} = -k(x - x_m), \tag{E.1.3.4}$$

where x_m represents the finally attainable highly resistant microbial concentration. The new expression may be solved:

$$x = (x_0 - x_m)e^{-kt} + x_m \tag{E.1.3.5}$$

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MATLAB® CODE E.1.3.a

Command Window:

```
clear all
close all
format compact

global k % make k available to all the m-functions where the word
global is written

k = 0.003; % death rate constant

[t,x] = ode45('deathkinetics1',[60 210], 4501854.5);
plot(t,log(x))
t = [60 90 120 150 180 210];
x = [4.5e006; 3.85e006; 3.45e006; 3.3e006; 3.1e006; 3.2e006];
% calculate x at t = 60, t = 90,...., t = 210 min with x0 = 4501854.5
[t,x2] = ode45('deathkinetics1', [60 90 120 150 180 210], 4501854.5);
d = log(x2)-log(x);
dsqr = d.^2;
sumdsqr = sum(dsqr);
% compute the standard error
se = sqrt(sumdsqr/6)
sy = std(log(x));
sx = std(t);
% compute the correlation coefficient with [1.6]
r1 = sqrt(1-se^2/sy^2)
sxy = sum(log(x).*t)/6-sum(log(x))/6*sum(t)/6;
% compute the correlation coefficient with [1.8]
r2 = sxy/(sx*sy)
hold on,plot(t,log(x),'x')
xlabel('t(min)'),ylabel('ln x')
```

M-File:

```
function y = deathkinetics1(t,x)
global k
% This function models microbial death in analogy with first order
irreversible unimolecular chemical reaction
y = -k*x;
```

When we run the code, the following lines and Figure E.1.3.1 will appear on the screen:

```
se =
    0.0651
r1 =
    0.8852
r2 =
   -0.7632
```

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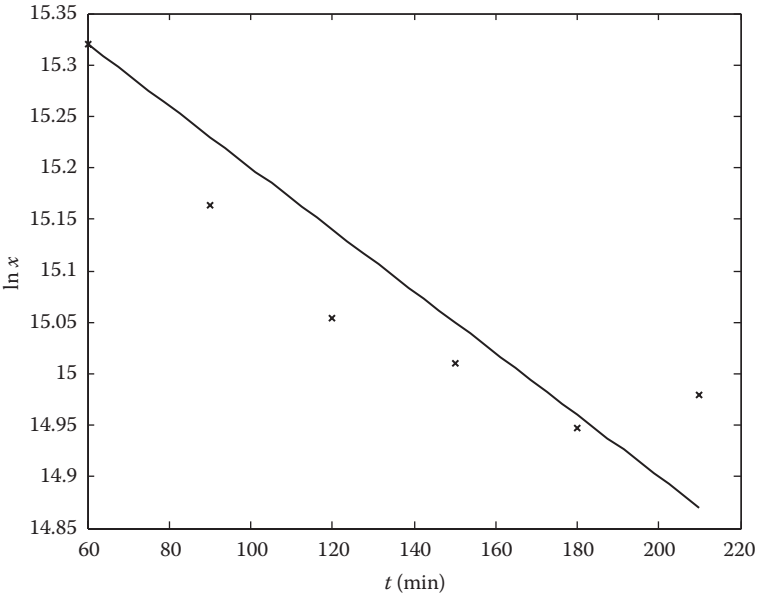


FIGURE E.1.3.1
Comparison of the model (-------) with the experimental data (x). Equation E.1.3.1 does not agree with the data ($r_1 = 0.89$, $r_2 = -0.76$, and $s_e = 0.0651$).

and linearized:

$$\ln(x - x_m) = \ln(x_0 - x_m) - kt, \tag{E.1.3.6}$$

when $x_m = 3.15 \times 10^6$ cfu/g constants of the linear equation may be evaluated with the linear regression as $\ln(x - x_m) = 15.64 - 0.025t$, with correlation coefficient $r = -0.999$ implying that $\ln(x_0 - x_m) = 15.64$ and $k = 0.025$ min^{-1}. MATLAB® code E.1.3.b compares Equation E.1.3.6 with the data.

Example 1.4: Kinetics of Galactose Oxidase Production
The logistic model (Chapter 3) is frequently used to simulate microbial growth:

$$\frac{dx}{dt} = \mu x\left(1 - \frac{x}{x_{\max}}\right), \tag{E.1.4.1}$$

where μ is the initial specific growth rate and $x_{\max}$ is the maximum attainable value of x. The logistic equation is an empirical model, because it simulates the data without any theoretical basis. It is based only on experimental observations: When $x << x_{max}$, the term in parenthesis is almost one and neglected, then the equation simulates the exponential growth ($dx/dt = \mu x$), and when x is comparable with $x_{\max}$, the term in parenthesis becomes important and simulates the inhibitory effect of overcrowding on microbial growth. When $x = x_{\max}$, the term in parenthesis becomes zero, then the equation will predict no growth ($dx/dt = 0$). The logistic equation may be integrated as

$$x = \frac{x_0 e^{\mu t}}{1 - \frac{x_0}{x_{\max}}(1 - e^{\mu t})}. \tag{E.1.4.2}$$

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MATLAB® CODE E.1.3.b

Command Window:

```
clear all
close all
format compact

% enter the data
tData = [60 90 120 150 180 210]; % times when the data were recorded
xData = [4.5e006 3.85e006 3.45e006 3.3e006 3.1e006 3.2e006];
xm = 3.15e006; % minimum attainable value of x
kDeath = 0.025; % death rate constant

global xm kDeath; % make xm and kDeath be available to all the
m-functions where the word global is written

plot(tData,log(xData),'*'); hold on % plot the data
xlabel('t(min)'),ylabel('ln x')
lsline % least squares line
[t,x] = ode45('deathkinetics2',[60 210], 4501854.5); % compute values
of x as a function of t
plot(t,log(x), ':') % plot the model

% evaluate the standard error and the correlation coefficients
xminusxm = xData-xm;
[t,x2] = ode45('deathkinetics2', [60 90 120 150 180 210], 4501854.5);
xminusxm2 = x2-xm;

for k = 1:1:size(x2)
    dsqr(k) = (xminusxm2(k)-xminusxm(k))^2;
    prod(k) = (xminusxm2(k))*tData(k);
end

sumdsqr = sum(dsqr);
se = sqrt(sumdsqr/6)
sy = std(xminusxm2) ;
sx = std(tData) ;
r1 = sqrt(1-((se^2)/(sy^2)))
sxy = std(prod);
r2 = sxy/(sx*sy)
legend('data','least squares line','model', 'location', 'NorthEast' )
```

M-File:

```
function y = deathkinetics2(t,x)
% This function models logistic microbial death, i.e, a minimum
microbial population described as xm survives
global xm kDeath
y = (-kDeath)*(x-xm); % death rate model
```

When we will run the code the following lines and Figure 1.3.2 will appear on the screen:

```
se =
    5.4663e+004
```

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```
r1 =
    0.9942
r2 =
    1.0125
```

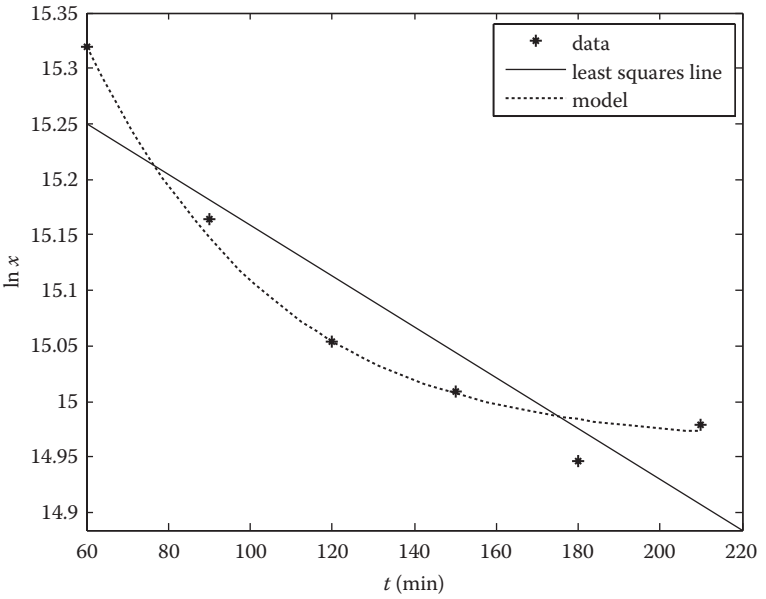


FIGURE E.1.3.2
Comparison of Equation E.1.3.4 with the experimental data. Parameters $s_e = 5.4663e+004$ (equals to 1.2% of the initial microbial population), $r_1 = 0.9942$ and $r_2 = 1.0125$ indicate almost perfect agreement between the model and the data. It is seen clearly that the least squares line goes far away from the data points.

MATLAB® code E.1.4.a compares the model Equation E.1.4.2 with the data.

Galactose oxidase production was simulated with the Luedeking–Piret model (details are explained in Chapter 3; Ogel and Özilgen 1995):

$$\frac{dc_P}{dt} = \alpha x + \beta \frac{dx}{dt}, \tag{E.1.4.3}$$

where α and β are constants. The term αx represents the galactose oxidase production by the microorganisms regardless of their growth; $\beta dx/dt$ represents the additional enzyme production in proportion with the growth rate. This is an empirical equation, because it simply relates the experimental observations without any theoretical basis. Integrated and differential forms of the logistic equation were used to simulate biomass concentration x and dx/dt, respectively, and the Luedeking–Piret model was integrated as

$$c_p = c_{p0} + \alpha A + \beta B, \tag{E.1.4.4}$$

where c_{p0} is the amount of the product in the fermentor when $t = 0$ and

$$A = \frac{x_{\max}}{m} \ln\left[1 - \frac{x_0}{x_{\max}}(1 - e^{\mu t})\right] \quad \text{and} \quad B = x_0\left(\left(e^{\mu t} \Big/ \left(1 - \frac{x_0}{x_{\max}}\left(1 - e^{\mu t}\right)\right)\right) - 1\right).$$

MATLAB code E.1.4.b compares the model Equation E.1.4.3 with the data.

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MATLAB® CODE E.1.4.a

Command Window:

```
clear all
close all
format compact
global mu xmax

% enter the constants
mu = 0.037;
xmax = 0.6;

% enter the data
tData1 = [25 48 72 97 132];
tData2 = [25 48 72 97 120 132];
a = [0.15 0.25 0.38 0.45 0.55];
b = [0.09 0.26 0.4 0.48 0.57 0.58];

plot(tData1,a,'x',tData2,b,'o'); hold on, % plot the data
xlabel('t (min)'),ylabel('gbiomass/L')
x1 = [0.15; 0.25; 0.38; 0.45; 0.55];
x2 = [0.09; 0.26; 0.4; 0.48; 0.57; 0.58];

[t,x] = ode45('logisticgrowth',150,0.068); % compute the model x
values
plot(t,x) % plot the model
legend('data','data','model', 'location', 'SouthEast' )
[t,x3] = ode45('logisticgrowth', [25 48 72 97 132], 0.068); % compute
the x values corresponding to tData1 (notice dimensions of t1 and t2
are not the same)
[t,x4] = ode45('logisticgrowth', [25 48 72 97 120 132], 0.068); %
compute the x values corresponding to tData2
dsqr1 = (x1-x3).^2;
dsqr2 = (x2-x4).^2;
sumdsqr = sum(dsqr1) + sum(dsqr2);
se = sqrt(sumdsqr/13)
```

M-File:

```
function y = logisticgrowth (t,x)
global mu xmax
y = mu*x*(1-(x/xmax));
```

When we run the code, the following lines and Figure E.1.4.1 will appear on the screen:

```
se =
    0.0858
```

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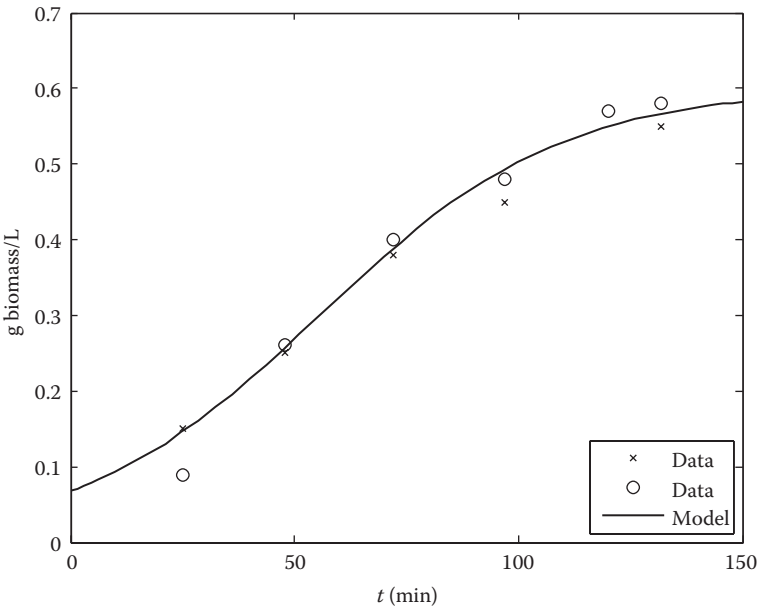


FIGURE E.1.4.1
Comparison of the biomass growth model with the data. (From Shatzman, A. R. and Kosman, D. J., *Journal of Bacteriology,* 130, 455–63, 1977.)

MATLAB® CODE E.1.4.b

Command Window:

```
clear all
close all

[t,x] = ode45('LuedekingPiret', 150, [0.068 0]);
plot(t, x( :,2))
xlabel('t(h)');
ylabel('Cp(Eu/L)');
c = [0 24 48 72 96 120];
d = [0 2400 5600 12000 14800 16400];
hold on, plot(c, d, 'r*')
```

M-File:

```
function dx = LuedekingPiret(t,x);
% This function models product formation with Luedeking-Piret model
mu = 0.037;
xmax = 0.6;
alpha = 43;
beta = 32000;
dx1 = mu*x(1)*(1-(x(1)/xmax));
dx2 = alpha*x(1) + beta*dx1;
dx = [dx1; dx2];
```

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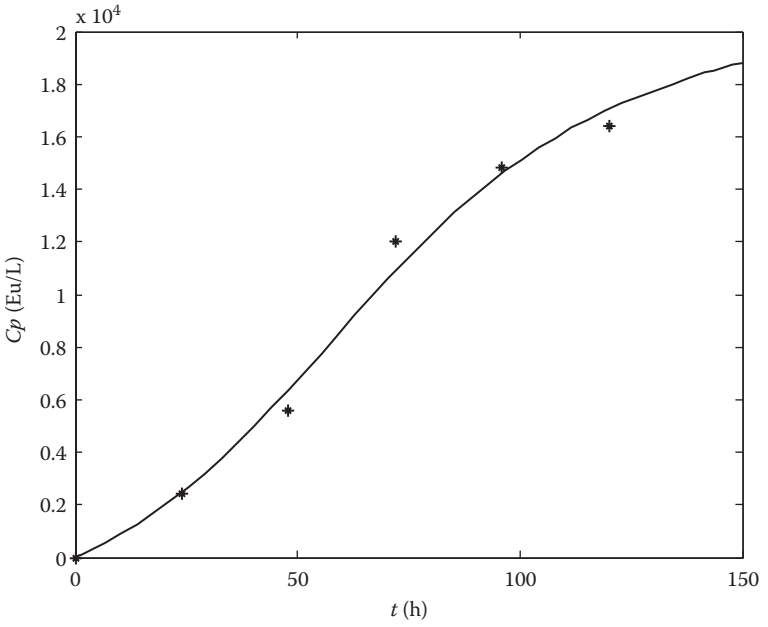


FIGURE E.1.4.2
Comparison of the product formation model (---) with the data (x). (Model parameters: $\alpha = 43$ Eu/g biomass h^{-1} and $\beta = 32 \times 10^3$ Eu/g biomass were taken from Ogel, B. Z. and Özilgen, M. *Enzyme and Microbial Technology*, 17, 870–76, 1995.)

Example 1.5: Kinetics of Lipid Oxidation in Foods

Lipid oxidation is one of the major reasons for spoilage of the lipid foods and occurs stagewise:

Initiation: $RH \rightarrow R\cdot + H\cdot$
Propagation: $R\cdot + O_2 \rightarrow RO_2\cdot$
$RO_2\cdot + RH \rightarrow RO_2H + R\cdot$
Termination: $R\cdot + R\cdot \rightarrow RR$
$R\cdot + RO_2\cdot \rightarrow RO_2R$
$RO_2\cdot + RO_2\cdot \rightarrow RO_2R + O_2$,

where RH represents the lipids, R**.**, H**.,** and RO_2**.** the free radicals, whereas RO_2H and RO_2R are the oxidation products. Parameter R actually represents different chemical species and too many reactions, involving many intermediary products, occurring simultaneously during lipid oxidation. Such a complex reaction mechanism makes it impossible to monitor the concentration of all the individual chemicals and it is difficult to use the conventional chemical kinetic rate expressions for modeling.

There is an analogy between lipid oxidation and microbial growth: both of them have initiation, propagation, and termination phases. Equation E.1.3.1 simulates microbial growth successfully. Microbial growth, like lipid oxidation, occurs through a large number of complex reactions. Therefore a logistic equation may be used to simulate lipid oxidation:

$$\frac{dc}{dt} = kc\left[1 - \frac{c}{c_{max}}\right], \tag{E.1.5.1}$$

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where c is the total amount of the oxidation products, dc/dt is the lipid oxidation rate, c_{max} is the total amount of the lipids available for oxidation, t is time, and k is the reaction rate constant. As the reaction rate constant k increases c_{max} is attained faster. At the beginning of the lipid oxidation process (i.e., when $c \ll c_{max}$) the term $(1 - c/c_{max})$ may be neglected and Equation E.1.5.1 becomes

$$\frac{dc}{dt} = kc.$$

At this stage of the process, the termination reactions do not occur and the free radicals accumulate in the food and the reaction rate seems to be increasing with the accumulation rate of the free radicals. In the termination phase, free radicals react with each other and the term $(1 - c/c_{max})$ becomes important. When $c = c_{max}$, the term $(1 - c/c_{max})$ becomes zero and Equation E.1.5.1 estimates the end of the lipid oxidation process. The solution to Equation E.1.5.1 is

$$c = \frac{c_0 e^{kt}}{1 - \frac{c_0}{c_{max}}(1 - e^{kt})}, \tag{E.1.5.2}$$

where c_0 is the concentration of the oxidized products at the beginning of oxidation. MATLAB® code E.1.5 carries out a sample set of simulations and compares the model with the data as shown in Figure E.1.5.

MATLAB® CODE E.1.5

Command Window:

```
clear all
close all

[t,c] = ode45('lipidoxidation1',20,2.61);
plot(t,c)
xlabel('t (days)');
ylabel('c (TBA)');
[t,c] = ode45('lipidoxidation2',20,0.73);
hold on, plot(t,c)
s = [0 2 6.4 10.8 14];
a = [2.2 6 10.4 14.2 14.6];
b = [0.8 1.92 3.96 4 5.4];
hold on, plot(s,a,'o')
hold on, plot(s,b,'x')
```

M-File:

```
function f = lipidoxidation1(t,c);
k = 0.38;
cmax = 14.9;
f = k*c*(1-(c/cmax));
```

M-File:

```
function f = lipidoxidation2(t,c);
k = 0.54;
cmax = 5;
f = k*c*(1-(c/cmax));
```

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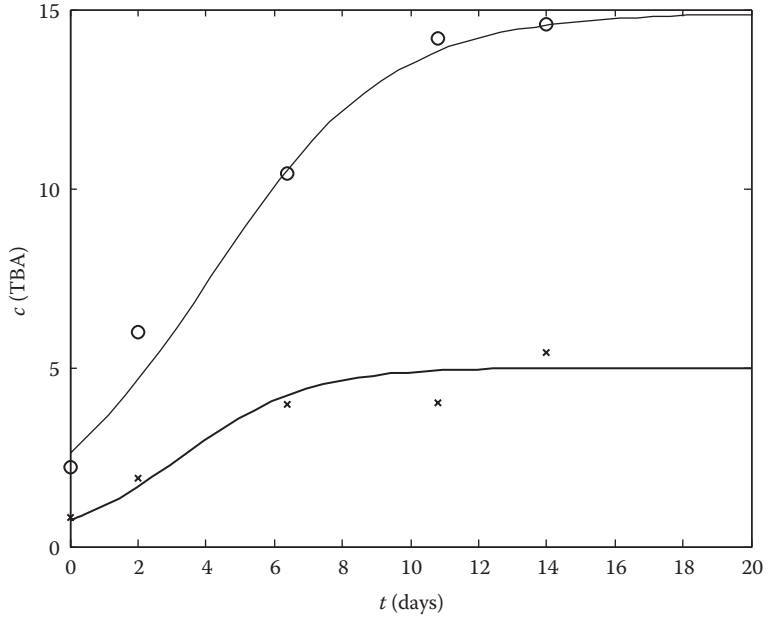


FIGURE E.1.5
Comparison of the model (lines) with the data (symbols, o:pH 4.70, $k = 0.38$, $c_{max} = 14.9$ TBA, $c_0 = 2.61$ TBA; x: pH 6.25, $k = 0.54$, $c_{max} = 5$ TBA, $c_0 = 0.73$ TBA) during lipid oxidation in ground raw poultry meat. (From Özilgen, S. and Özilgen, M., *Journal of Food Science*, 55, 498–502, 536, 1990.)

Example 1.6: Analogy Between Cake Filtration and Ultrafiltration Processes

In a cake filtration process (Chapter 4) the total pressure drop through the filter (ΔP) is

$$\Delta P = \Delta P_c + \Delta P_m, \tag{E.1.6.1}$$

where ΔP_c and ΔP_m are the pressure drops through the cake and the medium, respectively, and expressed theoretically as

$$\Delta P_c = \frac{\alpha \mu c V}{A^2} \frac{dV}{dt}, \tag{E.1.6.2}$$

and

$$\Delta P_m = \frac{R_m \mu}{A} \frac{dV}{dt}, \tag{E.1.6.3}$$

where α = specific resistance of the cake, μ = viscosity of the filtrate, c = mass of the solids per unit volume of the feed, A = filter area, V = volume of the filtrate, t = time, and R_m = filter medium resistance. Equations E.1.6.2 and E.1.6.3 may be substituted in Equation E.1.6.1 to obtain the Sperry's Equation:

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$$\frac{dV}{dt} = \frac{A\Delta P}{\mu}\frac{1}{R_m + \alpha c V/A}. \tag{E.1.6.4}$$

Equation E.1.6.4 has been based on theoretical considerations; therefore, it may be referred to as a phenomenological model. Foods are usually highly complex systems. Theoretical expressions are frequently found inefficient to simulate the processes involving foods and biological materials. De LaGarza and Boulton (1984) modified Equation E.1.6.4 to model wine filtrations:

$$\frac{dV}{dt} = \frac{A\Delta P}{\mu}\frac{1}{R_m + \alpha c (V/A)^n} \tag{E.1.6.5}$$

and

$$\frac{dV}{dt} = \frac{A\Delta P}{\mu}\frac{1}{R_m \exp(kV/A)}. \tag{E.1.6.6}$$

Equation E.1.6.6 may be integrated as

$$V = \frac{A}{\kappa}\left[\ln\left(\frac{\kappa\Delta P}{\mu R_m}t + 1\right)\right]. \tag{E.1.6.7}$$

MATLAB® code E.1.6.a compares Equation E.1.6.7 with the experimental data as shown in Figure E.1.6.1.

MATLAB® CODE E.1.6.a

Command Window:

```
clear all
close all

% introduce the data
tData = [0 30 55 120 190 250 290 300 340 415 500 700 900 1000];
vData = [0 80 120 162 190 210 220 222 230 245 255 277 295 300];
% introduce the constants
A = 30.2; % filtration area
deltaP = 6.5e4; % pressure difference
kappa = 0.447; % cake resistance coefficient
Rm = 2.05e8; % filter medium resistance
mu = 1.65e-3; % viscosity

% plot the data and insert labels
plot(tData, vData, '*'); hold on
xlabel('t (s)')
ylabel('V (cm3)')
```

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```
% compute the filtrate accumulation rate
for t = 0:1000;
v(t + 1) = A*(log(((kappa*deltaP)/(mu*Rm))*t + 1))/kappa;
time(t + 1) = t;
end;

% plot the model and insert the legends
plot(time,v)
legend('data','model', 'Location','SouthEast')
```

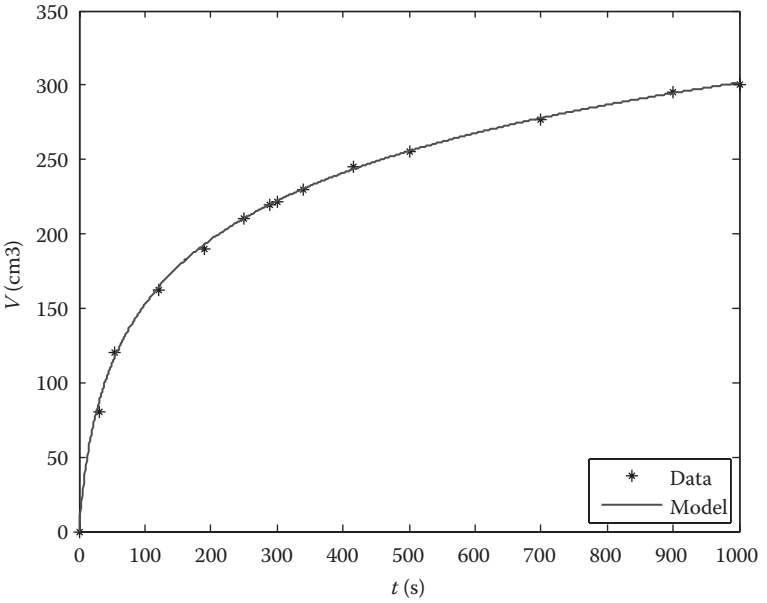


FIGURE E.1.6.1
Comparison of Equation E.1.6.7 (---) with the experimental data. (From Bayindirli, L., Ungan, S., and Özilgen, M., *Journal of Food Science,* 54, 1003–6, 1989.)

In an ultrafiltration process, a fraction of the solute is permitted to pass through the membrane and the remaining solutes are rejected. The use of batch ultrafiltration is limited to laboratory scale separations only due to an accumulation of the rejected particles on the membrane. Although Equations E.1.6.4, E.1.6.5, and E.1.6.6] are suggested for cake filtrations only, they may be used to simulate batch ultrafiltration based on the analogy between the processes: Resistance to flow by the membrane and the rejected solids in an ultrafiltration process is analogous to the medium and the cake resistance in cake filtration. MATLAB code E.1.6.b exemplifies the use of Equation E.1.6.5 with $n = 2$ to the model sequential batch ultrafiltration of red beet extract.

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MATLAB® CODE E.1.6.b

Command Window:

```
clear all
close all

% introduce the data
tData = [0 45 90 110 130 180 205 230 260 280 310 340 370 410 430 470
510];
vData = [0 80e-6 150e-6 210e-6 280e-6 340e-6 390e-6 440e-6 500e-6
550e-6 600e-6 640e-6 700e-6 750e-6 800e-6 830e-6 900e-6];

% plot the data
plot(tData, vData, '*'); hold on;
% put the labels
xlabel('t (min)'); hold on
ylabel('V (m3)'); hold on

% compute the filtrate accumulation rate
[t,V] = ode45('DeLaGarzaBoulton', 0:1:600, 0);

% plot the model and insert the legend
plot(t,V)
legend('data','model', 'Location','SouthEast')
```

M-File :

```
function dV = DeLaGarzaBoulton(t,V)
A = 30.2e-4;
deltaP = 4e5;
kappaA2 = 11.94e18; % kappa/Asquare
Rm = 6.29e13;
mu = 1e-5;
% DeLaGarza Boulton Model
dV = (deltaP*A/mu)*(1/(Rm + kappaA2*(V^2)));
```

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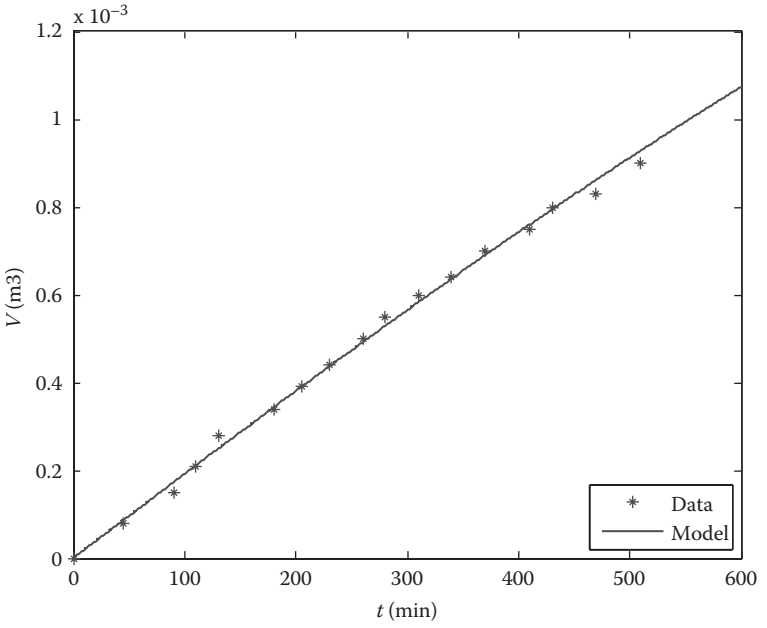


FIGURE E.1.6.2
Comparison of Equation E.1.6.5 ($n = 2$) (---) with the experimental data (cellulose nitrate isotropic membrane, 50,000 daltons molecular weight cutoff. (From Bayindirli, A., Yildiz, F., and Özilgen, M., *Journal of Food Science*, 53, 1418–22, 1988.)

Questions for Discussion and Problems

A. What is Process Modeling?
   1. Explain the philosophical reasoning of mathematical modeling.
   2. What are the properties of a good mathematical model?
   3. What are theoretical, analogy, and empirical modeling?
   4. What is the significance of the 80%–20% rule in process modeling?

B. Empirical Models and Linear Regression
   1. The active component of an artificial flavor decreases during the storage period as indicated by the following data

Time (months)	**1**	**2**	**4**	**6**	**8**	**12**	**18**	**24**	**28**	**36**	**40**	**43**
Active component (IU)	500	497	435	488	486	474	466	450	440	420	425	413

It is believed that the loss of an active ingredient in storage is a linear function of time

$$(\text{remaining active component, } IU) = \alpha - \beta t.$$

   i. Determine the constants α and β.
   ii. Determine the numerical value correlation coefficient and explain what it means to you.
   iii. Determine the numerical value of the standard error and explain what it means to you.

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2. The active number of the viable microorganisms per gram of a freeze-dried preparation is the major quality factor of the freeze-dried cultures. Variation in the number of the freeze-dried viable microorganisms with the time in storage may be expressed as

$$\frac{dx}{dt} = -k_d x. \tag{Q.1.B.2.1}$$

Equation 3.67 may be integrated as

$$\log x = \log x_0 - \frac{k_d}{2.303} t, \tag{Q.1.B.2.2}$$

where x_0 is the number of the viable microorganisms at $t = 0$. The following counts (number of viable microorganisms/ml) of the freeze-dried lactic acid starter culture microorganisms were reported by Alaeddinoglu, Guven, and Özilgen (1988):

***t*(days)**	**0**	**15**	**30**	**45**	**60**	**90**
log*x*	7.8	7.0	6.2	5.4	4.8	4.4

A. Calculate values of the constants $\log x_0$ and k_d and the correlation coefficient.
B. How many microorganisms/ml will remain viable on the 75th day of storage? State with 99.73% probability.

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2

Transport Phenomena Models

2.1 The Differential General Property Balance Equation

The phenomenological models are mostly based on conservation principles. Conservation of mass, energy, and momentum are mathematically analogous; discussion of either one equally applies to the others. A microscopic property (ψ) balance around a differential volume element gives

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \, \mathbf{v}) = \nabla \cdot \psi_G + (\nabla \cdot \delta \nabla \psi), \tag{2.1}$$

with constant δ (Equation 2.1) becomes

$$\frac{\partial \psi}{\partial t} + \nabla \cdot (\psi \, \mathbf{v}) = \nabla \cdot \psi_G + \delta \nabla^2 \psi, \tag{2.2}$$

where δ is diffusivity (Table 2.1). The $\nabla$and ∇^2 are del and Laplacian operators.

$\partial\psi/\partial t$ = accumulation rate of the property at a fixed point in the volume element
$\nabla \cdot (\psi \mathbf{v})$ = net input rate of the property to the point with convection
ψ_G = generation rate of the property at the point
$\delta\nabla^2\psi$ or $\nabla \cdot \delta \nabla\psi$ = net input rate of the property to the point with molecular diffusion.

A detailed discussion of derivation of the transport equations may be found in the classical *Transport Phenomena* books (Whitaker 1977; Brodkey and Hershey 1988; Bird, Stewart, and Lightfoot 2007).

Parameters α and ν are called the thermal diffusivity and kinematic viscosity (or viscous diffusivity), respectively, and defined as:

$$\nu = \frac{\mu}{\rho}, \tag{2.3}$$

and

$$\alpha = \frac{\rho c_p}{k}, \tag{2.4}$$

where k and μ are thermal conductivity and viscosity, respectively. Parameter D is the diffusion coefficient for mass transfer.

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TABLE 2.1

List of ψ and δ for Use in General Property Balance

Transport Phenomena	Flux	Flux Units	Diffusivity (m^2/s)	Concentration of Property y	Units of ψ
Heat	q	J/m^2s	α	$\rho c_p T$	$J\ m^{-3}$
Mass	J	kg/m^2s	D	c	$kg\ m^{-3}$
Momentum	σ	N/m^2	ν	ρν	$kg\ m^{-2}s^{-1}$

Source: Brodkey, R. S. and Hershey, H. C., *Transport Phenomena,* McGraw-Hill, New York, 1988.

TABLE 2.2

Empirical Laws for One Directional Fluxes

Mass transfer	Fick's Law	$J_z = -D\frac{dc}{dz}$	(2.5)
Heat transfer	Fourier's Law	$q_z = -k\frac{dT}{dz}$	(2.6)
Momentum transfer	Newton's Law	$\sigma_{zy} = -\mu\frac{dv_y}{dz}$	(2.7)

Equation 2.2 is the starting point of almost all the transport phenomena problems. We choose the appropriate ψ from Table 2.1, and expand ∇or ∇^2 in the appropriate coordinate systems, then solve the differential equation. Equations for the flux expressions are given in Table 2.2.

Equations 2.5 through 2.7 imply that the fluxes J_z, q_z, and σ_{zv} are proportional with the gradients dc/dz, dT/dz, and dv_y/dz, respectively. Parameters D, k, and μ are actually the proportionality constants. It should be noticed that mass and heat transfers occurs in the same direction with the gradient. The negative signs imply that the mass, heat, and momentum transfers occur from higher to lower concentration, temperature, or momentum regions, respectively. Liquid molecules are in contact with each other. When a layer of these molecules are set in motion in the y direction, momentum is transferred to the other liquid layers in the z direction due to the molecular interactions (σ_{zv} = viscous flux of y momentum in the z direction).

Choosing an appropriate coordinate system (Figure 2.1) with an appropriate origin may facilitate the modeling process substantially. A cylindrical coordinate system with z axis located on the center line of the cylinder will be preferred when the equation of continuity is used to describe drying behavior of a cylindrical rise grain (Example 2.12); the spherical coordinate system with the origin located to the center of the tuber will be preferred when an equation of energy will be used to evaluate the temperature profiles along a spherical potato (Example 2.9).

2.2 Equation of Continuity

Equations 2.1 and 2.2 become the equation of continuity when $\psi = c_A$, $\psi_G^{\bullet} = R_A$ and $\delta = D$:

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = R_A + (\nabla \cdot D \nabla c_A), \tag{2.8}$$

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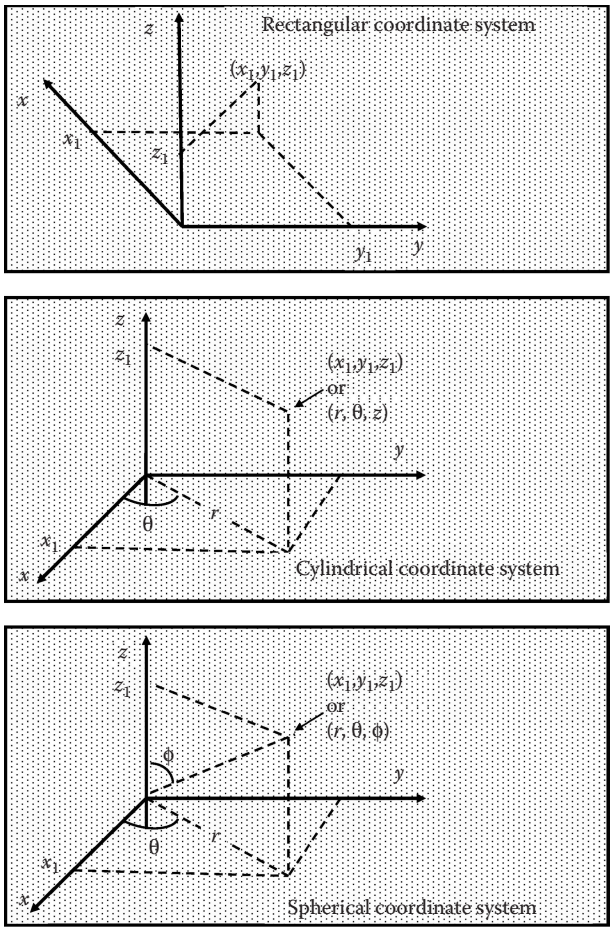


FIGURE 2.1
Coordinate systems employed with transport phenomena models.

$$\frac{\partial c_A}{\partial t} + \nabla \cdot (c_A \mathbf{v}) = R_A + D\nabla^2 c_A. \tag{2.9}$$

Total (convective + diffusive) flux of species A may also be expressed as:

$$N_A = x_A\left(N_A + N_B\right) - D_{AB}\frac{dc_A}{dz}, \tag{2.10}$$

where $N_A + N_B$ is the total flux in the system and $x_A(N_A + N_B)$ is the convective flux of A. The term $D_{AB}dc_A/dz$ represents the diffusive flux superimposed on convection. Equations 2.9 and 2.10 may be combined to express the equation of continuity as:

$$\frac{\partial c_A}{\partial t} + \nabla \cdot \left(N_A\right) = R_A. \tag{2.11}$$

Different forms of equation of continuity as written in rectangular, cylindrical and spherical coordinate systems are depicted in Table 2.3. The term $x_A(N_A + N_B)$ is associated with bulk

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TABLE 2.3

Equation of Continuity for Different Coordinate Systems

i) Rectangular coordinates:

$$\frac{\partial c_A}{\partial t}+\left(\frac{\partial N_{Ax}}{\partial x}+\frac{\partial N_{Ay}}{\partial y}+\frac{\partial N_{Az}}{\partial z}\right)=R_A. \tag{2.12}$$

ii) Cylindrical coordinates:

$$\frac{\partial c_A}{\partial t}+\left(\frac{1}{r}\frac{\partial\left(rN_{Ar}\right)}{\partial r}+\frac{1}{r}\frac{\partial N_{A\theta}}{\partial \theta}+\frac{\partial N_{Az}}{\partial z}\right)=R_A. \tag{2.13}$$

iii) Spherical coordinates:

$$\frac{\partial c_A}{\partial t}+\left(\frac{1}{r^2}\frac{\partial\left(r^2N_{Ar}\right)}{\partial r}+\frac{1}{r\sin\theta}\frac{\partial N_{A\theta}\sin\theta}{\partial \theta}+\frac{1}{r\sin\theta}\frac{\partial N_{A\phi}}{\partial \phi}\right)=R_A. \tag{2.14}$$

motion. When our kitchen smells after cooking, we may open the windows to supply air flow and refreshen the air. Here we encourage the bulk motion of the air described by $x_A(N_A + N_B)$. When x_A represents the chemicals causing the smell and after multiplying $(N_A + N_B)$ with x_A, we actually consider the fraction of the smelly chemicals in the bulk flow.

The gas molecules are in random motion in all directions. When we have smelly compounds at one point in the space in our kitchen, we may expect them to move to the neighbor points with molecular motion when there is no bulk flow. If the concentration of the smelly compounds are high at one point and low in the neighborhood, the molecular motion will tend to equalize them because the higher number of molecules leave the concentrated point with random motion. The term $D_{AB}dc_A/dz$ implies that the higher the concentration gradient dc_A/dz, the higher the diffusion rate. Constant D_{AB} is the diffusivity of A in B, where B is the medium that A is diffusing through. The term $D_{AB}dc_A/dz$ also implies that the rate of the diffusion will increase as D_{AB} gets larger.

Solute molecules in the solution, suspended microscopic solids in liquid, or liquid molecules in solids also make random motions and Equation 2.5 may also be used with these systems. The intensity of the random motions tend to decrease with liquid and solid systems as the molecular matrix of the diffusion medium gets more rigid.

Example 2.1: Diffusion of Water Through a Wine Barrel During Aging

During the aging of red wine in a cylindrical wooden barrel (Figure E.2.1.1, radius = R, length = L, thickness of the wood = λ) small amounts of water diffuses through the wood and evaporates. Assuming that all the barrel's surface is available for mass transfer, obtain an expression for the evaporation rate. The fraction of water at the inner surface of the wood is x_{in} and at the outer surface is x_{out}. Write a MATLAB® code and discuss the influence of R, L, λ, D, x_{in}, and x_{out} on the mass transfer rates with appropriate figures.

Solution: It was assumed that the barrel is a perfect cylinder and water diffuses out from all the surfaces. Since the thickness of the wood is much smaller than that of the barrel we may use the rectangular coordinates to simulate water transport through the wood with an equation of continuity:

$$c\frac{\partial x}{\partial t}+\frac{\partial N_w}{\partial z}=R_w.$$

Since $c\partial x/\partial t = 0$ at steady state and $R_w = 0$ (water does not react in the wood) the equation of continuity becomes $dN_w/dz = 0$, implying that N_w is a constant along the z direction. The flux of

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water in wood is $N_w = x(N_w + N_{wood}) - D_w(dc_w/dz)$, which becomes $N_w = -cD_w(dx/dz)$ since only a small amount of water is available in the wood ($x \ll 1$). After combining the final forms of the flux expression and the equation of continuity we will obtain $d^2x/dz^2 = 0$. Upon integration, a moisture profile along the wood will be $x = \mathcal{K}_1 z + \mathcal{K}_2$. Constants $\mathcal{K}_1$ and $\mathcal{K}_2$ may be evaluated from the boundary conditions as: $\mathcal{K}_1 = (x_{out} - x_{in})/\lambda$ and $\mathcal{K}_2 = x_{in}$. We may substitute $dx/dz = (x_{out} - x_{in})/\lambda$ in $N_w = -cD_w(dx/dz)$ and obtain $N_w = cD_w(x_{in} - x_{out})/\lambda$. The total evaporation rate through the barrel is $A_{barrel}N_w = 2\pi R(R + L)cD_w(x_{in} - x_{out})/\lambda$ where A_{barrel} is the total mass transfer area through the barrel. MATLAB® code E.2.1 simulates the effects of the barrel radius, barrel length, barrel wood thickness, numerical value of the diffusivity of water vapor through the barrel wood, and the fraction of the water vapor in the cellar and on the inside surface of the wood on the amounts of water loss from the barrel surface by evaporation (Figures E.2.1.2 through E.2.1.7).

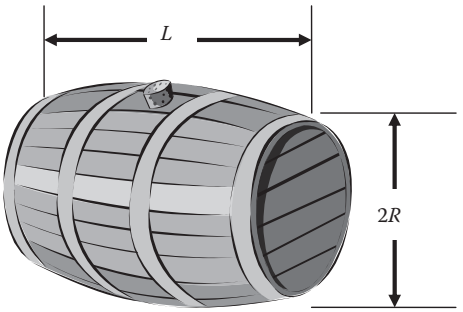


FIGURE E.2.1.1
The wine barrel. Variation of the radius along the longitudinal direction is neglected. Thickness of the wood is λ.

MATLAB® CODE E.2.1

Command Window:

```
clear all
close all

% effect of R on the evaporation rate
L=2; %m
lambda=0.025; % m
xin=0.15;
xout=0.10;
D=5e-6; % D=Dw*c, kg/ms
R1=[0.5: 0.05:1.5]; % m
for i=1:1:length(R1);
A1(i)=2*pi*R1(i)*(L+R1(i))*D*(xin-xout)/lambda; % A=Abarrel*Nw,
kg/s
end
plot(R1,A1, '*-')
ylabel('EVAPORATION RATE (kg/s)');
xlabel('R (m)')

% effect of L on the evaporation rate
R=1; % m
L2=[1:0.05:3]; % m
for k=1:1:length(L2);
```

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```
A2(k)=2*pi*R*(L2(k)+R)*D*(xin-xout)/lambda; % A=Abarrel*Nw, kg/s
end
figure
plot(L2,A2, 'o-')
ylabel('EVAPORATION RATE (kg/s)');
xlabel('L (m)')

% effect of barrel thickness on the evaporation rate
lambda3=[0.01:0.0005:0.03]; % m
for i=1:1:length(lambda3);
A3(i)=2*pi*R*(L+R)*D*(xin-xout)/lambda3(i); % A=Abarrel*Nw, kg/s
end
figure
plot(lambda3,A3, '*-')
ylabel('EVAPORATION RATE (kg/s)');
xlabel('lambda (m)')

% effect of diffusivity on the evaporation rate
D4=[4e-6: 1e-7: 6e-6]; % m2/s
for i=1:1:length(D4);
A4(i)=2*pi*R*(L+R)*D4(i)*(xin-xout)/lambda; % A=Abarrel*Nw, kg/s
end
figure
plot(D4,A4, '*-')
ylabel('EVAPORATION RATE (kg/s)');
xlabel('Diffusivity (kg/ms)')

% effect of xOut on the evaporation rate
xOut5=[0.0:0.01: 0.20]; % fraction of water at the inner side of
the wood
for i=1:1:length(xOut5);
A5(i)=2*pi*R*(L+R)*D*(xin-xOut5(i))/lambda; % A=Abarrel*Nw, kg/s
end
figure
plot(xOut5,A5, '*-')
ylabel('EVAPORATION RATE (kg/s)');
xlabel('xOut (fraction of water at the outside surface of the
wood)')

% effect of xIn on the evaporation rate
xIn6=[0.20: 0.01: 0.30]; % fraction of water at the inner side of
the wood
for i=1:1:length(xIn6);
A6(i)=2*pi*R*(L+R)*D*(xIn6(i)-xout)/lambda; % A=Abarrel*Nw, kg/s
end
figure
plot(xIn6,A6, '^-')
ylabel('EVAPORATION RATE (kg/s)');
xlabel('xIn (fraction of water at the inside surface of the wood)')
```

Figures E.2.1.2 through E.2.1.7, will appear on the screen after running the code.

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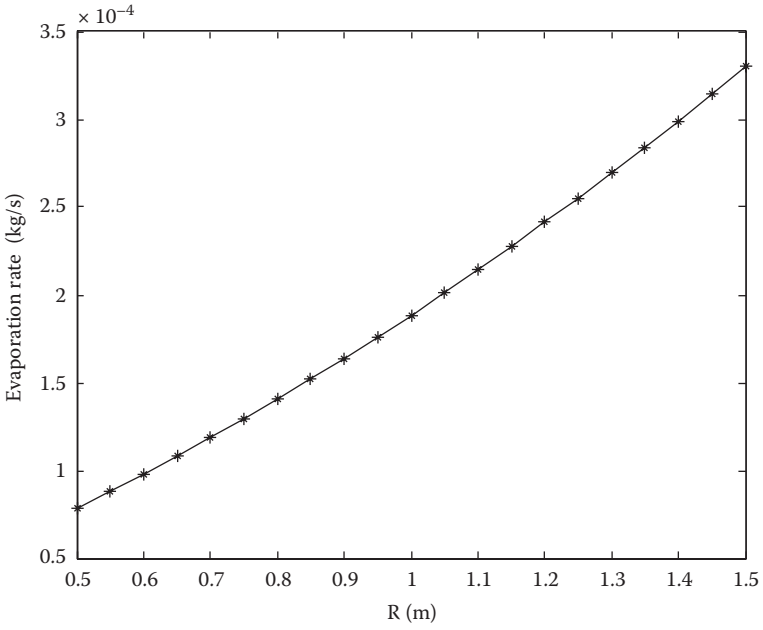


FIGURE E.2.1.2
Effect of the barrel radius on the amount of water lost by evaporation from the barrel surface.

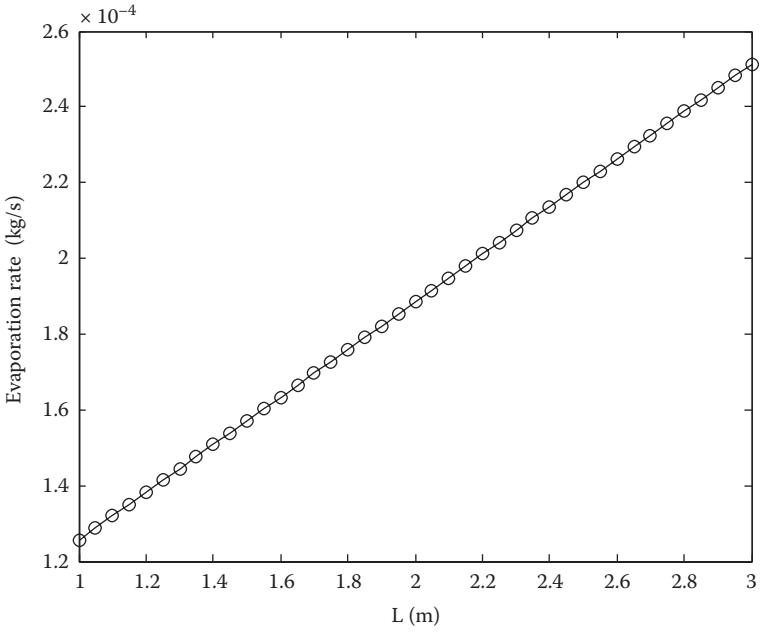


FIGURE E.2.1.3
Effect of the barrel length on the amount of water lost by evaporation from the barrel surface.

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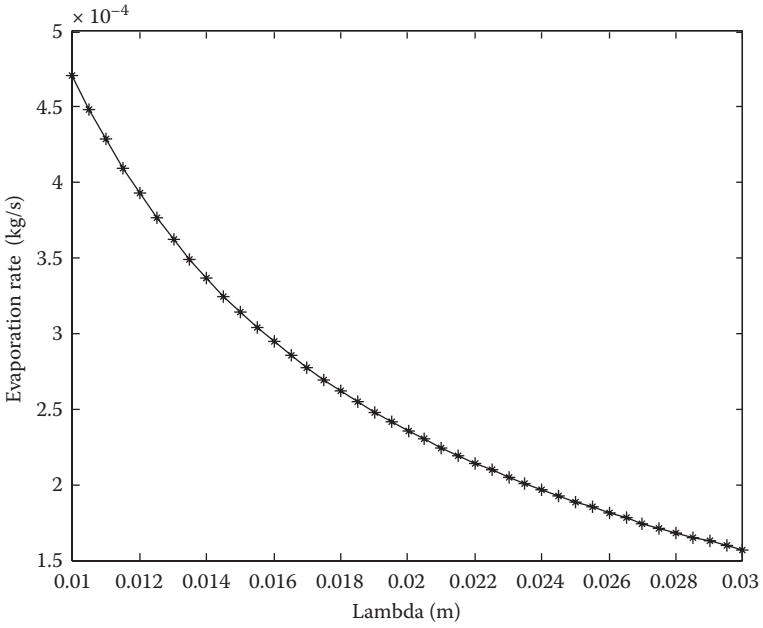


FIGURE E.2.1.4
Effect of the barrel wood thickness on the amount of water lost by evaporation from the barrel surface.

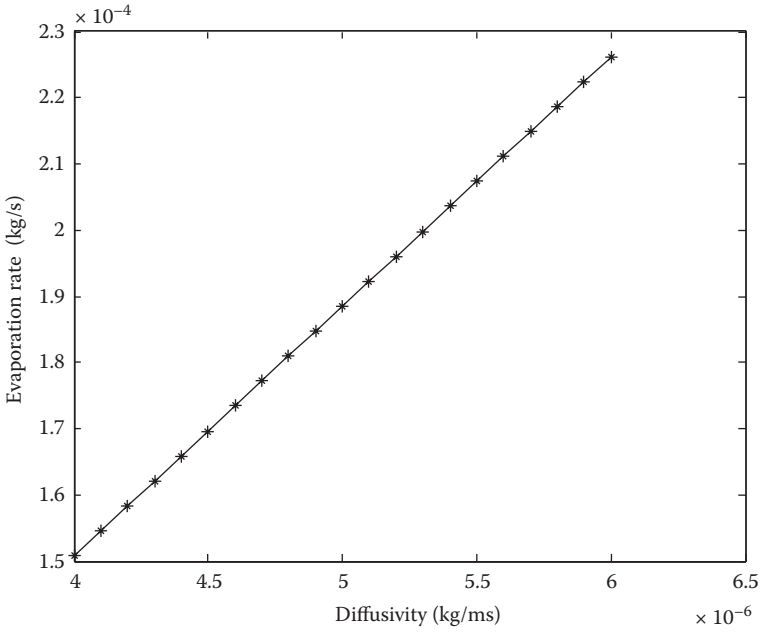


FIGURE E.2.1.5
Effect of the diffusivity on the amount of water lost by evaporation from the barrel surface.

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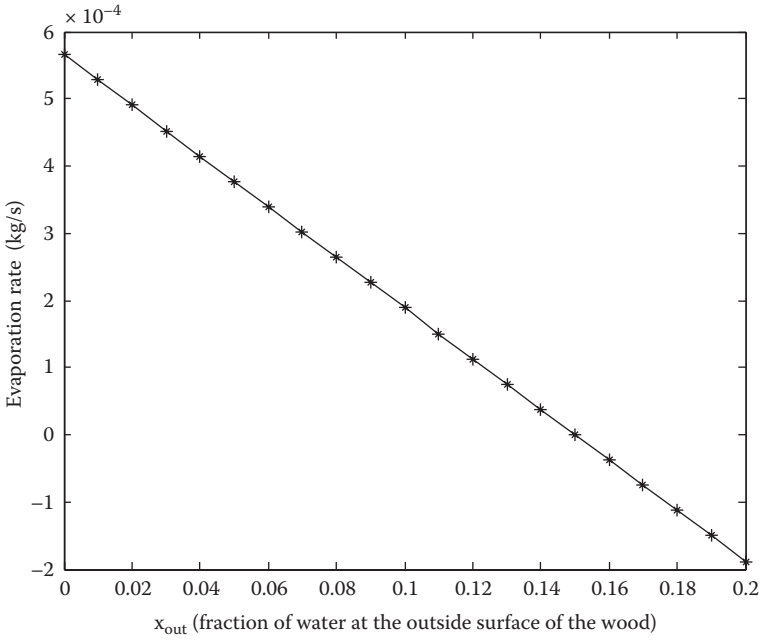


FIGURE E.2.1.6
Effect of x_{out} on the amount of water lost by evaporation from the barrel surface.

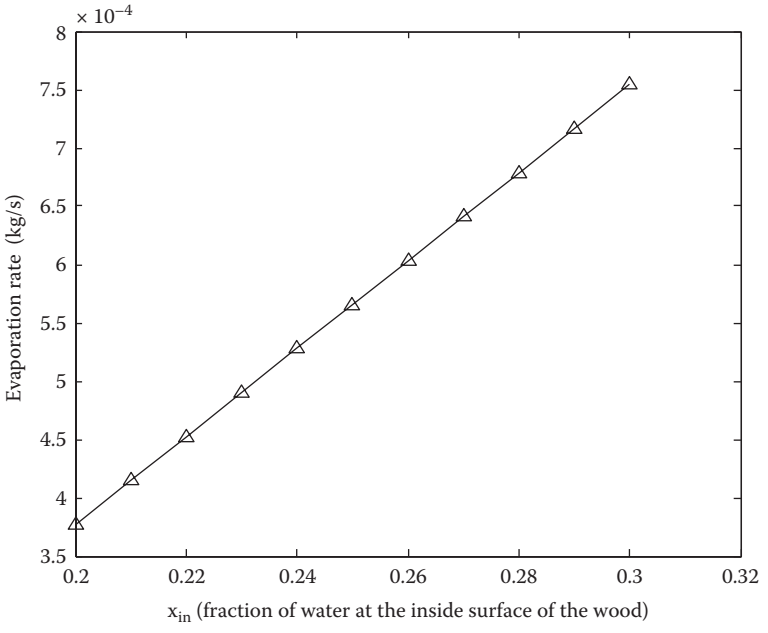


FIGURE E.2.1.7
Effect of x_{in} on the amount of water lost by evaporation from the barrel surface.

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TABLE 2.4

Equation of Energy for Different Coordinate Systems

i) Rectangular coordinates:

$$\frac{\partial T}{\partial t}+v_x\frac{\partial T}{\partial x}+v_y\frac{\partial T}{\partial y}+v_z\frac{\partial T}{\partial z}=\frac{\psi_G^{\bullet}}{\rho c}+\frac{\partial}{\partial x}\left(\alpha\frac{\partial T}{\partial x}\right)+\frac{\partial}{\partial y}\left(\alpha\frac{\partial T}{\partial y}\right)+\frac{\partial}{\partial z}\left(\alpha\frac{\partial T}{\partial z}\right). \tag{2.16}$$

ii) Cylindrical coordinates:

$$\frac{\partial T}{\partial t}+v_r\frac{\partial T}{\partial r}+\frac{v_\theta}{r}\frac{\partial T}{\partial \theta}+v_z\frac{\partial T}{\partial z}=\frac{\psi_G^{\bullet}}{\rho c}+\frac{1}{r}\frac{\partial}{\partial r}\left(r\alpha\frac{\partial T}{\partial r}\right)+\frac{1}{r^2}\frac{\partial}{\partial \theta}\left(\alpha\frac{\partial T}{\partial \theta}\right)+\frac{\partial}{\partial z}\left(\alpha\frac{\partial T}{\partial z}\right). \tag{2.17}$$

iii) Spherical coordinates:

$$\frac{\partial T}{\partial t}+v_r\frac{\partial T}{\partial r}+\frac{v_\theta}{r}\frac{\partial T}{\partial \theta}+\frac{v_\phi}{r\sin\theta}\frac{\partial T}{\partial \phi}=\frac{\psi_G^{\bullet}}{\rho c}+\frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\alpha\frac{\partial T}{\partial r}\right)+\frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\alpha\sin\theta\frac{\partial T}{\partial \theta}\right)+\frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial \phi}\left(\alpha\frac{\partial T}{\partial \phi}\right). \tag{2.18}$$

2.3 Equation of Energy

After substituting $\psi = \rho c_p T$, Equation 2.1 becomes

$$\frac{\partial(\rho\, c_p T)}{\partial t}+\nabla\cdot(\rho\, c_p T\, \mathbf{v})=\psi_G^{\bullet}+(\nabla\cdot\delta\,\nabla\rho\, c_p T). \tag{2.15}$$

The generation term $\psi_G^{\bullet}$ accounts for heat generation by viscous dissipation in the microwave field, radiation, and so on. Equation 2.15, for incompressible fluids, may be expanded for various coordinate systems as given in Table 2.4.

2.4 Equation of Motion

The equation of motion is more complicated than the equations of energy and continuity, because in momentum balance ψ is a vector composed of components ψ_x and ψ_y. When ψ_z is constant and after substituting $\psi_x = \rho v_x$ and $\delta = \nu$ in Equations 2.1 and 2.2, the x component of the momentum balance becomes

$$\frac{\partial v_x}{\partial t}+(\nabla\cdot\mathbf{v})v_x=\frac{\psi_{Gx}^{\bullet}}{\rho}+(\nabla\cdot\psi\nabla v_x), \tag{2.19}$$

and

$$\frac{\partial v_x}{\partial t}+(\nabla\cdot\mathbf{v})v_x=\frac{\psi_{Gx}^{\bullet}}{\rho}+\mathbf{v}\nabla^2 v_x. \tag{2.20}$$

It should be noticed that $\nabla\cdot\mathbf{v}=0$ when ρ is constant. Equations for the y and z components of the momentum balance may be written similarly as Equations 2.19 and 2.20.

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TABLE 2.5

Navier–Stokes Equation for Different Coordinate Systems

i) The x component in rectangular coordinates:

$$\frac{\partial v_x}{\partial t}+v_x\frac{\partial v_x}{\partial x}+v_y\frac{\partial v_x}{\partial y}+v_z\frac{\partial v_x}{\partial z}=-\frac{1}{\rho}\frac{\partial p}{\partial x}+g_x+\nu\left(\frac{\partial^2 v_x}{\partial x^2}+\frac{\partial^2 v_x}{\partial y^2}+\frac{\partial^2 v_x}{\partial z^2}\right) \tag{2.21}$$

ii) The r component in cylindrical coordinates:

$$\frac{\partial v_r}{\partial t}+v_r\frac{\partial v_r}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_r}{\partial \theta}+v_z\frac{\partial v_r}{\partial z}-\frac{v_\theta^2}{r}=-\frac{1}{\rho}\frac{\partial p}{\partial r}+g_r+\nu\frac{\partial^2 v_r}{\partial r^2}+\frac{\nu}{r}\frac{\partial v_r}{\partial r}-\nu\frac{v_r}{r^2}+\frac{\nu}{r^2}\frac{\partial^2 v_r}{\partial \theta^2}-\frac{2\nu}{r}\frac{\partial v_\theta}{\partial \theta}+\nu\frac{\partial^2 v_r}{\partial z^2}. \tag{2.22}$$

iii) The r component in spherical coordinates:

$$\begin{aligned}&\frac{\partial v_r}{\partial t}+v_r\frac{\partial v_r}{\partial r}+\frac{v_\theta}{r}\frac{\partial v_r}{\partial \theta}+\frac{v_\phi}{r\sin\theta}\frac{\partial v_r}{\partial \phi}-\frac{v_\theta^2}{r}-\frac{v_\phi^2}{r}\\&\quad=-\frac{1}{\rho}\frac{\partial p}{\partial r}+g_r+\frac{\nu}{r^2}\left[\frac{\partial}{\partial r}\left(r^2\frac{\partial v_r}{\partial r}\right)\right]+\left(\frac{\nu}{r^2\sin\theta}\right)\left[\frac{\partial}{\partial \theta}\left(\sin\theta\frac{\partial v_r}{\partial \theta}\right)\right]+\left(\frac{\nu}{r^2\sin^2\theta}\right)\left(\frac{\partial^2 v_r}{\partial \phi^2}\right).\end{aligned} \tag{2.23}$$

When the rate of momentum generation is proportional to the pressure gradient and x component of the gravitational acceleration; that is, $\psi_{Gx}^{\bullet}=-(\partial p/\partial x)+\rho g_x$, Equation 2.19 becomes the Navier–Stokes equation and its expansion for different coordinate systems is given in Table 2.5.

2.5 Theories for Liquid Transport Coefficients

Although viscosity, thermal conductivity, and mass diffusion coefficients are defined with empirical relations in Equations 2.5 through 2.7, there are theoretical explanations to these equations for simple systems. Foods are either liquid or solid or both liquid and solid. Theoretical models for viscosity, thermal conductivity, and mass diffusion coefficients are available for pure liquids or suspension of fine particles. Theoretical models are rarely used to evaluate values of μ, k, or D, empirical models or the actual experimental data are preferred in process calculations.

2.5.1 Eyring's Theory of Liquid Viscosity

In a pure liquid at rest, the individual molecules are considered to be confined in a large *cage* formed by its nearest neighbors (Figure 2.2). This cage represents an energy barrier of $\Delta G^{\#}/N_{Av}$ ($\Delta G^{\#}$ = energy barrier, N_{Av} = Avagadro number). The Glasstone, Laidler, and Eyring theory (1941) suggests that the liquid at rest undergoes rearrangements in which one molecule at a time is transferred to an adjoining *hole*. The rate (frequency) of jumps in each direction is

$$k=\left(\frac{\kappa T}{h}\right)\exp\left(-\frac{\Delta G_0^*}{RT}\right), \tag{2.24}$$

where h is the Planck constant, k is the Boltzman constant, T is temperature, $\Delta G_o^{\#}$ is the energy barrier (molar free energy of activation), and R is the gas constant.

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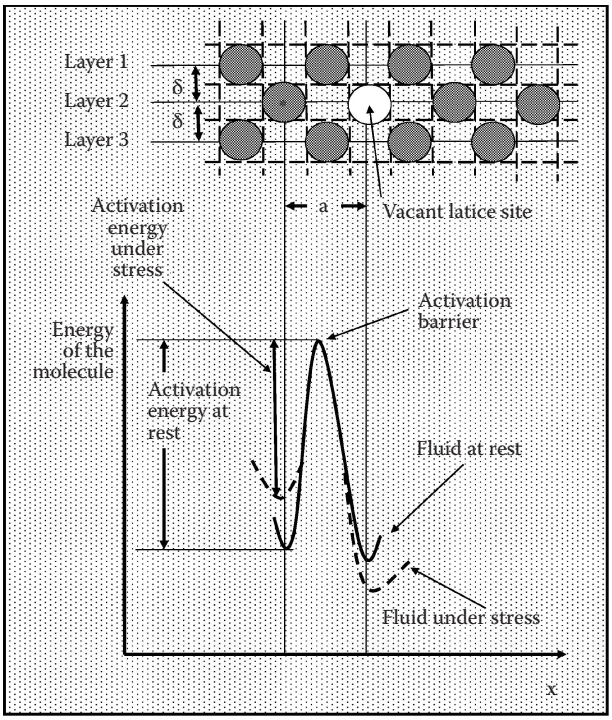


FIGURE 2.2
Illustration of the escape process in flow of a liquid. Molecule marked with * must pass over the activation barrier to reach the vacant site.

When liquid moves in x direction with velocity gradient dv_x/dy, the energy barrier is distorted and the frequency of molecular rearrangements increases. The distorted energy barrier is

$$-\Delta G^{\#} = -\Delta G_o^{\#} \pm \frac{a}{\delta}\frac{\sigma_{yx}V_m}{2}, \tag{2.25}$$

where $\Delta G^{\#}$ is the distorted mean free energy of activation, a is the length of molecular jump, δ is the distance between the molecular layers, V_m is the volume of one mole of liquid, σ_{xy} is the applied shear stress and $(a/\delta)(\sigma_{xy}V_m/2)$ is the approximation of the work done on the molecules as they move to the top of the energy barriers with the applied shear stress. The minus sign is employed to describe the movement of the molecules against the shear stress. When $(\sigma_{xy}aV_m/\delta RT) \ll 1$ and $\delta/a = 1$ product of the net frequency of jumps and a/δ is the shear rate:

$$-\frac{dv_x}{dt} = \frac{\kappa T}{h}\left(-\Delta G_o^{\#}/RT\right)\frac{\sigma_{xy}V_m}{2RT}, \tag{2.26}$$

where h = Planck constant. Equation 2.26 is Newton's Law of viscosity with (Bird, Stewart, and Lightfoot 2007)

$$\mu = \frac{N_{Av}h}{V_m}e^{\Delta G_o^{\#}/RT}. \tag{2.27}$$

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Temperature effects on liquid viscosity may be expressed with the Arrhenius expression:

$$\mu = \mu_0 e^{(E_a/RT)}, \tag{2.28}$$

where μ_0 is the preexponential constant, E_a is the activation energy, and R is the gas constant.

Example 2.2: Kinetic Compensation Relations for the Viscosity of Fruit Juices

Gibbs free energy of activation at rest may be expressed as (Özilgen and Bayindirli 1992)

$$\Delta G_o^{\#} = \Delta H^{\#} - T\Delta S^{\#},$$

where $\Delta H^{\#}$ = activation enthalpy and $\Delta S^{\#}$ = activation entropy. After substituting this expression, Equation 2.27 becomes

$$\mu = \frac{N_{Av}h}{V_m}\exp\left(\Delta H^{\#}/RT\right)\exp\left(-\Delta S^{\#}/RT\right).$$

Comparing this equation with Equation 2.28 requires

$$E_a = \Delta H^{\#} + RT$$

and

$$\mu_0 = \frac{N_{Av}h}{2.72V_m}\exp\left(-\Delta S^{\#}/RT\right).$$

In the experiments performed under slightly different experimental conditions, generally linear relationships are observed between the activation energy E_a and the frequency factor μ_0, and the activation enthalpy $\Delta H^{\#}$ and the activation entropy $\Delta S^{\#}$:

$$\ln\mu_0 = \alpha E_a + \beta$$

and

$$\Delta S^{\#} = \delta\Delta H^{\#} + \phi.$$

These equations are called the compensation relations. Since μ_0 and $\Delta S^{\#}$ and E_a and $\Delta H^{\#}$ are interrelated, the validity of either equation implies that the other one is also valid. Although E_a, μ_0, $\Delta H^{\#}$, and $\Delta S^{\#}$ varies with the experimental conditions, α, β, δ, and ϕ are constants through the range of the experiments. A sample set of compensation relations are given in Figure E.2.2.

The compensation relations may be used for interpolation in process design when data are available in the close range, but not under the exactly required conditions (Özilgen and Özilgen 1996). MATLAB® code E.2.2 plots the kinetic compensation model for the viscosity of fruit juices and compares it with the data (Figure E.2.2).

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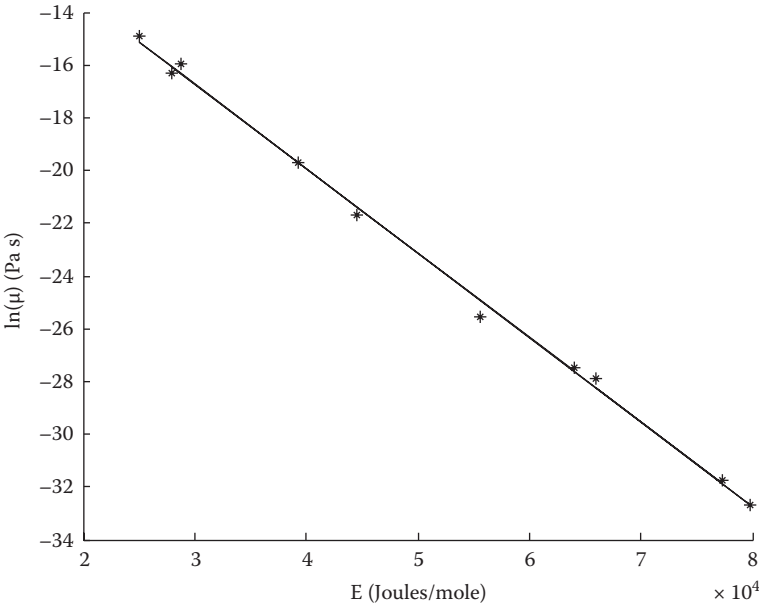


FIGURE E.2.2
Variation of parameter $\ln(\mu_0)$ of apple juice with activation energy. Equation of the line: $\ln(\mu_0) = -7.09 - 3.19 \times 10\text{-}4E_a$. Standard error ($s_e = 0.3054$) and correlation coefficient ($r = 0.9988$) are calculated by using tools of MATLAB®. Standard error was about 2% of the magnitude of the measurements. (From Özilgen, M. and Bayindirli, L., *Journal of Food Engineering*, 17, 143–51, 1992.)

MATLAB® CODE E.2.2

Command Window:

```
clear all
close all

% introduce the data
mu=[8.09e-8 1.61e-14 7.95e-13 6.55e-15 3.38e-7 1.18e-7 2.7e-9
3.91e-10 7.93e-12 1.15e-12];
E = [2.8e4 7.73e4 6.6e4 7.98e4 2.51e4 2.88e4 3.93e4 4.46e4 5.56e4
6.4e4];

% plot the data
ylabel('ln(mu) (Pa s)');
xlabel('E (Joules/mole)');
hold on, plot(E,log(mu),'k*');

% find the best fitting line equation
f = polyfit(E,log(mu),1);
y = polyval(f,E);

% plot the model
plot(E, y);
```

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```
% find the correlation coefficient and the standard error
rmatrix=corrcoef(E,log(mu));
   r=rmatrix(1,2)
for i=1:length(E);
d(i) = (log(mu(i))-(f(2)+f(1)*E(i)))^2;
end;
Se = sqrt(sum(d)/length(E))
```

The following lines and Figure E.2.2. will appear in the screen after running the code:

```
r =
   -0.9988

Se =
    0.3054
```

2.5.2 Thermal Conductivity of Liquids

Thermal conductivity of monatomic low density gases is $k = (1/3)c_v u\lambda$ (c_v = specific heat, u = mean molecular velocity, λ = collision length). This equation may be modified for liquids after assuming that pure liquid molecules are arranged in cubic lattice, energy is transferred from one lattice plane to the next, the heat capacity of monatomic liquids at constant volume is about the same as for a solid at high temperature and the mean molecular speed is the same as the sonic velocity v_s and the distance that energy travels per single collision is the same as the lattice spacing $\left(\bar{V}/N_{Av}\right)^{1/2}$ as (Bird, Stewart, and Lightfoot 2007)

$$k = 3\left(\frac{N_{Av}}{\bar{V}}\right)^{1/3}\kappa v_s, \tag{2.29}$$

where $\bar{V}$ is specific volume.

2.5.3 Hydrodynamic Theory of Diffusion in Liquids

Diffusion of a single particle or solute molecule through a stationary medium is calculated after making force balance around the particle as

$$D_{AB} = \kappa T\frac{v}{F}, \tag{2.30}$$

where v is the velocity of the particle, F is the drag force on the particle, and v/F is the mobility of the particle. When $N_{re} \ll 1$ and there is no tendency for fluid to slip at the surface of the diffusing particle:

$$F_A = 6\pi\mu v d_p, \tag{2.31}$$

where d_p is the effective particle diameter. Substituting Equation 2.31 into Equation 2.30 gives

$$D_{AB} = \frac{\kappa T}{6\pi\mu v d_p}. \tag{2.32}$$

Equation 2.32 is called the Stokes–Einstein equation.

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When there is no tendency for the fluid to stick to the surface of the diffusing particle then Equations 2.31 and 2.32 becomes

$$F_A = 4\pi\mu v d_p, \tag{2.33}$$

and

$$D_{AB} = \frac{\kappa T}{4\pi\mu v d_p}. \tag{2.34}$$

2.5.4 Eyring's Theory of Liquid Diffusion

As explained for viscosity, Eyring's theory assumes that the liquid molecules are entrapped into a *cage* made by neighbor molecules. The molecule is expected to exceed an activation barrier to jump into the neighboring *holes* with a first-order reaction. A constant average distance is involved into each jump. Derivation of the expression for diffusivity is very similar to that of the viscosity. The resulting equation is

$$D_{AB} = \frac{\kappa T}{\mu}\left(\frac{N_{Av}}{V}\right)^{1/3}. \tag{2.35}$$

Temperature effects on diffusivity may be described with the Arrhenius expression:

$$D = D_0 \exp\left\{-\frac{E_a}{RT}\right\}, \tag{2.36}$$

where D_0 = preexponential constant.

Example 2.3: Temperature Effects on Diffusivity of Water in Starch

Parameters E_a and D_0 were given for diffusion in the hydrated amylopectin (fraction of starch) and potatoes as (Özilgen 1993)

Diffusion System	D_0 (m²/s)	E_a (J/mol)
Water in hydrated amylopectin	3.37×10^{-6}	2.55×10^4
Glucose in potato tissue	1.78×10^{-6}	2.03×10^4
Potassium in potato tissue	4.08×10^{-6}	2.09×10^4

a. Compare the diffusivities of water in amylopectin, glucose in potato tissue, and potassium in potato tissue at 65°C.

Solution: $D = D_0 \exp\{-E_a/RT\}$ and $R = 8.314$ J/mol K after substituting the numbers we will have

Diffusion System	D (m²/s)
Water in hydrated amylopectin	2.04×10^{-9}
Glucose in potato tissue	1.34×10^{-9}
Potassium in potato tissue	2.40×10^{-9}

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Water molecules are smaller than the potassium molecules and both of them are smaller than the glucose molecules; potato tissue is cellular, and amylopectin has a simpler structure. The results indicate that the diffusivity of smaller molecules is greater in structurally simpler systems.

b. Compare the diffusivity of potassium in potato tissue at 65°C and 90°C.

Solution: After substituting the numbers in Equation 2.36 we will have

Diffusion System	D (m^2/s)
Potassium in potato tissue at 65°C	2.40×10^{-9}
Potassium in potato tissue at 90°C	4.00×10^{-9}

The results show a 1.67-fold increase in D with 25°C increase in *T*.

Example 2.4: Compensation Relations for Diffusivity of Water in Starch

The compensation relations, similarly as those of viscosity, applies to diffusivity:

$$\ln D_0 = \alpha E_a + \beta.$$

These equations may also be used for interpolation in process design (Özilgen and Özilgen 1996). Figure E.2.4 describes a variation of ln D_0 with the activation energy in a different media. MATLAB® code E.2.4 plots the kinetic compensation model for diffusivity of water in starch and compares it with the data (Figure E.2.4).

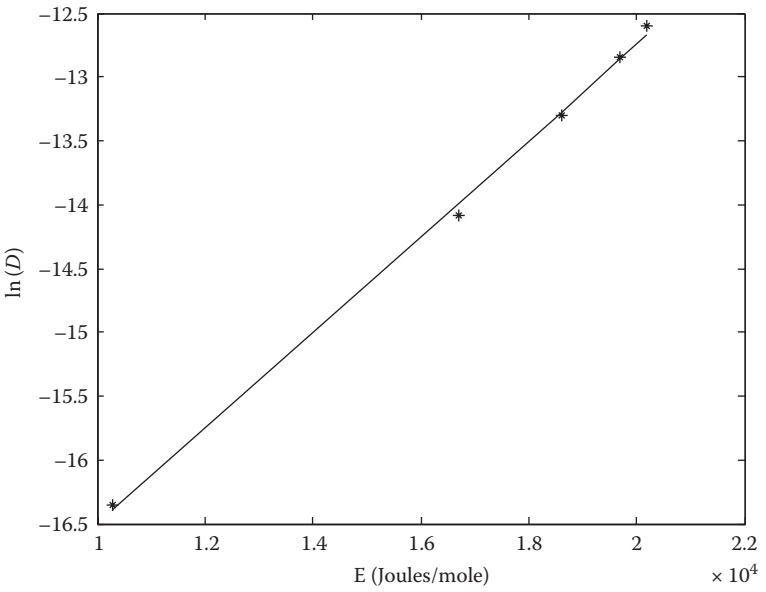


FIGURE E.2.4
Variation of parameter ln(D_0) with activation energy during diffusion of water in hydrated. Standard error (s_e = 0.0572) and correlation coefficient (r = 0.9991) are calculated by using MATLAB® tools. Standard error was less than 0.5% of the mean value of ln(D). (From Özilgen, M., *Starch*, 45, 48–51, 1993.)

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MATLAB® CODE E. 2.4

Command Window:

```
clear all
close all
format compact

% introduce the data
lnDdata = [-12.60 -12.85 -13.30 -14.08 -16.35];
Edata= [2.02e4 1.97e4 1.86e4 1.67e4 1.03e4];

% plot the data
plot(Edata,lnDdata,'*'); hold on
ylabel('ln(D)');
xlabel('E (Joules/mole)');

% find the equation of the best fitting line
f = polyfit(Edata,lnDdata,1);
lnDmodel= polyval(f,Edata);

% plot the model
plot(Edata, lnDmodel);

% find the correlation coefficient and the standard error
rmatrix=corrcoef(Edata,lnDmodel);
  r=rmatrix(1,2)

for i=1:length(Edata);
  d(i) = (lnDdata(i)-(f(2)+f(1)*Edata(i)))^2;
end;
Se = sqrt(sum(d)/length(Edata))
```

The following lines and Figure E.2.4 will appear on the screen after running the code:

```
r =
  0.9991

Se =
  0.3657
```

2.6 Analytical Solutions to Ordinary Differential Equations

In most transport phenomena problems we choose an equation from Tables 2.3, 2.4, and 2.5, to describe the system, then simplify it by eliminating the negligible terms. The next step is solving this differential equation. *Differential equation*s involve derivatives or differentials of one or more dependent variables with respect to one or more independent variables. If the dependent variable is a function of one independent variable, the differential equation involves only ordinary derivatives and is called an *ordinary differential equation*. If the dependent variable is a function of two or more independent variables,

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its derivatives with respect to each independent variable are called partial derivatives, and the equation is called a *partial differential equation*. When we simplify the equation of continuity (Table 2.3) and if concentration of species A remains as the single dependent variable as a function of the independent variable of the location in x direction and time (i.e., $c_A = c_A(t,x)$), the final differential equation will be a partial differential equation. If we can make a steady state assumption and neglect the time dependence of concentration (i.e., $c_A = c_A(x)$), the differential equation will be converted into an ordinary differential equation. *Solution* is a relation between the variables, which involves no derivatives and satisfies the original differential equation. If this relation contains unknown constants, then it is called a general solution. The specifications of the problem may require the dependent and the independent variables to satisfy certain requirements at some geometric boundaries, these requirements are called the *boundary conditions*. The relation between the dependent and the independent variables at the beginning of the process is called the *initial condition*. Since the solution should also be valid at the geometric boundaries and at the beginning of the process, the boundary and the initial conditions may be used to evaluate the unknown constants of the general solution. When all the unknown constants are obtained we will have the *complete (particular) solution*.

The order of the highest order derivative is called the *order of the differential equation*. The power of the highest order derivative after the equation is cleared of fractions and roots in the dependent variable and its derivatives is called the *degree of the differential equation*. If every dependent variable and every derivative are of the first degree and there are no products of the dependent variable with the derivatives, the differential equation is called a *linear differential equation*. If all the terms in the equation contains the dependent variable and its derivatives, the differential equation is *homogeneous*.

Example 2.5: Characterization of a Differential Equation

Characterize the differential equation

$$\frac{d^2y}{dx^2} = f(x)\left[1+\left(\frac{dy}{dx}\right)^2\right]^{3/2}.$$

Solution: The highest order derivative is d^2y/dx^2; therefore, this is a second-order differential equation. We may clear this differential equation from the fractions in the dependent variable and its derivatives as $(d^2y/dx^2)^2 = f(x)[1+(dy/dx)^2]^3$, the power of the highest order derivative is 2 and therefore this is a second degree differential equation. The equation is nonlinear because it contains a second-order term $(d^2y/dx^2)^2$, and another nonlinear term $[1+(dy/dx)^2]^3$. This is a nonhomogeneous equation, because an $f(x)$ term will appear after expanding the right-hand side of the equation and it does not have a dependent variable or its derivatives. This is an ordinary differential equation, because dependent variable y is a function of a single independent variable x.

Techniques for solving the ordinary differential equations are discussed in the classical differential equation books (i.e., Ross 1984). The solutions are usually time-consuming and the techniques may be forgotten if not used for a while. We are very lucky in the sense that only limited types of differential equations arise after simplifying the general transport equations in most of the food engineering analysis, and we may find the general solutions to those differential equations in Table 2.6.

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TABLE 2.6

General Solutions to Common Ordinary Differential Equations

i) First order, first degree

Separable first order, first degree equation

$$g(y)dx + f(x)dy = 0$$

Solution: $\int_{x_1}^{x_2} dx/f(x) = -\int_{y_1}^{y_2} dy/g(y)$

Exact first order, first degree equation

$$M(x,y)dx + N(x,y)dy = 0 \text{ with } \frac{\partial M}{\partial y} = \frac{\partial N}{\partial x}$$

Solution: $$-\left[\int^{x} M dx\right]_{y} + \left[\int^{y} R dy\right]_{x} = C \text{ with } R = N - \frac{\partial}{\partial y}\int^{x} M dx$$

or

$$-\left[\int^{y} N dy\right]_{x} + \left[\int^{x} S dx\right]_{y} = C \text{ with } S = M - \frac{\partial}{\partial x}\int^{y} N dy$$

Homogeneous first order, first degree equation

$M(x,y)dx + N(x,y)dy = 0$ with $M(\lambda x, \lambda y) = \lambda^n M(x,y)$ and $N(\lambda x, \lambda y) = \lambda^n N(x,y)$

where λ is a constant, then M and N are homogeneous of degree n

Solution: Substitute $y = \nu x$, then the equation becomes separable

Linear first order, first degree equation

$$\frac{dy}{dx} + P(x)y = Q(x)$$

Solution: $$y = \exp\left\{-\int^{x} P dx\right\}\left(\int^{x} Q \exp\left\{\int^{x} P dx\right\} dx\right) + C\exp\left\{-\int^{x} P dx\right\}$$

ii) First order, special ordinary differential equations

Bernoulli's equation

$$\frac{dy}{dx} + P(x)y = Q(x)y^n \text{ with } n \neq 1$$

Solution: Substitute $\nu = y^{n-1}$, then equation becomes linear

$$\frac{d\nu}{dx} + P_1(x)\nu = Q_1(x)$$

where $P_1(x) = (1-n)P(x)$ and $Q_1(x) = (1-n)Q(x)$

Riccati equation

$$\frac{dy}{dx} + P(x)y + Q(x)y^2 = R(x)$$

Solution: Substitute $y = \frac{du}{dx}\frac{1}{Q(x)u}$ equation becomes linear $\frac{d^2u}{dx^2} + P(x)\frac{du}{dx} + R(x)Q(x)u = 0$

iii) Simultaneous linear equations

$$(\alpha_{11}D + \beta_{11})x_1 + (\alpha_{12}D + \beta_{12})x_2 + (\alpha_{13}D + \beta_{13})x_3 = \gamma_1(t)$$

$$(\alpha_{21}D + \beta_{21})x_1 + (\alpha_{22}D + \beta_{22})x_2 + (\alpha_{23}D + \beta_{23})x_3 = \gamma_2(t)$$

$$(\alpha_{31}D + \beta_{31})x_1 + (\alpha_{32}D + \beta_{32})x_2 + (\alpha_{33}D + \beta_{33})x_3 = \gamma_3(t)$$

where $D = d/dt$, α's and β's are constants

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TABLE 2.6 (CONTINUED)

General Solutions to Common Ordinary Differential Equations

Solution: Equations are transformed into single linear ordinary differential equations as $\Delta x_1 = Dx_1$, $\Delta x_2 = Dx_2$, and $\Delta x_3 = Dx_3$

where $\Delta = \begin{vmatrix} (\alpha_{11}D+\beta_{11}) & (\alpha_{12}D+\beta_{12}) & (\alpha_{13}D+\beta_{13}) \\ (\alpha_{21}D+\beta_{21}) & (\alpha_{22}D+\beta_{22}) & (\alpha_{23}D+\beta_{23}) \\ (\alpha_{31}D+\beta_{31}) & (\alpha_{32}D+\beta_{32}) & (\alpha_{33}D+\beta_{33}) \end{vmatrix}$ $\mathcal{D}x_1 = \begin{vmatrix} \gamma_1(t) & (\alpha_{12}D+\beta_{12}) & (\alpha_{13}D+\beta_{13}) \\ \gamma_2(t) & (\alpha_{22}D+\beta_{22}) & (\alpha_{23}D+\beta_{23}) \\ \gamma_3(t) & (\alpha_{32}D+\beta_{32}) & (\alpha_{33}D+\beta_{33}) \end{vmatrix}$

$\mathcal{D}x_2 = \begin{vmatrix} (\alpha_{11}D+\beta_{11}) & \gamma_1(t) & (\alpha_{13}D+\beta_{13}) \\ (\alpha_{21}D+\beta_{21}) & \gamma_2(t) & (\alpha_{23}D+\beta_{23}) \\ (\alpha_{31}D+\beta_{31}) & \gamma_3(t) & (\alpha_{33}D+\beta_{33}) \end{vmatrix}$ $\mathcal{D}x_3 = \begin{vmatrix} (\alpha_{11}D+\beta_{11}) & (\alpha_{12}D+\beta_{12}) & \gamma_1(t) \\ (\alpha_{21}D+\beta_{21}) & (\alpha_{22}D+\beta_{22}) & \gamma_2(t) \\ (\alpha_{31}D+\beta_{31}) & (\alpha_{32}D+\beta_{32}) & \gamma_3(t) \end{vmatrix}$

iv) First order, higher degree differential equations

Solvable for *y*

$$y = f\left(x, \frac{dy}{dx}\right) \quad \frac{dy}{dx} = P = \frac{\partial f}{\partial x} + \frac{\partial f}{\partial P}\frac{\partial P}{\partial x} \quad y = \int^x P dx + C$$

Solvable for *x*

$$y = f\left(y, \frac{dy}{dx}\right) \quad \frac{dy}{dx} = \frac{1}{P} = \frac{\partial f}{\partial y} + \frac{\partial f}{\partial P}\frac{\partial P}{\partial y} \quad x = \int^y \frac{1}{P} dy + C$$

v) Second order, linear differential equations

Second order homogeneous linear differential equations with constant coefficients

$$\frac{d^2y}{dx^2} + \alpha_1 \frac{dy}{dx} + \alpha_2 y = 0$$

calculate $\lambda_{1,2} = \dfrac{-\alpha_1 \pm \sqrt{\alpha_1^2 - 4\alpha_2}}{2}$

Solutions:

i) $\lambda_1 \neq \lambda_2$ real numbers $y = C_1 \exp\{\lambda_1 x\} + C_2 \exp\{\lambda_2 x\}$
ii) $\lambda_1 = \lambda_2$ real numbers $y = (C_1 + C_2 x)\ \{\lambda_2 x\}$
iii) $\lambda_{1,2} = a \pm ib$ imaginary numbers $y = e^{ax}\ [C_1 \sin(bx) + C_2 \cos(bx)]$
iv) With higher order equations assume a solution $y = Ce^{\lambda x}$, substitute in the differential equation and obtain the characteristic equation to solve λ

Special cases

a) $\alpha_1 = 0$, $\alpha_2 = \lambda^2$ $y = C_1 \exp\{\lambda_1 x\} + C_2 \exp\{\lambda_2 x\}$
b) $\alpha_1 = 0$, $\alpha_2 = -\lambda^2$ $y = C_1 \sinh(x) + C_2 \cosh(x)$

Second order nonhomogeneous linear differential equations with constant coefficients

$$\frac{d^2y}{dx^2} + \alpha_1 \frac{dy}{dx} + \alpha_2 y = r(x)$$

Solution:

$y = y_h + y_p$
y_h = homogeneous solution is found as shown above
y_p = particular solution, may be found with the method of undetermined coefficients:
Assume particular solution $y_p(x)$ according to $r(x)$, then substitute $y_p(x)$ in the equation and determine the unknown coefficients (α) after equating the coefficients of the equal power terms on both sides.

$r(x)$	$y_p(x)$ (assumed solution)
kx^n	

(*Continued*)

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TABLE 2.6 (CONTINUED)

General Solutions to Common Ordinary Differential Equations

$a_1x^n + a_2x^{n-1} + \ldots + a_{n-1}x + a_n$	
ke^{px}	
ae^{px}	
$k\cos(qx)$ or $k\sin(qx)$	
$\alpha_1\sin(qx) + \alpha_1\cos(qx)$	
Cauchy–Euler equation	
$\alpha_0x^2\frac{d^2y}{dx^2} + \alpha_1x\frac{dy}{dx} + \alpha_2y = h(x)$	**Solution:** substitute $x = e^t$, then equation becomes linear $\frac{d^2y}{dt^2} + \beta_1\frac{dy}{dx} + \beta_2y = H(t)$ where $\beta_1 = \frac{\alpha_1 - \alpha_0}{\alpha_0}$, $\beta_2 = \frac{\alpha_2}{\alpha_0}$, $H(t) = \frac{h(e^t)}{\alpha_0}$
Contains no *dy/dx* and no *x*	
$d^2y/dx^2 = f(y)$	**Solution:** substitute $\frac{dy}{dx} = P$, $\frac{d^2y}{dx^2} = \frac{dP}{dx}$, $\frac{dP}{dx} = P\frac{dP}{dy} = f_1(y)$ then original equation becomes $\int^P \frac{dP}{f_1(P)} - x = C_1$, since $dy/dx = P$ integrate once more to obtain the solution $\int^y \frac{dy}{f_2(y)} - y = C_2$
Contains no *x* and no *y*	
$d^2y/dx^2 = f(dy/dx)$	**Solution:** substitute $dy/dx = P$, $d^2y/dx^2 = dP/dx = f_1(P)$, then original equation becomes $\int^P PdP - \int^y f_1(y)dy = C_1$, since $dy/dx = P$ integrate once more to obtain the solution
vi) Second order, nonlinear differential equations	
Contains no *y* $f\left(\frac{d^2y}{dx^2}, \frac{dy}{dx}, x\right) = 0$	a. Substitute $dy/dx = P$ and $d^2y/dx^2 = dP/dy$ in $f(d^2y/dx^2, dy/dx, x) = 0$ b. Rearrange $f(dP/dx, P, x) = 0$ to obtain $dP/dy = f_2(P, x)$ c. Solve for P to obtain $P = f_3(x)$ d. Integrate $P = dy/dx$ to obtain $y = \int^x f_3(x)dx + C$
Contains no *x* $f\left(\frac{d^2y}{dx^2}, \frac{dy}{dx}, y\right) = 0$	e. Substitute $dy/dx = P$ and $d^2y/dx^2 = dP/dy$ f. Solve $f(dP/dx, P, y) = 0$ for P to obtain $P = f_1(y)$. g. Since $P = dy/dx$ the final solution is $\int^y dy/f_1(y) - x = C$

Example 2.6: Heat Transfer in a Continuous Plug Flow Sterilization Reactor

In a continuous plug flow (Chapter 3.6) sterilization process milk enters into a heating tube at a constant temperature T_O and temperature changes along the flow direction only.

a. Obtain the governing ordinary differential equation of heat transfer.

Solution: The equation of energy in cylindrical coordinates is

$$\frac{\partial T}{\partial t} + v_r\frac{\partial T}{\partial r} + \frac{v_\theta}{r}\frac{\partial T}{\partial \theta} + v_z\frac{\partial T}{\partial z} = \frac{\Psi_G^{\bullet}}{\rho c} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\alpha\frac{\partial T}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \theta}\left(\alpha\frac{\partial T}{\partial \theta}\right) + \frac{\partial}{\partial z}\left(\alpha\frac{\partial T}{\partial z}\right). \quad (2.17)$$

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The following simplifications may be made:

$\frac{\partial T}{\partial t} = 0$ (steady state)

$v_r = v_\theta = 0$ (no flow in r and q directions)

$\psi_G^{\bullet} =$ (no heat generation)

$v_z \frac{\partial T}{\partial z} >> \frac{\partial}{\partial z}\left(\alpha \frac{\partial T}{\partial z}\right)$ (in z direction heat transfer with conduction is much smaller than heat transfer with convection).

Equation 2.17 becomes

$$v_z \frac{\partial T}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\alpha \frac{\partial T}{\partial r}\right)$$

or

$$v_z \frac{\partial T}{\partial z} = \frac{\alpha}{r}\frac{\partial T}{\partial r} + \alpha \frac{\partial^2 T}{\partial^2 r}.$$

We may average each term along the r direction as

$$\frac{1}{\pi R^2}\int_0^R v_z \frac{\partial T}{\partial z} 2\pi r dr = \frac{1}{\pi R^2} v_z \frac{\partial T}{\partial z}(\pi R^2 - 0) = v_z \frac{\partial T}{\partial z},$$

$$\frac{1}{\pi R^2}\int_0^R \frac{\alpha}{r}\frac{\partial T}{\partial z} 2\pi r dr = \frac{2\alpha}{R^2}\int_0^R \frac{\partial T}{\partial r} dr = \frac{2\alpha}{R^2}\int_T^{T_w} dT = \frac{2\alpha}{R^2}(T_w - T),$$

$$\frac{1}{\pi R^2}\int_0^R \alpha \frac{\partial^2 T}{\partial r^2} 2\pi r dr = \frac{2\alpha}{R^2}\int_0^R r \frac{\partial^2 T}{\partial r^2} dr.$$

We may use integration by parts as

$$\frac{2\alpha}{R^2}\int_0^R r \frac{\partial^2 T}{\partial r^2} dr = \frac{2\alpha}{R^2}\left\{ r\left[\frac{dT}{dr}\right]_{r=0}^{r=R} - \int_0^R \frac{\partial T}{\partial r} dr \right\} \text{ then } -k\left[\frac{dT}{dr}\right]_{r=R} = h\left(T - T_w\right)$$

to obtain

$$\frac{1}{\pi R^2}\int_0^R \alpha \frac{\partial^2 T}{\partial r^2} 2\pi r dr = \frac{2\alpha h}{Rk}(T - T_w) - \frac{2\alpha}{R^2}(T_w - T).$$

After substituting all the averaged terms and $K = (Rkv_z)/(2\alpha h)$ into the simplified energy equation we will obtain

$$\frac{dT}{dz} + \frac{1}{K}T - \frac{1}{K}T_w = 0.$$

b. Solve the differential equation when $T_w =$ constant. Show that the solution confirms the boundary conditions $T = T_0$ at $z = 0$ and $T = T_w$ when $z \to \infty$.

Solution: The governing equation

$$\frac{dT}{dz} + \frac{1}{K}T - \frac{1}{K}T_w = 0$$

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is separable and its solution is given in Table 2.6:

Equation	Solution
$g(y)dx + f(x)dy = 0$	$\int_{x_1}^{x_2} \frac{dx}{f(x)} = \int_{y_1}^{y_2} \frac{dy}{g(y)}$

with the following substitutions

dx	dT
$f(x)$	$(T - T_w)/K$
dy	dz
$g(y)$	1

therefore,

$$\int_{T_w - T_0}^{T_w - T} \frac{K}{T - T_w} dT = -\int_0^z dz.$$

Upon integration we will obtain an expression for a variation of T along the z direction:

$$T = T_w + (T_0 - T_w)\exp\left(-\frac{z}{K}\right).$$

When we substitute $z = 0$ and $z \to \infty$ the model predicts $T = T_0$ and $T = T_w$, respectively.

c. Solve the differential equation when the wall temperature increases with distance $T_{wall} = T_{w0} + \alpha z$. Where T_{w0} and α are constants.

Solution: The governing equation $(dT/dz) + (1/K)T = (\alpha z/K) + (T_{w0}/K)$. The solution may be assumed to be $T = T^c + T^p$, where T^c is the complementary and T^p is the particular solution.

i. A complementary solution: $(dT^c/dz) + (1/K)T^c = 0$, this is a simple separable equation and its solution is: $T^c = Ce^{-z/K}$ where C is a constant.

ii. A particular solution may be obtained from the equation $(dT^p/dz) + (1/K)T^p = (\alpha z/K) + (T_{w0}/K)$. This equation has constant coefficients and may be solved with the method of undetermined coefficients. According to the right-hand side, the equation may be T^p assumed by the help of Table 2.6 as: $T^p = A_1 z + A_2$, therefore $(dT^p/dz) = A_1$. After substituting equivalents of T^p and dT^p/dz into the equation, we will have $A_1 + (1/K)(A_1 z + A_2) = (\alpha z/K) + (T^p_{w0}/K)$.
Coefficients of the equal powers of z should be the same on both sides of the equation:

Power of z	Equal Coefficients
Z^0	$A_1 + \frac{A_2}{K} = \frac{T_{w0}}{K}$
Z^1	$\frac{A_1}{K} = \frac{\alpha}{K}$

The unknown constants are: $A_1 = \alpha$ and $A_2 = T_{w0} - \alpha K$ and the particular solution is

$$T^p = \alpha(z - K) + T_{w0}.$$

The model for variation of the milk temperature along the tube is

$$T = T^p + T^c = \alpha(z - K) + T_{w0} + Ce^{-z/K}.$$

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The boundary condition $T = T_0$ at $z = 0$ requires $C = T_0 - \alpha K - T_{w0}$; therefore, the model is

$$T = T_{w0} + \alpha(z - K) + (T_0 - \alpha K - T_{w0})e^{-z/K}.$$

d. Solve the differential equation when $T_{wall} = T_{w0}e^{\alpha z} + \beta$.

Solution: The governing equation $(dT/dz) + (1/K)T = (T_{w0}e^{\alpha z}/K) + (\beta/K)$. The solution may be assumed to be $T = T^c + T^p$ where T^c is the complementary and T^p is the particular solution.

i. A complementary solution: $(dT^c/dz) + (1/K)T^c = 0$; therefore, the complementary solution is the same as in the previous case: $T^c = Ce^{-z/K}$.

ii. A particular solution may be obtained from the equation $(dT^p/dz) + (1/K)T^p + (T_{w0}e^{\alpha z}/K) + (\beta/K)$. This equation has constant coefficients and may be solved by following the same procedure as in the previous case. According to the right-hand side, the equation may be T^p assumed by the help of Table 2.6 as: $T^p = A_1e^{\alpha z} + A_2$; therefore, $dT^p/dz = A_1\alpha e^{\alpha z}$. After substituting equivalents of T^p and dT^p/dz into the equation we will have $A_1\alpha e^{\alpha z} + (1/K)(A_1\alpha e^{\alpha z} + A_2) = (T_{w0}e^{\alpha z}/K) + (\beta/K)$. This equation may be rearranged as $(A_1\alpha + A_1/K)e^{\alpha z} + (A_2/K) = (T_{w0}e^{\alpha z}/K) + (\beta/K)$.

Coefficients of the equal powers of z should be the same on both sides of the equation:

Term	Equal Coefficients
Z^0	$\frac{A_2}{K} = \frac{\beta}{K}$
$e^{\alpha z}$	$A_1\alpha + \frac{A_1}{K} = \frac{T_{w0}}{K}$

The unknown constants are $A_1 = T_{w0}/(\alpha K + 1)$ and $A_2 = \beta$ and the particular solution is $T^p = [T_{w0}/(\alpha K + 1)]e^{\alpha z} + \beta$. The model for variation of the milk temperature along the tube is $T = T^p + T^c = [T_{w0}/(\alpha K + 1)]e^{\alpha z} + \beta + Ce^{-z/K}$. The boundary condition $T = T_0$ at $z = 0$ requires $C = T_0 - [T_{w0}/(\alpha K + 1)] - \beta$; therefore, the model is

$$T = \frac{T_{w0}}{\alpha K + 1}e^{\alpha z} + \beta + \left(T_0 - \frac{T_{w0}}{\alpha K + 1} - \beta\right)e^{-z/K}.$$

e. Solve the differential equation when $T_{wall} = 3z^2 + e^z + 2ze^z + 3z + 3e^{5z}$.

Solution: The governing equation

$$\frac{dT}{dz} + \frac{1}{K}T = \frac{1}{K}\left(3z^2 + e^z + 2ze^z + 3z + 3e^{5z}\right).$$

The solution may be assumed to be $T = T^c + T^p$ where T^c is the complementary and T^p is the particular solution.

i. A complementary solution: $(dT^c/dz) + (1/K)T^c = 0$; therefore, the complementary solution is the same as in the previous case: $T^c = Ce^{-z/K}$.

ii. A particular solution may be obtained from the equation $(dT^p/dz) + (1/K)T^p = (1/K)(3z^2 + e^z + 2ze^z + 3z + 3e^{5z})$. This equation has constant coefficients and may be solved by following the same procedure as in the previous case. According to the right-hand side, the equation may be T^p assumed by the help of Table 2.6 as:

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Term	T^p
z^2	$A_1z^2 + A_2z + A_3$
e^z	$A_4{}^{ez}$
ze^z	A_5ze^z (z^0 terms are the same as that of e^z)
z	Solution is included in that of z^2
e^{5z}	A_6e^{5z}

therefore,

$$\frac{dT^p}{dz} = 2A_1z + A_2 + A_4e^z + A_5ze^z + A_5e^z + 5A_6e^{5z}.$$

After substituting equivalents of T^p and dT^p/dz into the equation we will have

$$\left(A_2 + \frac{A_3}{K}\right) + \left(2A_1 + \frac{A2}{K}\right)z + \left(\frac{A_1}{K}\right)z^2 + \left(A_4 + A_5 + \frac{A_4}{K}\right)e^z + \left(5A_6 + \frac{A_6}{K}\right)e^{5z} + \left(\frac{A_5}{K}\right)ze^z$$
$$= \frac{1}{K}\left(3z^2 + e^z + 2ze^z + 3z + 3e^{5z}\right)$$

Coefficients of the equal powers of z should be the same on both sides of the equation:

Term	Equal Coefficients
z^0	$A_2 + \frac{A_3}{K} = 0$
z^1	$2A_1 + \frac{A_2}{K} = \frac{3}{K}$
z^2	$\frac{A_1}{K} = \frac{3}{K}$
e^z	$A_4 + A_5 + \frac{A_4}{K} = \frac{1}{K}$
e^{5z}	$5A_6 + \frac{A_6}{K} = \frac{3}{K}$
ze^z	$\frac{A_5}{K} = 0$

The unknown constants are $A_1 = 3$, $A_2 = 3(1 - 2K)$, $A_3 = 3K(2K - 1)$, $A_4 = 1/(1 + K)$, $A_5 = 0$, and $A_6 = 3/(5K + 1)$.

The model for variation of the milk temperature along the tube is

$$T = T^p + T^c = 3Kz^2 + 3(1-2K)z + 3K(2K-1) + [1/(1+K)]e^z + [3+(5K+1)]e^{5z} + Ce^{-z/K}.$$

BC: $T = T_0$ at $z = 0$, requires

$$C = T_0 - \frac{30K^4 + 21K^3 - 12K^2 + 5K + 4}{5K^2 + 6K + 1};$$

therefore, the model is:

$$T = \left\{T_0 - \frac{30K^4 + 21K^3 - 12K^2 + 5K + 4}{5K^2 + 6K + 1}\right\}e^{-z/K} + 3Kz^2 + 3(1-2K)z + 3K(2K-1) + \frac{1}{1+K}e^z + \frac{3}{5K+1}3e^{5z}.$$

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Example 2.7: Diffusion of the Modified Atmosphere Gas Mixtures Through a Polymer Film

Gas mixtures of 3–15% oxygen, 5–20% carbon dioxide, and the balance being nitrogen are referred to as modified atmospheres and are used to replace normal air in storage processes to extend the shelf life of fresh produce. Diffusion of oxygen and carbon dioxide from a low density polyethylene package was studied (Ilter, Özilgen, and Orbey 1991) by using a diffusion cell associated with the experimental setup shown in Figure E.2.7.1.

The diffusion cell has two major compartments: upstream and downstream sides. The upstream side of the cell was maintained at a constant gas composition. The downstream side of the diffusion cell is a closed system, separated from the upstream side by means of a polymer film and filled initially with nitrogen. The gas composition changes in the downstream side of the cell due to the permeation of the gases through the film, and these data are used to evaluate the permeation characteristics of the film to the gas mixtures. Carbon dioxide and oxygen balances within the downstream side of the diffusion cell are

$$N_c S = V \frac{dc_c}{dt}$$

and

$$N_o S = V \frac{dc_o}{dt},$$

where N_c, N_o = carbon dioxide and oxygen fluxes through the film; S = mass transfer area; V = volume of the downstream side of the cell; c_c, c_o = carbon dioxide and oxygen concentrations in the downstream side of the cell; and t = time. We may use the equation of continuity in a rectangular coordinate system to simulate carbon dioxide flux through the film (Ilter, Özilgen, and Orbey 1991):

$$\frac{\partial c_c}{\partial t} + \left(\frac{\partial N_c}{\partial x} + \frac{\partial N_c}{\partial y} + \frac{\partial N_c}{\partial z} \right) = R_c. \tag{2.12}$$

This expression may be simplified under steady state conditions (i.e., $dc_c/dt = 0$) with one-dimensional flux; that is, $dN_c/dx = dN_c/dy = 0$ and carbon dioxide do not involve into any chemical reactions (i.e., $R_c = 0$) as

$$\frac{dN_c}{dz} = 0.$$

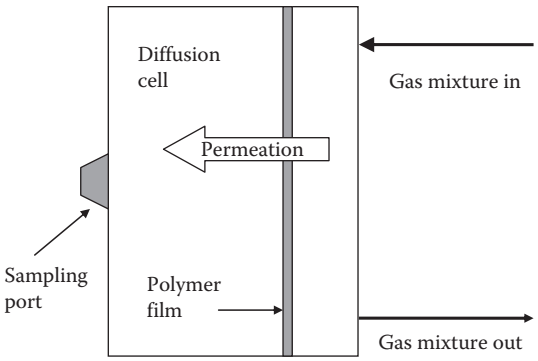


FIGURE E.2.7.1
Schematic description of *the diffusion cell.*

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A similar expression may be obtained for the oxygen flux:

$$\frac{dN_o}{dz} = 0.$$

Flux was previously expressed for a noninterfering species as

$$N_A = x_A\left(N_A + N_B\right) - D_{AB}\frac{dc_A}{dz} \tag{2.10}$$

In the present system, carbon dioxide and oxygen fluxes may interfere with each other, therefore Equation 2.10 may be modified as (Ilter, Özilgen, and Orbey 1991)

$$N_c = x_c\left(N_c + N_o + N_n\right) - D_{Ac}\frac{d\bar{c}_A}{dz} - \beta_o N_o,$$

where $\bar{c}_c$ is the carbon dioxide concentration in the membrane, N_n = nitrogen flux through the film, D_c = diffusivity of carbon dioxide through the film, and β_o = constant. Since pressure is constant within the diffusion cell, we may state that the total flux of carbon dioxide and oxygen into the diffusion cell equals the nitrogen flux from the cell to upstream gas mixture, implying that

$$N_c + N_o + N_n = 0,$$

then the flux expression for carbon dioxide will be

$$N_c = -D_c\frac{d\bar{c}_c}{dz} - \beta_o N_o.$$

A similar flux expression may be obtained for oxygen as

$$N_o = -D_o\frac{d\bar{c}_o}{dz} - \beta_c N_c.$$

We may substitute the simplified flux expressions in the final forms of the equation of continuity and obtain

$$\frac{d^2\bar{c}_c}{dz^2} = 0$$

and

$$\frac{d^2\bar{c}_o}{dz^2} = 0$$

with the BCs:

$$\bar{c}_c = H_c c_{cu} \text{ at } Z = 0 \text{ when } t > 0$$

$$\bar{c}_c = H_c c_c \text{ at } Z = L \text{ when } t > 0$$

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and

$$\bar{c}_o = H_o c_{ou} \text{ at } Z = 0 \text{ when } t > 0$$

$$\bar{c}_o = H_o c_o \text{ at } Z = L \text{ when } t > 0.$$

Where H_c and H_o are the Henry's Law constants for carbon dioxide and oxygen, respectively, c_{cu} and c_{ou} are the upstream gas concentrations and L is the thickness of the membrane. We may integrate these equations twice to obtain the concentration profiles along the membranes:

$$\bar{c}_c = \frac{H_c}{L}(c_c - c_{cu})z + H_c c_{cu}$$

and

$$\bar{c}_o = \frac{H_o}{L}(c_o - c_{ou})z + H_o c_{ou}.$$

Then the fluxes of carbon dioxide and oxygen become (assumption $\beta_c\beta_o \ll 1$):

$$N_c = -D_c \frac{d\bar{c}_c}{dz} - \beta_o N_o = -\frac{D_c H_c}{L}(c_c - c_{cu}) + \beta_o \frac{D_o H_o}{L}(c_o - c_{ou})$$

$$N_o = -D_o \frac{d\bar{c}_o}{dz} - \beta_c N_c = -\frac{D_o H_o}{L}(c_o - c_{ou}) + \beta_c \frac{D_c H_c}{L}(c_c - c_{cu}).$$

Carbon dioxide and oxygen balances around the diffusion cells were $N_c S = V(dc_c/dt)$ and $N_o S = V(dc_o/dt)$. After substituting the expressions for N_c and N_o we will have

$$\frac{dc_c}{dt} = -\phi_1(c_c - c_{cu}) + \phi_2(c_o - c_{ou}),$$

$$\frac{dc_o}{dt} = -\phi_3(c_o - c_{ou}) + \phi_4(c_c - c_{cu}),$$

where

$$\phi_1 = \frac{D_c S H_c}{VL},\ \phi_1 = \beta_o \frac{D_o S H_o}{VL},\ \phi_3 = \frac{D_o S H_o}{VL},\ \phi_4 = \beta_c \frac{D_c S H_c}{VL}.$$

We will rearrange these equations as

$$(D + \phi_1)c_c - \phi_2 c_o = \phi_1 c_{cu} - \phi_2 c_{ou}$$
$$-\phi_4 c_c + (D + \phi_3)c_o = -\phi_4 c_{cu} + \phi_3 c_{ou}.$$

We will use Table 2.6 to solve these equations simultaneously:

$$\Delta c_c = \boldsymbol{D} c_c,$$

$$\Delta c_o = \boldsymbol{D} c_o,$$

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and

$$\Delta = \begin{vmatrix} D+\phi_1 & -\phi_2 \\ -\phi_4 & D+\phi_3 \end{vmatrix} \quad \boldsymbol{D}c_c = \begin{vmatrix} \phi_1 c_{cu} - \phi_2 c_{ou} & -\phi_2 \\ -\phi_4 c_{cu} + \phi_3 c_{ou} & D+\phi_3 \end{vmatrix} \text{ and } \boldsymbol{D}c_o = \begin{vmatrix} D+\phi_1 & -\phi_1 c_{cu} - \phi_2 c_{ou} \\ -\phi_4 & \phi_4 c_{cu} + \phi_3 c_{ou} \end{vmatrix}.$$

Then we will have

$$\frac{d^2 c_c}{dt^2} + (\phi_1 + \phi_3)\frac{dc_c}{dt} + (\phi_1\phi_3 - \phi_2\phi_4)c_c = (\phi_1\phi_3 - \phi_2\phi_4)c_{cu}$$

and

$$\frac{d^2 c_o}{dt^2} + (\phi_1 + \phi_3)\frac{dc_o}{dt} + (\phi_1\phi_3 - \phi_2\phi_4)c_o = (\phi_1\phi_3 - \phi_2\phi_4)c_{ou}.$$

These are second-order ordinary differential equations with constant coefficients and their solutions obtained by using Table 2.6 and the ICs:

$$c_c = 0 \text{ at } t = 0,$$

$$c_o = (c_{ou})_{\text{initial}} \text{ at } t = 0,$$

$$c_c = r_3\{\exp(r_1 t) - \exp(r_2 t)\} + c_{cu}\{1 - \exp(r_2 t)\},$$

$$c_o = r_4\{\exp(r_1 t) - \exp(r_2 t)\} + c_{ou}\{1 - \exp(r_2 t)\} + (c_{ou})_{\text{initial}}\exp(r_2 t).$$

Adjustable constants $r_1 - r_4$ were obtained from the data with regression in MATLAB® code E.2.7 and a variation of c_c and c_0 with time is plotted in Figure E.2.7.2.

MATLAB® CODE E. 2.7

Command Window:

```
clear all
close all

% enter the data
tData=[0 6 12 24 48]; % h
tModel=[0:1:50];
ccu=0.13;
cou=0.143;
cou0=0.035;
Cco2Data=[0e-3 17e-3 20e-3 30e-3 48e-3]; % kg mol/m3
Co2Data=[32e-3 50e-3 51e-3 54e-3 68e-3]; % kg mol/m3

% plot the data
plot(tData,Cco2Data, '*'); hold on
plot(tData,Co2Data, 'o'); hold on
ylabel('Cco2 (kmol/m3)')
xlabel('time (h)')
legend('CO2 concentrations','O2 concentrations',
2,'Location','SouthEast')
```

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```
% call the nonlinear least squares data fitting function nlinfit
for carbon dioxide
[COEFFS,resid,J]=nlinfit(tData, Cco2Data, 'diffusionC',
[1e-1 1e-3 1e-1]);
Cco2Model=COEFFS(3)*((exp(COEFFS(1)*tModel))-
(exp(COEFFS(2)*tModel)))+ccu*(1-exp(COEFFS(2)*tModel));
plot(tModel,Cco2Model, ':'); hold on

% call the nonlinear least squares data fitting function nlinfit
for oxgen
[COEFFS2,resid,J]=nlinfit(tData, Co2Data, 'diffusionO',
[1e-1 1e-3 1e-1 1e-2]);
Co2Model=COEFFS2(4)*((exp(COEFFS2(1)*tModel))-
(exp(COEFFS2(2)*tModel)))+cou*(1-exp(COEFFS2(2)*tModel))+
cou0*(exp((COEFFS2(2))*tModel));
plot(tModel,Co2Model, ':'); hold on
```

M-file1:

```
function Cco2Model=diffusionC(coeff, tData)

% introduce the constants and coefficients and the independent
variable
ccu=0.13;
r1=coeff(1);
r2=coeff(2);
r3=coeff(3);
t=tData;

% model:
Cco2Model=r3*((exp(r1*t))-(exp(r2*t)))+ccu*(1-exp(r2*t));
```

M-file2:

```
function Co2Model=diffusionO(coeff, tData)

% introduce the constants and coefficients and the independent
variable
ccu=0.13;
cou=0.143;
cou0=0.035;
r1=coeff(1);
r2=coeff(2);
r3=coeff(3);
r4=coeff(4);
t=tData;

% model:
Co2Model=r4*((exp(r1*t))-(exp(r2*t)))+cou*(1-(exp(r2*t)))+
cou0*(exp(r2*t));
```

Figure E.2.7.2 will appear on the screen when we run the code.

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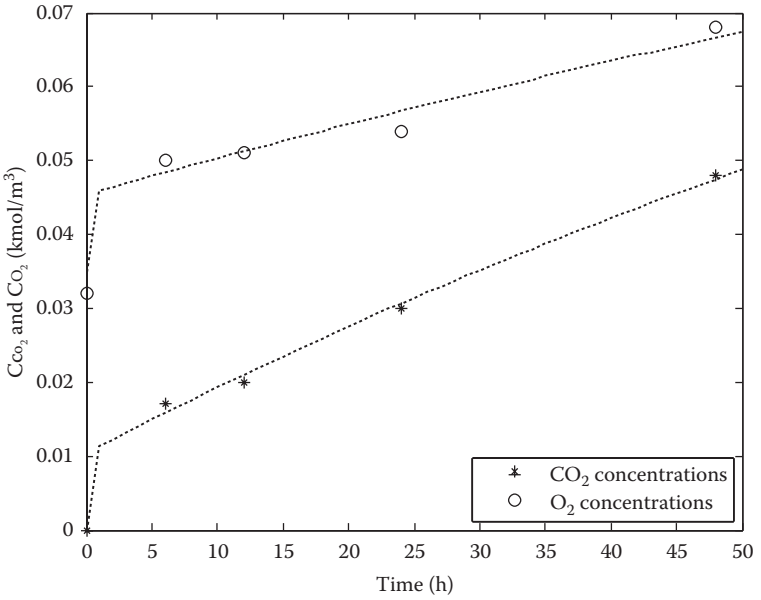


FIGURE E.2.7.2
Comparison of the model and experimental CO_2 and O_2 concentrations in the downstream side of the diffusion cell with the upstream consisting of 13.0% CO_2, 14.3% O_2, and balance nitrogen. (From Ilter, M., Özilgen, M., and Orbey, N., *Polymer International,* 25, 211–17, 1991.)

2.7 Transport Phenomena Models Involving Partial Differential Equations

We will solve the problems involving the partial differential equations by using three different techniques: (i) separation of variables, (ii) combination of variables, and (iii) the Laplace transformations. All of these techniques help us to reduce the problem into ordinary differential equations and make it possible to obtain the solution through the use of simple techniques.

Example 2.8: Temperature Profiles in a Steak During Frying and in the Meat Analog During Cooking

A steak ($\alpha = 8\ 10^{-8}$ m^2/s, dimensions = 10 × 10 × 1 cm, $T_0 = 4$°C) is dipped into vegetable oil ($T = 177$°C) for frying. We may assume that the surfaces attain the oil temperature immediately. If heat transfer within the steak may be simulated with conduction only, draw the temperature profiles of the steak 5 and 10 minutes after the beginning of frying.

Solution: The equation of energy in a rectangular coordinate system is

$$\frac{\partial T}{\partial t} + v_x \frac{\partial T}{\partial x} + v_y \frac{\partial T}{\partial y} + v_z \frac{\partial T}{\partial z} = \frac{\psi_G^{\bullet}}{\rho c} + \frac{\partial}{\partial x}\left(\alpha \frac{\partial T}{\partial x}\right) + \frac{\partial}{\partial y}\left(\alpha \frac{\partial T}{\partial y}\right) + \frac{\partial}{\partial z}\left(\alpha \frac{\partial T}{\partial z}\right). \tag{2.16}$$

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The process conditions imply $v_x = v_y = v_z = 0$ and $\psi_G^{\bullet}$. The steak is a thin sheet, therefore conduction through the longer dimensions may be neglected:

$$\frac{\partial}{\partial x}\left(\alpha\frac{\partial T}{\partial x}\right)=0,\quad \frac{\partial}{\partial y}\left(\alpha\frac{\partial T}{\partial y}\right)=0,$$

then Equation 2.16 becomes

$$\frac{\partial T}{\partial t}=\frac{\partial}{\partial z}\left(\alpha\frac{\partial T}{\partial z}\right). \tag{E.2.8.1}$$

Since α is constant it may be rearranged as

$$\frac{\partial^2 T}{\partial z^2}-\frac{1}{\alpha}\frac{\partial T}{\partial t}=0.$$

This is a partial differential equation with

BC1: $T = T_1$ at $z = -L$ when $t > 0$ ($2L$ = thickness of the steak)
BC2: $T = T_1$ at $z = L$ when $t > 0$
BC3: $dT/dz = 0$ at $z = 0$ when $t > 0$
BC4: $T = T_1$ for all z when $t \to \infty$
IC: $T = T_0$ when $t = 0$ for all z,

where T_1 = surface temperature = 177°C and L = half of the thickness of the steak = 0.5 cm. We may introduce the dimensionless variables

$$\theta=\frac{T-T_1}{T_0-T_1},\quad \eta=\frac{z}{L},\quad \text{and}\quad \tau=\frac{\alpha T}{L^2}.$$

We may write the equation, BCs and the IC in dimensionless variables:

$$\frac{\partial^2\theta}{\partial\eta^2}-\frac{\partial\theta}{\partial\tau}=0$$

BC1: $\theta = 0$ at $\eta = -1$
BC2: $\theta = 0$ at $\eta = 1$
BC3: $d\theta/d\eta$ at $\eta = 0$
BC4: $\theta = 0$ for all η when $\tau \to \infty$
IC: $\theta = 1$ when $\tau = 0$.

Solution of this partial differential equation was also described by Bird, Stewart, and Lightfoot (2007). We may use the method of *separation of variables* for a solution since both the partial differential equation, boundary conditions, and the initial condition are homogeneous; the boundaries are fixed and the boundary and the initial conditions are convenient to use with the orthogonality principle (i.e., they are equal to 0, 1, or –1).

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The method of the separation of variables requires separation of θ into two functions $f(\eta)$ and $g(\tau)$:

$$\theta = f(\eta)\, g(\tau),$$

where f is a function of η, and g is a function of τ.

The partial differential equation may be rewritten in terms of the new functions as

$$g\frac{\partial^2 f}{\partial h^2} - f\frac{\partial g}{\partial t} = 0.$$

We may rearrange this equation as

$$\frac{1}{f}\frac{\partial^2 f}{\partial \eta^2} = \frac{1}{g}\frac{\partial g}{\partial \tau} = \lambda.$$

Different variables appear on both sides of the equation. This equation may be satisfied if both sides equals a constant λ. Solution to $1/g\ \partial g/\partial\tau = \lambda$ is $g = C_1 e^{\lambda t}$. We may determine the sign of λ by considering the boundary conditions:

Assumption	Consequences of the BCs	Conclusions
$\lambda > 0$	$g \to \infty$ when $\tau \to \infty$, therefore $T \to \infty$	Impossible
$\lambda = 0$	$g = C_1$, therefore $\theta = f(\eta)$ only	Impossible
$\lambda < 0$	$g = 0$ when $\tau \to \infty$, therefore $\theta = 0$	Satisfies BC4

These results require $\lambda^2 = -C^2$ and consequently $g = C_1 e^{-C^2\tau}$. The square of any real number C is always positive, but the preceding negative sign makes it negative. Solution to

$$\frac{1}{f}\frac{\partial^2 f}{\partial \eta^2} = \lambda \text{ is } f(\eta) = C_2 \sin(C\eta) + C_3 \cos(C\eta)$$

(Table 2.6).

The original solution was $\theta = f(\eta)g(\tau) = C_1 e^{-C^2\tau}\left\{C_2 \sin(C\eta) + C_3 \cos(C\eta)\right\}$, temperature profiles within the steak should be symmetrical. The cos function is symmetrical: $\cos(C\eta) = \cos(-C\eta)$, but the sin function is not: $\sin(C\eta) \neq \sin(-C\eta)$; therefore, we may not have a sin function in the solution, and $C_2 = 0$ then the solution becomes

$$\theta = C_n \exp(-C^2\tau)\cos(C\eta),$$

where $C_n = C_1 C_3$.

Constants C_n and C are still not determined. We may use BC2 to determine C:

$\theta = 0$ at $\eta = 1$ implying $0 = C_n \exp(-C^2\tau)\cos(C)$.

This equation holds if $C = [n + (1/2)]\pi$ and the solution becomes

$$\theta_n = \sum_{i=0}^{\infty} C_n \exp\left\{-\left(n+\frac{1}{2}\right)^2 \pi^2 \tau\right\} \cos\left[\left(n+\frac{1}{2}\right)\pi\eta\right].$$

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Constant C_n still needs to be determined. We may use the IC to determine C_n:

$$\text{IC: when } \tau=0,\ \theta=1,\ \text{and } 1=\sum_{i=0}^{\infty} C_n \exp\left\{-\left(n+\frac{1}{2}\right)^2 \pi^2 \tau\right\}.$$

The cos function is an orthogonal function and the orthogonality principle may be applied as

$$\int_a^b \cos\left[\left(n+\frac{1}{2}\right)\pi\tau\right]\cos\left[\left(m+\frac{1}{2}\right)\pi\tau\right]d\eta = 0 \quad \text{if } m\neq n \text{ within the range of } -1\le\eta\le 1.$$

After multiplying both sides of the final expression for θ_n with $\cos\{[m + (1/2)]\pi\eta\}$ and applying the orthogonality principle we may obtain $C_n = \{2(-1)^n/[n + (1/2)\pi]\}$ and the solution becomes

$$\frac{T-T_1}{T_0-T_1} = \sum_{n=0}^{\infty} \frac{2(-1)^n}{\left(n+\frac{1}{2}\right)\pi} \exp\left\{-\left(n+\frac{1}{2}\right)\pi^2\alpha t/L^2\right\}\cos\left[\left(n+\frac{1}{2}\right)\pi z/L\right]. \tag{E.2.8.2}$$

Temperatures along the steak 5 and 10 minutes after the beginning of frying are simulated in Figure E.2.8.

In a bacon analog production process, red, pink, and white proteinaceous slurries are alternately layered and cooked. Heat coagulates the slurries into a solid mass; then the product is sliced, prefried, and packaged. It was reported that the cooked slab may be sliced without smearing only when the center temperature reaches 90.5°C (Altomare 1988). MATLAB® code E.2.8 computes the time needed to achieve the required center temperature in slabs of different thicknesses by using Equation E.2.8.2 (Figure 2.8).

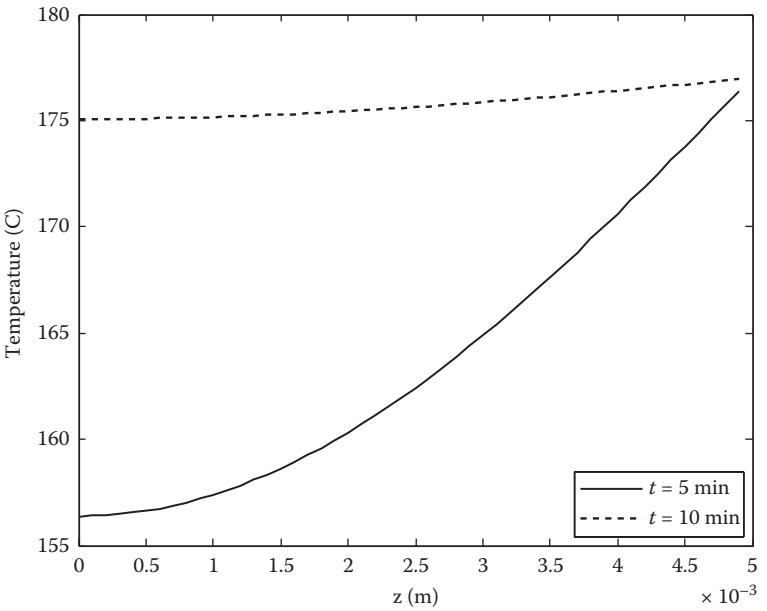


FIGURE E.2.8
Temperature profiles along the steak after 5 and 10 minutes after the beginning of the frying process.

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MATLAB® CODE E. 2.8

Command Window:

```
clear all
close all

T1 = 177;
T0 =4;
time(1) = 0;
alpha= 4.8e-6; % m2/min
L = 5e-3; % half of the thickness (m)

% model
deltaZ=1e-4;
for j=1:1:10;
     time(j)=j;
     z=0;
 for k=1:1:50;
  Z(k)=z;
     ssum=0 ;
        for n=1:1:10;
            N=(n-1)+(1/2);
               s(n)=(((-1)^(n-1))/(N*pi))*exp(-(N^2)*(pi^2)
               *alpha*time(j)/(L^2))*cos(N*pi*Z(k)/L);
            end
     ssum=sum(s) ;
     T(j,k)=T1+2*(T0-T1)*ssum;
     z=z+deltaZ ;
  end
end
plot(Z,T(5,:), '-'); hold on
plot(Z,T(10,:), ':'); hold on
ylabel('Temperature (C)')
xlabel('z (m)')
legend('t=5 min','t=10 min', 2,'Location','SouthEast')
```

Figure E.2.8 will appear on the screen when we run the code.

Example 2.9: Temperature Profiles in a Spherical Potato Tuber During Blanching

A spherical potato tuber ($\alpha = 0.19\ 10^{-6}$ m^2/s, radius = 4.1 cm, $T_0 = 18$°C) is dipped into blanching water where its surface temperature raised to T_1 °C. If the heat transfer within the potato tuber may be simulated with conduction only, plot variation of the temperature with time at $r = 3.1$ cm and $r = 0$ cm from the center (Sarikaya and Özilgen 1991).

Solution: The equation of energy in a spherical coordinate system is

$$\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + \frac{v_\theta}{r}\frac{\partial T}{\partial \theta} + \frac{v_\phi}{r\sin\theta}\frac{\partial T}{\partial \phi} = \frac{\psi_G^{\bullet}}{\rho C} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\alpha\frac{\partial T}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\alpha\sin\theta\frac{\partial T}{\partial \theta}\right) + \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial \phi}\left(\alpha\frac{\partial T}{\partial \phi}\right). \quad (2.18)$$

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The process conditions imply $v_\theta = v_\phi = v_r = 0$ and $\psi_G^{\bullet} = 0$. The potato tuber is symmetrical; therefore, conduction through the radial directions may be neglected:

$$\frac{1}{r^2 \sin\theta}\frac{\partial}{\partial\theta}\left(\alpha \sin\theta \frac{\partial T}{\partial\theta}\right) = 0, \quad \frac{1}{r^2 \sin^2\theta}\frac{\partial}{\partial\phi}\left(\alpha \frac{\partial T}{\partial\phi}\right) = 0,$$

then Equation 2.18 becomes

$$\frac{\partial T}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2 \alpha \frac{\partial T}{\partial r}\right).$$

Since a is constant it may be rearranged as

$$\frac{\partial T}{\partial t} = \alpha\left[\frac{2}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial r^2}\right].$$

This is a partial differential equation with

BC1: $T = T_1$ at $r = R$ when $t > 0$
BC2: $dT/dr = 0$ at $r = 0$ when $t > 0$
BC3: $T = T_1$ for all r when $t \to \infty$
IC: $T = T_0$ when $t = 0$ for all r.

We may introduce the dimensionless variables

$$\theta = \frac{T - T_1}{T_0 - T_1}, \quad \eta = \frac{r}{R} \quad \text{and} \quad \tau = \frac{\alpha t}{R^2}.$$

We may write the equation, BCs, and the IC in dimensionless variables:

$$\frac{\partial\theta}{\partial\tau} = \frac{2}{\eta}\frac{\partial\theta}{\partial\eta} + \frac{\partial^2\theta}{\partial\eta^2}$$

BC1: $\theta = 0$ at $\eta = 1$ when $\tau > 0$
BC2: $d\theta/d\eta = 0$ (θ is finite) at $\eta = 0$ when $\tau > 0$
BC3: $\theta = 0$ for all η when $\tau \to \infty$
IC: $\theta = 1$ when $\tau = 0$.

The method of the separation of variables requires separation of θ into two functions $f(\eta)$ and $g(\tau)$:

$$\theta(\eta,\tau) = f(\eta)\, g(\tau),$$

where f is the function of η, and g is the function of τ.

The partial differential equation may be rewritten in terms of the new functions as

$$\frac{1}{f}\left[\frac{\partial^2 f}{\partial\eta^2} + \frac{2}{\eta}\frac{\partial f}{\partial\eta}\right] = \frac{1}{g}\frac{\partial g}{\partial\tau} = \lambda.$$

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After following the same principle with the previous example, we will find $\lambda = -C^2$ and consequently $g = C_1 e^{-C^2\tau}$.

The other equation,

$$\frac{1}{f}\left[\frac{\partial^2 f}{\partial \eta^2} + \frac{2}{\eta}\frac{\partial f}{\partial \eta}\right] = -C^2,$$

may be rearranged as

$$\eta^2 \frac{\partial^2 f}{\partial \eta^2} + 2\eta \frac{\partial f}{\partial \eta} + \eta^2 C^2 f = 0.$$

We may define a new variable: $u = f\eta$, then this differential equation may be written as $(d^2u/d\eta^2) + C^2u = 0$ and its solution is (Table 2.6)

$$u = C_2 \cos(C\eta) + C_3 \sin(C\eta) \quad \text{or} \quad f = (C_2/\eta)\cos(C\eta) + (C_3/\eta)\sin(C\eta).$$

BC2 implies θ is finite when $\eta = 0$, but $(C_2/\eta)\cos(C\eta) \to \infty$; therefore, $(C_2/\eta)\cos(C\eta)$ may not be a solution, and we conclude that $C_2 = 0$; therefore, the solution is: $\theta = (C_n/\eta)C_1 e^{-C^2\tau}\sin(C\eta)$.

BC1 requires $\theta = 0$ at $\eta = 1$ when $\tau > 0$; therefore, $0 = C_n e^{-C^2\tau}\sin(C)$. The BC is satisfied when $C = \pi n$, and the solution becomes

$$\theta = \frac{1}{\eta}\sum_{n=0}^{\infty}\left\{C_n e^{-(\pi n^2 \tau)}\sin(\pi n \eta)\right\}.$$

The IC requires $\theta = 1$ when $\tau = 0$; that is,

$$1 = \frac{1}{\eta}\sum_{n=0}^{\infty}\left\{C_n \sin(\pi n \eta)\right\},$$

we may determine C_n after applying the orthogonality principle as

$$C_n = 2\frac{(-1)^{n+1}}{\pi n},$$

then the solution is

$$\theta = \frac{1}{\eta}\sum_{n=0}^{\infty}\left\{2\frac{(-1)^{n+1}}{\pi n} e^{-(\pi n^2 \tau)}\sin(\pi n \eta)\right\},$$

or

$$\frac{T - T_1}{T_0 - T_1} = \frac{R}{r}\sum_{n=0}^{\infty}\left\{2\frac{(-1)^{n+1}}{\pi n} e^{-(\pi n^2 \tau)}\sin\left(\frac{\pi n r}{R}\right)\right\}.$$

MATLAB® code E.2.9 generates Figures E.2.9.1 and E.2.9.2 to compare the model with the data at $r = 3.1$ cm and $r = 0.1$ cm from the center.

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MATLAB® CODE E. 2.9

Command Window:

```
clear all
close all

% Enter the data
timeD=[0 10 20 30 40 50 60 70];
TData1=[20 61 71 73 78 79 80 80;20 55 63 65 67 69 71 72;20 50 58 60
61 62 63 64]; % r=3.1 cm
TData2=[20 22 48 62 71 76 78 80;20 23 44 55 61 68 69 71;20 24 38 49
56 61 62 65]; % r=0 cm
T1 = [65 72 80];
T0 =18;
time(1) = 0;
alpha= 1.14e-5;
R = 0.041;

% plot the data (r=3.1 cm)
plot(timeD,TData1(1,: ),'*' ); hold on;
plot(timeD,TData1(2,: ),'o' ); hold on;
plot(timeD,TData1(3,: ),'+' ) ; hold on;
ylabel('Temperature (C)')
xlabel('Time (min)')
legend('T1=80 C','T1=72 C','T1=65 C', 3,'Location','SouthEast')

% plot the data (r=3.1 cm)
plot(timeD,TData1(1,: ),'*' ); hold on;
plot(timeD,TData1(2,: ),'o' ); hold on;
plot(timeD,TData1(3,: ),'+' ) ; hold on;
ylabel('Temperature (C)')
xlabel('Time (min)')
legend('T1=80 C','T1=72 C','T1=65 C', 3,'Location','SouthEast')

% model (r=0 cm)
r = 3.1e-2; %Enter the distance for r=0 cm
for i=1:length(T1);
T(1)=T0;
    for j=1:1:70;
       time(j)=j;
         tau=alpha* time(j)/(R^2);
         for n=1:1:100
s(n)=(((-1)^(n+1))/(pi*n))*(exp(-tau*(pi*n)^2))*(sin(pi*n*r/R));
         end
         ssum=sum(s) ;
         T(j)=T1(i)+(T0-T1(i))*(2*R/r)*ssum ;
end
plot(time,T, '-');
end

figure
% plot the data (r=0 cm)
plot(timeD,TData2(1,: ),'*' ); hold on;
plot(timeD,TData2(2,: ),'o' ); hold on;
plot(timeD,TData2(3,: ),'+' ) ; hold on;
ylabel('Temperature (C)')
```

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```
xlabel('Time (min)')
legend('T1=80 C','T1=72 C','T1=65 C', 3,'Location','SouthEast')

% model (r=0 cm)
r = 0.1e-2; %Enter the distance for r=0 cm
for i=1:length(T1);
T(1)=T0;
    for j=1:1:70;
       time(j)=j;
         tau=alpha* time(j)/(R^2);
         for n=1:1:100
s(n)=(((-1)^(n+1))/(pi*n))*(exp(-tau*(pi*n)^2))*(sin(pi*n*r/R));
         end
         ssum=sum(s) ;
         T(j)=T1(i)+(T0-T1(i))*(2*R/r)*ssum ;
end
plot(time,T, '-');
end
```

Figures E.2.9.1 and E.2.9.2 will appear on the screen when we run the code.

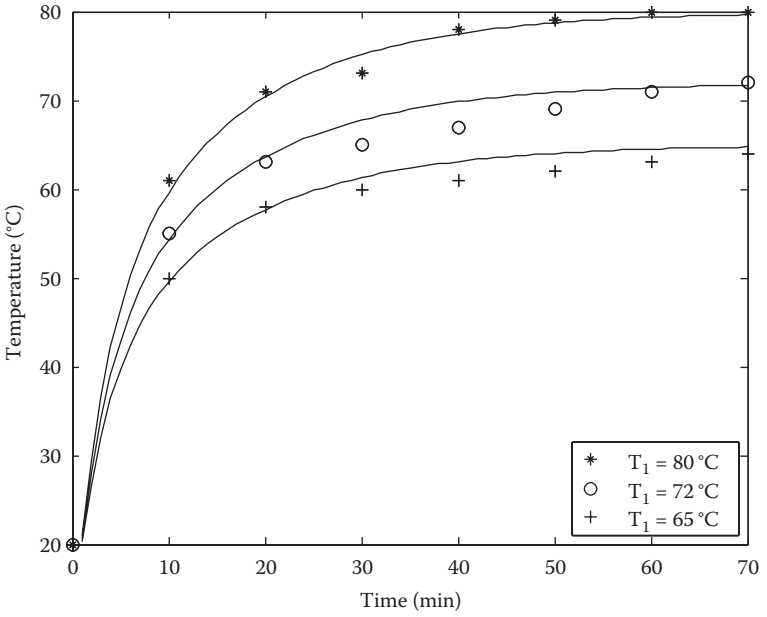


FIGURE E.2.9.1
Temperature profiles at $r = 3.1$ m during thermal processing of whole potatoes. (From Sarikaya, A. and Özilgen, M., *Lebensmittel-Wissenschaft und Technologie,* 24, 159–63, 1991.)

Example 2.10: Temperature Profiles in a Sausage During Cooking

A sausage ($\alpha = 6.5\ 10^{-8}$ m²/s, length = 10 cm radius = 0.8 cm, $T_0 = 4$°C) is dipped into boiling water where its surface temperature raised to $T_1 = 102$°C. If heat transfer within the sausage may be simulated with conduction only, plot the temperature profiles along the radius 3 and 7 minutes after the beginning of the process.

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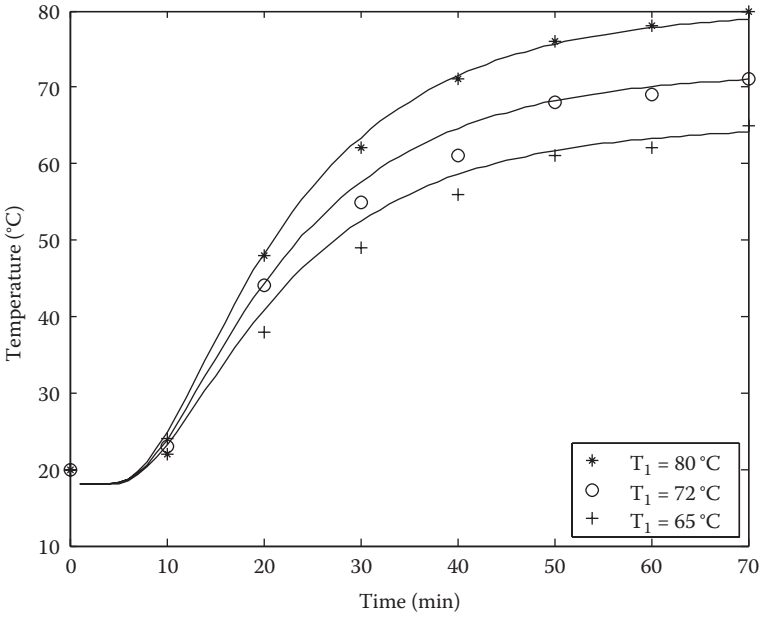


FIGURE E.2.9.2
Temperature profiles at $r = 0.01$ m during thermal processing of whole potatoes. (From Sarikaya, A. and Özilgen, M., *Lebensmittel-Wissenschaft und Technologie,* 24, 159–63, 1991.)

Solution: The equation of energy in a cylindrical coordinate system is:

$$\frac{\partial T}{\partial t} + v_r \frac{\partial T}{\partial r} + \frac{v_\theta}{r}\frac{\partial T}{\partial \theta} + v_z \frac{\partial T}{\partial z} = \frac{\psi_G^{\bullet}}{\rho c} + \frac{1}{r}\frac{\partial}{\partial r}\left(r\alpha \frac{\partial T}{\partial r}\right) + \frac{1}{r^2}\frac{\partial}{\partial \theta}\left(\alpha \frac{\partial T}{\partial \theta}\right) + \frac{\partial}{\partial z}\left(\alpha \frac{\partial T}{\partial z}\right). \tag{2.17}$$

The process conditions imply $v_\theta = v_r = v_z = 0$ and $\psi_G^{\bullet} = 0$. The sausage is a thin cylinder therefore conduction through the longer dimension may be neglected:

$$\frac{1}{r^2}\frac{\partial}{\partial \theta}\left(\alpha \frac{\partial T}{\partial \theta}\right) = 0, \quad \frac{\partial}{\partial z}\left(\alpha \frac{\partial T}{\partial z}\right) = 0,$$

then Equation 2.17 becomes

$$\frac{\partial T}{\partial t} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\alpha \frac{\partial T}{\partial r}\right).$$

Since α is constant it may be rearranged as

$$\frac{1}{\alpha}\frac{\partial T}{\partial t} - \frac{1}{r}\frac{\partial}{\partial r}\left(r \frac{\partial T}{\partial r}\right) = 0.$$

This is a partial differential equation with

BC1: $T = T_1$ at $r = R$ when > 0
BC2: $dT/dR = 0$ at $r = 0$ when $t > 0$
BC3: $T = T_1$ for all r when $t \to \infty$
IC: $T = T_0$ when $t = 0$ for all r,

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where T_1 = surface temperature = 102°C and R = radius of the sausage = 0.8 cm. We may introduce the dimensionless variables $\theta = (T - T_1)/(T_0 - T_1)$, $\eta = r/R$ and $\tau = (\alpha t/R^2)$.

We may write the equation, BCs, and the IC in dimensionless variables:

$$\frac{1}{\eta}\frac{\partial}{\partial\eta}\left(\eta\frac{\partial\theta}{\partial\eta}\right) - \frac{\partial\theta}{\partial\tau} = 0$$

BC1: $\theta = 0$ at $\eta = 1$ when $\tau > 0$
BC2: $d\theta/d\eta = 0$ (θ is finite) at $\eta = 0$ when $\tau > 0$
BC3: $\theta = 0$ for all η when $t \to \infty$
IC: $\theta = 1$ when $\tau = 0$.

The method of the separation of variables requires separation of θ into two functions $f(\eta)$ and $g(\tau)$:

$$\theta = f(\eta)\, g(\tau),$$

where f is the function of η, and g is the function of τ.

The partial differential equation may be rewritten in terms of the new functions as: $(1/f)[(\partial^2 f/\partial\eta^2) + (1/\eta)(\partial f/\partial\eta)] = (1/g)(\partial g/\partial\tau) = \lambda$. After following the same principle with the previous example, we will find $\lambda = -C^2$ and consequently $g = C_1 e^{-C^2\tau}$. The other equation $(1/f)[(\partial^2 f/\partial\eta^2) + (1/\eta)(\partial f/\partial\eta)] = -C^2$ may be rearranged as

$$\frac{1}{f}\left[\frac{\partial^2 f}{\partial\eta^2} + \frac{2}{\eta}\frac{\partial f}{\partial\eta}\right] = -C^2.$$

This is Bessel's equation with $\nu = 0$ and its solution is (Tables 2.7 and 2.8)

TABLE 2.7(A)

Bessel's Equations and their Solutions

Bessel's equation

$$x^2\frac{d^2y}{dx^2} + x\frac{dy}{dx} + \left(x^2 - \nu^2\right)y = 0$$

i. When ν is positive but not an integer or zero the solutions are $y(x) = C_1J_\nu(x) + C_2J_{-\nu}(x)$ or $y(x) = C_1J_\nu(x) + C_2Y_\nu(x)$

ii. When $\nu = n$ = positive integer $J_{-n}(x)$ and $J_n(x)$ are not independent solutions and related as $J_{-n}(x) = (-1)^nJ_n(x)$, therefore the only solution is $y(x) = C_1J_n(x) + C_2Y_n(x)$

Where Bessel's functions are defined as:

i. Bessel's function of the first kind of order ν

$$J_\nu(x) = \sum_{m=0}^{\infty}\frac{(-1)^m(0.5x)^{2m+\nu}}{m!\Gamma(m+\nu+1)} \quad J_{-\nu}(x) = \sum_{m=0}^{\infty}\frac{(-1)^m(0.5x)^{2m-\nu}}{m!\Gamma(m-\nu+1)}$$

where gamma function $\Gamma(m+\nu+1) = (m+\nu)\Gamma(m+\nu) = (m+\nu)(m+\nu-1)\Gamma(m+\nu-1) = ...$

ii. Bessel's function of the second kind of order ν

$$Y_\nu(x) = \sum_{m=0}^{\infty}\frac{\mathrm{Cos}(\nu\pi)J_\nu(x) - J_{-\nu}(x)}{\mathrm{Sin}(\nu\pi)}$$

iii. Bessel's function of the first kind of order n

$$J_n(x) = \frac{x^n}{2^n n!}\left\{1 - \frac{x^2}{2^2 1!(n+1)} + \frac{x^4}{2^4 2!(n+1)(n+2)} - \frac{x^6}{2^6 3!(n+1)(n+2)(n+3)} + \ldots\right\}$$

iv. Bessel's function of the second kind of order n

$$Y_n(x) = \frac{2}{\pi}\left\{\left[\ln(0.5x) + 0.5772\right]J_n(x) - 0.5\sum_{m=0}^{\infty}\left[(-1)^{m+1}\left[\phi(m) + \phi(m+n)\frac{(0.5)^{2m+n}}{m!(m+n)!}\right]\right]\right\}$$

Where $\phi(m) = \sum_{k=1}^{\infty}\frac{1}{k}$ with $\phi(0) \equiv 0$

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TABLE 2.7(B)

Modified Bessel's Equation and Its Solutions

Modified Bessel's equation

$$x^2\frac{d^2y}{dx^2}+x\frac{dy}{dx}-(x^2+\nu^2)y=0$$

i. When ν is positive but not an integer or zero the solutions are $y(x)=C_1I_\nu(x)+C_2I_{-\nu}(x)$ or $y(x)=C_1I_\nu(x)+C_2K_\nu(x)$

ii. When $\nu=n=$ positive integer $I_{-n}(x)$ and $I_n(x)$ are not independent solutions and related as $I_{-n}(x)=I_n(x)$ therefore the only solution is $y(x)=C_1I_n(x)+C_2K_n(x)$

Where modified Bessel's functions are defined as:

i. Modified Bessel's function of the first kind of order ν

$$I_\nu(x)=\sum_{m=0}^{\infty}\frac{(0.5x)^{2m+\nu}}{m!\Gamma(m+\nu+1)}\qquad I_{-\nu}(x)=\sum_{m=0}^{\infty}\frac{(0.5x)^{2m-\nu}}{m!\Gamma(m-\nu+1)}$$

ii. Modified Bessel's function of the second kind of order ν

$$K_\nu(x)=(0.5\pi)\frac{I_{-\nu}(x)-I_\nu(x)}{\mathrm{Sin}(\nu\pi)}$$

iii. Modified Bessel's function of the first kind of order n

$$I_n(x)=\frac{x^n}{2^n n!}\left\{1+\frac{x^2}{1^2 1!(n+1)}+\frac{x^4}{2^4 2!(n+1)(n+2)}+\frac{x^6}{2^6 3!(n+1)(n+2)(n+3)}+\ldots\right\}$$

iv. Modified Bessel's function of the second kind of order n

$$K_n(x)=(-1)^{n+1}\left[\ln(0.5x)+0.5772\right]I_n(x)+0.5\sum_{m=0}^{n-1}\left\{(-1)^{m+1}\left[\frac{(-1)^m(n-m-1)!\,2^{n-2m}}{m!\,x^{n-2m}}\right]\right\}$$

$$+\frac{(-1)^n}{2}\sum_{m=0}^{\infty}\left\{\frac{n+2m}{m!(n+m)!\,2^{n-2m}}\left[\left(1+\frac{1}{2}+\ldots..+\frac{1}{m}\right)+\left(1+\frac{1}{2}+\ldots..+\frac{1}{n+m}\right)\right]\right\}$$

$$f=C_2J_0(C\eta)+C_3Y_0(C\eta).$$

Plots of J_0 and Y_0 versus η were given in Figure 2.3 and shows that at $\eta=0$ $Y_0\to\infty$. The presence of the term $C_3Y_0(C\eta)$ in the solution will cause f (and θ) $\to\infty$ at $\eta=0$, but contradict the fact that $\theta=$ finite at $\eta=0$; therefore $C_3Y_0(C\eta)$ cannot be a solution and $C_3=0$. The combined solution is:

$$\theta=f(\eta)g(\tau)=C_ne^{-C^2\tau}J_0(C),$$

where $C_n=C_1C_2$.

BC1: $\theta=0$ at $\eta=1$ when $\tau>0$ requires $0=C_ne^{-C^2\tau}J_0(C)$. The requirement is satisfied when $C=B_n=$ Eigen values of J_0. Definition: Values of x, which make $J_0(x)=0$ are called the Eigen values of J_0 and given in Table 2.13, then the solution becomes

$$\theta=\sum_{n=1}^{\infty}C_n\exp(-B_n^2\tau)J_0(B_n\eta)$$

IC: $\theta=1$ when $\tau=0$ requires $1=\sum_{n=1}^{\infty}C_nJ_0(B_n\eta)$.

J_0 is an orthogonal function and requires

$$\int_0^1 J_0(B_n\eta)J_0(B_m\eta)\eta d\eta=0\quad\text{if } n\neq n$$

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TABLE 2.8

Important Properties for Bessel's Equation; Bessel and Modified Bessel Functions and their Derivatives

i. $x^2\frac{d^2y}{dt^2}+x\frac{dy}{dx}+\left(C^2x^2-\nu^2\right)y=0$ (C = constant) becomes Bessel's equation after substituting $t = Cx$: $t^2\frac{d^2y}{dt^2}+x\frac{dy}{dt}+\left(t^2-\nu^2\right)y=0$

ii. Half order functions

$$J_{1/2}(x)=\sqrt{\frac{2}{\pi x}}\sin(x)\quad J_{-1/2}(x)=\sqrt{\frac{2}{\pi x}}\cos(x)$$

$$I_{1/2}(x)=\sqrt{\frac{2}{\pi x}}\sinh(x)\quad I_{-1/2}(x)=\sqrt{\frac{2}{\pi x}}\cosh(x)$$

iii. *Differential properties*

$$J_{n-1}(x)+J_{n+1}(x)=\left(\frac{2n}{x}\right)J_n(x)\qquad Y_{n-1}(x)+Y_{n+1}(x)=\left(\frac{2n}{x}\right)Y_n(x)$$

$$J_{n-1}(x)-J_{n+1}(x)=2\frac{d\left(J_n(x)\right)}{dx}\qquad Y_{n-1}(x)-Y_{n+1}(x)=2\frac{d\left(Y_n(x)\right)}{dx}$$

$$nJ_n(x)+x\frac{d\left(J_n(x)\right)}{dx}=J_{n-1}(x)\qquad nY_n(x)+x\frac{d\left(Y_n(x)\right)}{dx}=xY_{n-1}(x)$$

$$nJ_n(x)-x\frac{d\left(J_n(x)\right)}{dx}=J_{n+1}(x)\qquad nY_n(x)-x\frac{d\left(Y_n(x)\right)}{dx}=xY_{n+1}(x)$$

$$I_{n-1}(x)+I_{n+1}(x)=\left(\frac{2n}{x}\right)I_n(x)\qquad K_{n-1}(x)+K_{n+1}(x)=\left(\frac{2n}{x}\right)K_n(x)$$

$$I_{n-1}(x)+I_{n+1}(x)=2\frac{d\left(I_n(x)\right)}{dx}\qquad K_{n-1}(x)+K_{n+1}(x)=-2\frac{d\left(K_n(x)\right)}{dx}$$

$$nI_n(x)+x\frac{d\left(I_n(x)\right)}{dx}=xI_{n-1}(x)\qquad nK_n(x)+x\frac{d\left(K_n(x)\right)}{dx}=-xK_{n-1}(x)$$

$$nI_n(x)-x\frac{d\left(I_n(x)\right)}{dx}=-xI_{n+1}(x)\qquad nK_n(x)-x\frac{d\left(K_n(x)\right)}{dx}=xK_{n+1}(x)$$

iv. *Integral properties*

$$\int\alpha x^kJ_{k-1}(\alpha x)dx=x^kJ_k(\alpha x)\qquad \int\alpha x^kY_{k-1}(\alpha x)dx=x^kY_k(\alpha x)$$

$$\int\alpha x^kI_{k-1}(\alpha x)dx=x^kI_k(\alpha x)\qquad \int\alpha x^kK_{k-1}(\alpha x)dx=-x^kK_k(\alpha x)$$

$$\int_{n=0}^{\infty}\left[J_k(\alpha x)\right]^2xdx=\frac{1}{2}x^2\left[J_k^2(\alpha x)-J_{k-1}(\alpha x)\,J_{k+1}(\alpha x)\right]$$

$$\int_{n=0}^{\infty}\left[I_k(\alpha x)\right]^2xdx=\frac{1}{2}x^2\left[I_k^2(\alpha x)-J_{k-1}(\alpha x)\,I_{k+1}(\alpha x)\right]$$

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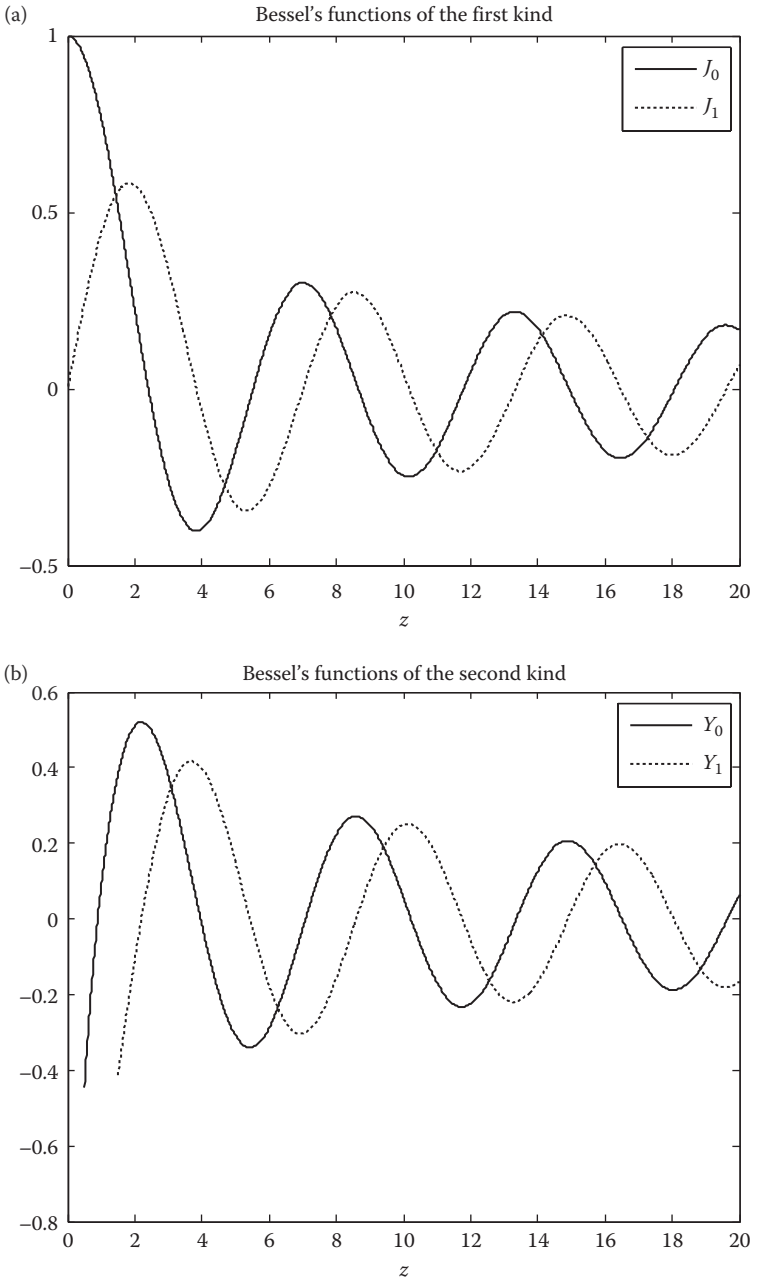


FIGURE 2.3
(a) Variation of Bessel functions of the first kind with independent variable z. (b) Variation of Bessel functions of the second kind with independent variable z. (c) Variation of modified Bessel functions of the first kind with independent variable z. (d) Variation of modified Bessel functions of the second kind with independent variable z.

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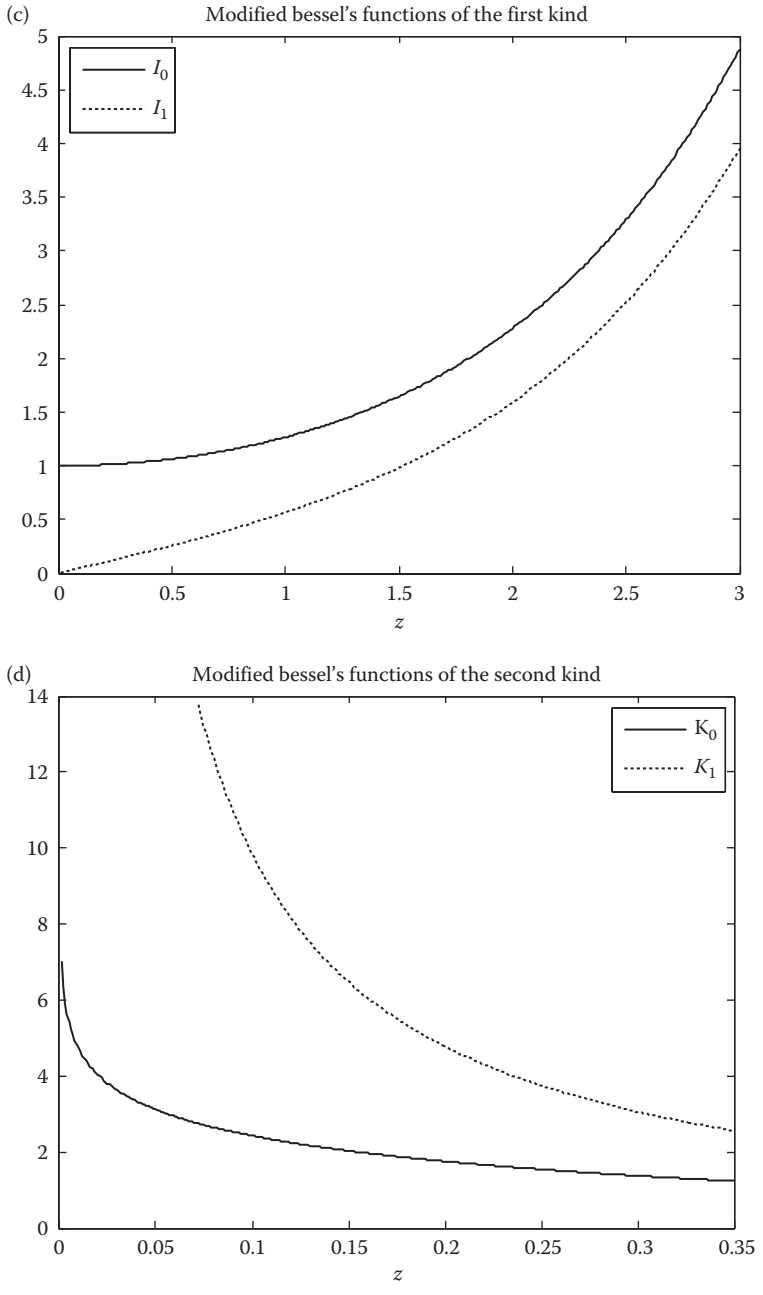


FIGURE 2.3 (CONTINUED)
(a) Variation of Bessel functions of the first kind with independent variable z. (b) Variation of Bessel functions of the second kind with independent variable z. (c) Variation of modified Bessel functions of the first kind with independent variable z. (d) Variation of modified Bessel functions of the second kind with independent variable z.

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We may apply the orthogonality principle to the IC equation as:

$$\int_0^1 J_0(B_n\eta)\,\eta d\eta = C_n \int_0^1 (J_0(B_n\eta))^2\,\eta d\eta.$$

We use identities

$$\int \alpha x^k J_{k-1}(\alpha x)dx = x^k J_k(\alpha x), \quad J_{-n}(x) = (-1)^n J_n(x)$$

and

$$\int_{n=0}^{\infty} \left[J_k(\alpha x)\right]^2 x dx = \frac{1}{2}x^2\left[J_k^2(\alpha x) - J_{k-1}(\alpha x)\,J_{k+1}(\alpha x)\right]$$

(see Table 2.8) then calculate $C_n = 2/[B_n J_1(B_n)]$. The final solution is:

$$\theta = \sum_{n=1}^{\infty} \frac{2}{B_n^2 J_1(B_n)} \exp\left(-B_n^2\tau\right) J_0\left(B_n\eta\right).$$

Temperature profiles along the radius 3 and 7 minutes after the beginning of the process are computed with MATLAB® code E.2.10 and plotted in Figure E.2.10.

MATLAB® CODE E. 2.10

Command Window:

```
clear all
close all

T1 = 102;
T0 =4;
time(1) = 0;
alpha= 3.9e-6; % m2/min
Radius = 0.008;
Bn=[2.405 5.520 8.654 11.792 14.93 18.07 21.212 24.353 27.494];

% model (r=0.0001 cm)
deltaR=0.0001;
for j=1:1:10;
        time(j)=j;
        r=0;
      for k=1:1:80;
       R(k)=r;
          ssum=0 ;
               for n=1:9;
                   z= Bn(n)*R(k)/Radius;
                   s(n)=exp(-(alpha* time(j)/(Radius^2))*(Bn(n)^2))
                   *besselj(0,z)/((Bn(n)^2)*besselj(1,Bn(n)));
                end
          ssum=sum(s) ;
          T(j,k)=T1+2*(T0-T1)*ssum ;
          r=r+deltaR ;
       end
```

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```
end
plot(R,T(3,:), '-'); hold on
plot(R,T(7,:), ':'); hold on
ylabel('Temperature (C)')
xlabel('r (m)')
legend('t=3 min','t=7 min', 2,'Location','SouthEast')
```

Figure E.2.10 will appear on the screen when we run the code.

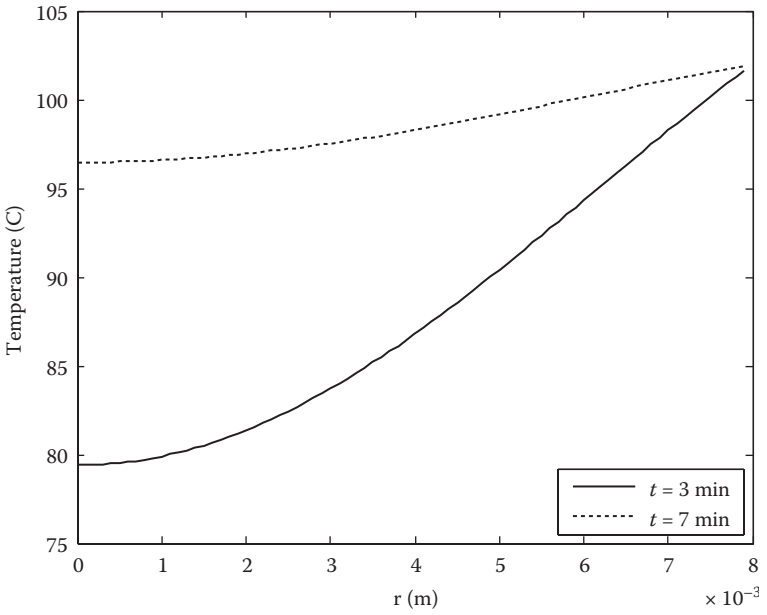


FIGURE E.2.10
Temperature profiles along the sausage 3 and 7 minutes after dipping into boiling water.

Some of the properties and values of Bessel's and modified Bessel's functions are given in Tables 2.7 through 2.15. MATLAB code 2.1 computes and plots these functions as depicted in Figures 2.3a–d.

Example 2.11: Determination of the Temperature Profiles in a Spherical Potato Tuber by Using the Generalized Bessel's Equation

It was shown that temperature profiles in a spherical potato tuber (Example 2.9) may be described as (Sarikaya and Özilgen 1991)

$$\frac{\partial\theta}{\partial\tau}=\frac{2}{\eta}\frac{\partial\theta}{\partial\eta}+\frac{\partial^2\theta}{\partial\eta^2}$$

with

BC1: $\theta = 0$ at $\eta = 1$ when $\tau > 0$
BC2: $d\theta/d\eta = 0$ (θ is finite) at $\eta = 0$ when $\tau > 0$
BC3: $\theta = 0$ for all η when $t \to \infty$
IC: $\theta = 1$ when $\tau = 0$,

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TABLE 2.9

Generalized Form of the Bessel's Equation

$$x^2\frac{d^2y}{dx^2}+x(a+2bx^r)\frac{dy}{dx}+\left[c+dx^{2s}-b(1-a-r)x^r+b^2x^{2r}\right]y=0$$

is called the generalized Bessel's equation and its solution is:

$$y=x^{(1-a)/2}\exp\left\{-\frac{bx^r}{r}\right\}\left[C_1Z_p\left(\frac{\sqrt{|d|}}{s}x^s\right)+C_2Z_{-p}\left(\frac{\sqrt{|d|}}{s}x^s\right)\right]$$

where $p=\frac{1}{s}\sqrt{\left(\frac{1-a}{2}\right)^2-c}$

if $\frac{\sqrt{d}}{s}$ = real, $p\neq 0$ or $p\neq$ integer	$Z_p=J_p, Z_{-p}=J_{-p}$
if $\frac{\sqrt{d}}{s}$ = real, $p=0$ or $p=$ integer	$Z_n=J_p, Z_{-p}=Y_n$
if $\frac{\sqrt{d}}{s}$ = imaginary, $p\neq 0$ or $p\neq$ integer	$Z_p=I_p, Z_{-p}=I_{-p}$
if $\frac{\sqrt{d}}{s}$ = imaginary, $p=0$ or $p=$ integer	$Z_p=I_p, Z_{-p}=K_n$

where

$$\theta=\frac{T-T_1}{T_0-T_1},\quad \eta=\frac{r}{R},\quad \text{and}\quad \tau=\frac{\alpha t}{R^2}.$$

After using the method of the separation of variables

$$\theta(\eta,\tau)=f(\eta)\,g(\tau)$$

it was found that

$$g=C_1e^{-C^2\tau},$$

and the other equation was rearranged as

$$\eta^2\frac{\partial^2 f}{\partial\eta^2}+2\eta\frac{\partial f}{\partial\eta}+\eta^2C^2f=0.$$

Use the generalized Bessel's equation to obtain the same solution.

Solution: The generalized Bessel's equation and its solution are (Table 2.9)

$$\eta^2\frac{d^2f}{d\eta^2}+\eta\left(a+2\,b\,x^r\right)\frac{df}{d\eta}+\left[c+d\eta^{2s}-b(1-a-r)\eta^r+b^2\eta^{2r}\right]f=0,$$

and

$$f=\eta^{(1-a)/2}\exp\left\{-\frac{b\,\eta^r}{r}\right\}\left[C_1Z_p\left(\frac{\sqrt{|d|}}{s}\eta^s\right)+C_2Z_{-p}\left(\frac{\sqrt{|d|}}{s}x^s\right)\right],$$

where

$$p=(1/s)\sqrt{((1-a)/2)^2-c}.$$

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TABLE 2.10

Bessel Functions $J_0(x)$ and $J_1(x)$

x	$J_0(x)$	$J_1(x)$	x	$J_0(x)$	$J_1(x)$	x	$J_0(x)$	$J_1(x)$	x	$J_0(x)$	$J_1(x)$
0.0	1.0000	0.0000	4.0	–0.3971	–0.0660	8.0	0.1717	0.2346	12.0	0.0477	–0.2234
0.1	0.9975	0.0499	4.1	–0.3887	–0.1033	8.1	0.1475	0.2476	12.1	0.0697	–0.2157
0.2	0.9900	0.0995	4.2	–0.3765	–0.1386	8.2	0.1222	0.2580	12.2	0.0908	–0.2050
0.3	0.9776	0.1483	4.3	–0.3610	–0.1719	8.3	0.0960	0.2657	12.3	0.1108	–0.1943
0.4	0.9604	0.1960	4.4	–0.3423	–0.2028	8.4	0.0692	0.2708	12.4	0.1296	–0.1807
0.5	0.9385	0.2423	4.5	–0.3205	–0.2311	8.5	0.0419	0.2731	12.5	0.1469	–0.1655
0.6	0.9120	0.2867	4.6	–0.2961	–0.2566	8.6	0.0146	0.2728	12.6	0.1626	–0.1487
0.7	0.8812	0.3290	4.7	–0.2693	–0.2791	8.7	–0.0125	0.2697	12.7	0.1766	–0.1307
0.8	0.8463	0.3688	4.8	–0.2404	–0.2985	8.8	–0.0392	0.2641	12.8	0.1887	–0.1114
0.9	0.8075	0.4059	4.9	–0.2097	–0.3147	8.9	–0.0653	0.2559	12.9	0.1988	–0.0912
1.0	0.7652	0.4401	5.0	–0.1776	–0.3276	9.0	–0.0903	0.2453	13.0	0.2069	–0.0703
1.1	0.7196	0.4709	5.1	–0.1443	–0.3371	9.1	–0.1142	0.2324	13.1	0.2129	–0.0489
1.2	0.6711	0.4983	5.2	–0.1103	–0.3432	9.2	–0.1367	0.2174	13.2	0.2167	–0.0271
1.3	0.6201	0.5220	5.3	–0.0758	–0.3460	9.3	–0.1577	0.2004	13.3	0.2183	–0.0052
1.4	0.5669	0.5419	5.4	–0.0412	–0.3453	9.4	–0.1768	0.1816	13.4	0.2177	0.0166
1.5	0.5118	0.5579	5.5	–0.0068	–0.3414	9.5	–0.1939	0.1613	13.5	0.2150	0.0380
1.6	0.4554	0.5699	5.6	0.0270	–0.3343	9.6	–0.2090	0.1395	13.6	0.2101	0.0590
1.7	0.3980	0.5778	5.7	0.0599	–0.3241	9.7	–0.2218	0.1166	13.7	0.2032	0.0791
1.8	0.3400	0.5815	5.8	0.0917	–0.3110	9.8	–0.2323	0.0928	13.8	0.1943	0.0984
1.9	0.2818	0.5812	5.9	0.1220	–0.2951	9.9	–0.2403	0.0684	13.9	0.1836	0.1165
2.0	0.2239	0.5767	6.0	0.1506	–0.2767	10.0	–0.2459	0.0435	14.0	0.1711	0.1334
2.1	0.1666	0.5683	6.1	0.1773	–0.2559	10.1	–0.2490	0.0184	14.1	0.1570	0.1488
2.2	0.1104	0.5560	6.2	0.2017	–0.2329	10.2	–0.2496	–0.0066	14.2	0.1414	0.1626
2.3	0.0555	0.5399	6.3	0.2238	–0.2081	10.3	–0.2477	–0.0313	14.3	0.1245	0.1747
2.4	0.0025	0.5202	6.4	0.2433	–0.1816	10.4	–0.2434	–0.0555	14.4	0.1065	0.1850
2.5	–0.0484	0.4971	6.5	0.2601	–0.1538	10.5	–0.2366	–0.0789	14.5	0.0875	0.1934
2.6	–0.0968	0.4708	6.6	0.2740	–0.1250	10.6	–0.2276	–0.1012	14.6	0.0679	0.1999
2.7	–0.1424	0.4416	6.7	0.2851	–0.0953	10.7	–0.2164	–0.1224	14.7	0.0476	0.2043
2.8	–0.1850	0.4097	6.8	0.2931	–0.0652	10.8	–0.2032	–0.1422	14.8	0.0271	0.2066
2.9	–0.2243	0.3754	6.9	0.2981	–0.0349	10.9	–0.1881	–0.1603	14.9	0.0064	0.2069
3.0	–2.601	0.3391	7.0	0.3001	–0.0047	11.0	–0.1712	–0.1768			
3.1	–0.2921	0.3009	7.1	0.2991	0.0252	11.1	–0.1528	–0.1913			
3.2	–0.3202	0.2613	7.2	0.2951	0.0543	11.2	–0.1330	–0.2039			
3.3	–0.3443	0.2207	7.3	0.2882	0.0826	11.3	–0.1121	–0.2143			
3.4	–0.3643	0.1792	7.4	0.2786	0.1096	11.4	–0.0902	–0.2225			
3.5	–0.3801	0.1374	7.5	0.2663	0.1352	11.5	–0.0677	–0.2284			
3.6	–0.3918	0.0955	7.6	0.2516	0.1592	11.6	–0.0446	–0.2320			
3.7	–0.3992	0.0538	7.7	0.2346	0.1813	11.7	–0.0213	–0.2333			
3.8	–0.4026	0.0128	7.8	0.2154	0.2014	11.8	–0.0020	–0.2323			
3.9	–0.4018	–0.0272	7.9	0.1944	0.2192	11.9	–0.0250	–0.2290			

Notes: You may compute this table by using MATLAB® functions: $J_0(x)$ = besselj(0,x) and $J_1(x)$ = besselj(1,x). besselj(0:1,(0:0.1:15)′) generates the values given in the entire table. See the note in Table 2.14.

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TABLE 2.11

Bessel Functions $Y_0(x)$ and $Y_1(x)$

x	$Y_0(x)$	$Y_1(x)$	x	$Y_0(x)$	$Y_1(x)$	x	$Y_0(x)$	$Y_1(x)$
0.0	–∞	–∞	1.50	0.382	–0.412	3.50	0.189	0.410
0.05	–1.979	–12.790	1.60	0.420	–0.347	3.60	0.148	0.415
0.10	–1.534	–6.459	1.70	0.452	–0.285	3.70	0.106	0.417
0.15	–1.271	–4.364	1.80	0.477	–0.224	3.80	0.064	0.414
0.20	–1.081	–3.324	1.90	0.497	–0.164	3.90	0.023	0.408
0.25	–0.932	–2.704	2.00	0.510	–0.107	4.00	–0.017	0.398
0.30	–0.807	–2.293	2.10	0.518	–0.052	4.10	–0.056	0.384
0.35	–0.700	–2.000	2.20	0.521	0.0015	4.20	–0.094	0.368
0.40	–0.606	–1.781	2.30	0.518	0.052	4.30	–0.130	0.348
0.45	–0.521	–1.610	2.40	0.510	0.100	4.40	–0.163	0.326
0.50	–0.444	–1.471	2.50	0.498	0.146	4.50	–0.195	0.301
0.60	–0.308	–1.260	2.60	0.481	0.188	4.60	–0.223	0.274
0.70	–0.191	–1.103	2.70	0.460	0.228	4.70	–0.249	0.244
0.80	–0.087	–0.978	2.80	0.436	0.263	4.80	–0.272	0.213
0.90	0.0056	–0.873	2.90	0.408	0.296	4.90	–0.292	0.181
1.00	0.088	–0.781	3.00	0.377	0.325	5.00	–0.308	0.148
1.10	0.162	–0.698	3.10	0.343	0.350			
1.20	0.228	–0.621	3.20	0.307	0.371			
1.30	0.286	–0.548	3.30	0.269	0.338			
1.40	0.338	–0.479	3.40	0.230	0.401			

Notes: You may compute this table by using MATLAB® functions: $Y_0(x) = \text{bessely}(0,x)$ and $Y_1(x) = \text{bessely}(1,x)$. bessely(0:1,(0:0.05:5)′) generates the values given in the entire table. See note in Table 2.14.

In the given example $a = 2$, $b = 0$, $c = 0$, $d = C^2$, and $s = 1$, therefore, $p = ½$.

Since $C^2 > 0$, $\sqrt{d}/s = \text{real}$, $Z_p = J_p$, $Z_{-p} = J_{-p}$ then the solution is

$$f = \eta^{-1/2}\left[C_1 J_{1/2}(C\eta) + C_2 J_{-1/2}(C\eta)\right].$$

Table 2.8 shows that

$$J_{1/2}(x) = \sqrt{\frac{2}{\pi x}}\sin(x)$$

and

$$J_{-1/2}(x) = \sqrt{\frac{2}{\pi x}}\cos(x),$$

therefore,

$$f = \frac{1}{\eta}\left[C_1\sqrt{\frac{2}{\pi}}\text{Sin}(C\eta) + C_2\sqrt{\frac{2}{\pi}}\text{Cos}(C\eta)\right].$$

BC2 implies θ is finite when $\eta = 0$, but

$$\frac{C_2}{\eta}\sqrt{\frac{2}{\pi}}\text{Cos}(C\eta) \to \infty,$$

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TABLE 2.12

Modified Bessel Functions $I_0(x)$ and $I_1(x)$

x	$I_0(x)$	$I_1(x)$	x	$I_0(x)$	$I_1(x)$	x	$I_0(x)$	$I_1(x)$
0.0	1.000	0.0000	1.80	1.990	1.317	3.60	8.028	6.793
0.10	1.002	0.050	1.90	2.128	1.448	3.70	8.739	7.436
0.20	1.010	0.100	2.00	2.280	1.591	3.80	9.517	8.140
0.30	1.023	0.152	2.10	2.446	1.745	3.90	10.369	8.913
0.40	1.040	0.204	2.20	2.629	1.914	4.00	11.30	9.759
0.50	1.063	0.258	2.30	2.830	2.098	4.10	12.32	10.69
0.60	1.092	0.314	2.40	3.049	2.298	4.20	13.44	11.70
0.70	1.126	0.372	2.50	3.290	2.517	4.30	14.67	12.82
0.80	1.166	0.433	2.60	3.553	2.755	4.40	16.01	14.04
0.90	1.213	0.497	2.70	3.842	3.016	4.50	17.48	15.39
1.00	1.266	0.565	2.80	4.157	3.301	4.60	19.09	16.86
1.10	1.326	0.637	2.90	4.503	3.613	4.70	20.86	18.48
1.20	1.394	0.715	3.00	4.881	3.953	4.80	22.79	20.25
1.30	1.469	0.797	3.10	5.294	4.326	4.90	24.91	22.20
1.40	1.553	0.886	3.20	5.747	4.734	5.00	27.24	24.34
1.50	1.647	0.982	3.30	6.243	5.181			
1.60	1.750	1.085	3.40	6.785	5.670			
1.70	1.864	1.196	3.50	7.378	6.206			

Notes: You may compute this table by using MATLAB® functions: $I_0(x)$ = besseli(0,x) and $I_1(x)$ = besseli(1,x). besseli(0:1,(0:0.1:5)′) generates the values given in the entire table. See the note in Table 2.14.

therefore,

$$\frac{C_2}{\eta}\sqrt{\frac{2}{\pi}}\mathrm{Cos}(C\eta)$$

may not be a solution, and we conclude that $C_2 = 0$, therefore, the solution is

$$\theta = fg = \frac{C_n}{\eta}e^{-C^2\tau}\sqrt{\frac{2}{\pi}}\mathrm{Sin}(C\eta).$$

Constants C and C_n will be evaluated the same way as in the previous solution and we will obtain (Sarikaya and Özilgen 1991)

$$\frac{T-T_1}{T_0-T_1} = \frac{R}{r}\left(\frac{2}{\pi}\right)\sum_{n=0}^{\infty}\left\{\frac{(-1)^{n+1}}{n}e^{-C^2\tau}\sin\left(\frac{\pi nR}{R}\right)\right\}.$$

Example 2.12: Liquid Diffusion Model for Drying Rough Rice

The rice grain may be represented by a finite cylinder of radius R and length $2L$. The moisture removal is assumed to be in a liquid state and described by the equation of continuity in a cylindrical coordinate system:

$$\frac{\partial c_A}{\partial t} + \left(\frac{1}{r}\frac{\partial rN_{Ar}}{\partial r} + \frac{1}{r}\frac{\partial N_{A\theta}}{\partial \theta} + \frac{\partial N_{Az}}{\partial z}\right) = R_A. \tag{2.13}$$

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TABLE 2.13

Modified Bessel Functions $K_0(x)$ and $K_1(x)$

x	$K_0(x)$	$K_1(x)$	x	$K_0(x)$	$K_1(x)$	x	$K_0(x)$	$K_1(x)$
0.0	–∞	–∞	1.50	0.214	0.277	3.50	0.0196	0.0222
0.05	3.114	19.910	1.60	0.188	0.241	3.60	0.0175	0.0198
0.10	2.427	9.854	1.70	0.165	0.209	3.70	0.0156	0.0176
0.15	2.030	6.477	1.80	0.146	0.183	3.80	0.0140	0.0157
0.20	1.753	4.776	1.90	0.129	0.160	3.90	0.0125	0.0140
0.25	1.541	3.747	2.00	0.114	0.140	4.00	0.0112	0.0125
0.30	1.327	3.056	2.10	0.101	0.123	4.10	0.0100	0.0111
0.35	1.233	2.559	2.20	0.0893	0.108	4.20	0.0089	0.0099
0.40	1.114	2.184	2.30	0.0791	0.0950	4.30	0.0080	0.0089
0.45	1.013	1.892	2.40	0.0702	0.0837	4.40	0.0071	0.0079
0.50	0.924	1.656	2.50	0.0623	0.0739	4.50	0.0064	0.0071
0.60	0.778	1.303	2.60	0.0554	0.0653	4.60	0.0057	0.0063
0.70	0.660	1.050	2.70	0.0492	0.0577	4.70	0.0051	0.0056
0.80	0.565	0.862	2.80	0.0438	0.0511	4.80	0.0046	0.0050
0.90	0.487	0.716	2.90	0.0390	0.0453	4.90	0.0041	0.0045
1.00	0.421	0.602	3.00	0.0347	0.0402	5.00	0.0037	0.0040
1.10	0.366	0.510	3.10	0.0310	0.0356			
1.20	0.318	0.434	3.20	0.0276	0.0316			
1.30	0.278	0.372	3.30	0.0246	0.0281			
1.40	0.244	0.321	3.40	0.0220	0.0250			

Notes: You may compute this table by using MATLAB® functions $K_0(x)$ = besselk(0,x) and $K_1(x)$ = besselk(1,x). It is possible to generate all the $K_0(x)$ and $K_1(x)$ values of the table with besselk(0:1,(0:0.05:5)′). See the note in Table 2.14.

We may neglect the diffusion in angular direction $1/r\ \partial N_{A\theta} / \partial\theta = 0$, since water does not involve into any reactions $R_A = 0$, then Equation 2.13 becomes

$$\frac{\partial c_A}{\partial t} + \left(\frac{1}{r} \frac{\partial r N_{Ar}}{\partial r} + \frac{\partial N_{Az}}{\partial z} \right) = 0.$$

Total flux of water in z direction is

$$N_{AZ} = x_A \left(N_A + N_B \right) - D_{AB} \frac{dc_A}{dz}. \tag{2.10}$$

Total flux of water in r direction may be stated as

$$N_{Ar} = x_A \left(N_A + N_B \right) - D_{AB} \frac{dc_A}{dr},$$

we may assume that the fraction of water in rice x_A is small and neglects the term $x_A(N_A + N_B)$ we will obtain the expressions for N_{Az} and N_{Ar} as

$$N_{AZ} = -D_{AB} \frac{dc_A}{dz}$$

$$N_{Ar} = -D_{AB} \frac{dc_A}{dr}.$$

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TABLE 2.14

Values of B_n for Which $J_0(B_n) = 0$ and Corresponding Values of $J_1(B_n)$

n	B_n	$J_1(B_n)$
1	2.4048	0.5191
2	5.5201	–0.3404
3	8.6537	0.2715
4	11.7915	–0.2324
5	14.9309	0.2065

Note: For an extensive list of the mathematical functions given in Tables 2.10 through 2.14 an interested reader may refer to *Mathematical Tables*, Volume 6, Part 1, *Bessel Functions of Orders Zero and Unity*, British Association of Advancement of Science, Cambridge University Press, 1958.

You may obtain the values of B_n after running the following MATLAB® code. You may produce values of $J_1(B_n)$ with the MATLAB function $J_1(B_n)$ = besselj(1,B_n).

MATLAB CODE T.2.14

Command Window:

```
clear all
close all
x=1:0.1:16
x0=15; % run the code by entering a value of x0, around which you
are searching for the zero value of the function. fzero finds only
one value, which makes the function zero, so you have to enter only
one x0 value at a time.
for i=1:length(x);
Bn(i)=fzero('besselj(0,x)',x0)
end
```

When you run this code, the code will find the value of $B_n = 5.5201$ for all the trials. If you should choose $x_0 = 13$ the answer will be $B_n = 11.7915$. If you should choose $x_0 = 15$ the answer will be $B_n = 14.9309$. It is recommended plotting $J_0(x)$ versus x then search for *Bn* by looking for the points where $J_0(x)$ changes sign.

The rice used in this study has 22–24% water. Neglecting the term $x_A(N_A + N_B)$ simplifies the solution of the problem, but exaggerates the effect of diffusion described by the terms $D_{AB}(dc_A/dz)$ or $D_{AB}(dc_A/dr)$. Since the process is treated like pure diffusion in contrast to the actual mechanism, we will refer the constant D_{AB} as the *apparent diffusivity*. Apparent constants are frequently used in modeling. After substituting the final forms of N_{Az} and N_{Ar} in the simplified form of the equation of continuity and neglecting the subscripts we will have

$$\frac{\partial c}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right) + \frac{\partial}{\partial z}\left(\frac{\partial c}{z}\right)\right].$$

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TABLE 2.15

Values of $K_{1/4}(x)$ and Its Derivatives $d[K_{1/4}(x)]/dx$

x	$K_{1/4}(x)$	$d[K_{1/4}(x)]/dx$	x	$K_{1/4}(x)$	$d[K_{1/4}(x)]/dx$
0.1	2.69	12.3	3.1	0.031229	0.036030
0.2	1.878	5.50	3.2	0.027833	0.031983
0.3	1.448	3.39	3.3	0.024817	0.028409
0.4	1.1651	2.370	3.4	0.022137	0.025251
0.5	0.9603	1.772	3.5	0.019755	0.022457
0.6	0.80399	1.3795	3.6	0.017635	0.019983
0.7	0.68058	1.1037	3.7	0.015749	0.017791
0.8	0.58086	0.90026	3.8	0.014069	0.015847
0.9	0.49893	0.74502	3.9	0.012572	0.014121
1.0	0.37342	0.62346	4.0	0.011238	0.012589
1.1	0.32486	0.52635	4.1	0.010049	0.011228
1.2	0.28345	0.44754	4.2	0.0089877	0.010018
1.3	0.28345	0.38278	4.3	0.0080407	0.0089420
1.4	0.24794	0.32900	4.4	0.0071953	0.0079841
1.5	0.21736	0.28396	4.5	0.0064404	0.0071312
1.6	0.19091	0.24597	4.6	0.0057660	0.0063714
1.7	0.16797	0.21372	4.7	0.0051633	0.0056943
1.8	0.14801	0.18621	4.8	0.0046247	0.0050906
1.9	0.13060	0.16262	4.9	0.0041430	0.0045522
2.0	0.11538	0.14233	5.0	0.0037123	0.0040718
2.1	0.10204	0.12480	6.0	0.0012500	0.0013514
2.2	0.090341	0.10961	8.0	0.0001470	0.0001560
2.3	0.080054	0.096426	10.0	0.0000178	0.0000187
2.4	0.070999	0.084941			
2.5	0.063017	0.074919			
2.6	0.055973	0.066156			
2.7	0.049750	0.058480			
2.8	0.044246	0.051744			
2.9	0.039374	0.045826			
3.0	0.035057	0.040618			

Source: Carsten, H. R. F. and McKerrow, N. W., *Philosophy Magazine,* 35, 812–18, 1944.
Note: You may compute the $K_{1/4}(x)$ values given in this table by using MATLAB® functions K(x) = besselk(0.25,x).

This equation may be simplified further

$$\frac{\partial c}{\partial t} = D\left[\frac{\partial^2 c}{\partial r^2} + \frac{1}{r}\frac{\partial c}{\partial r} + \frac{\partial^2 c}{\partial z^2}\right].$$

The boundary and the initial conditions are

BC1: $c(t,R,z) = c_e$
BC2,3 : $c(t,r,L) = c_e$ $t > 0$
BC4: $[dc/dr_{r=0}] = 0$
BC5: $[dc/dz]_{z=0} = 0$
IC: $c(0,r,z) = c_0$.

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MATLAB® CODE 2.1

Command Window:

```
clear all
close all

% compute Bessel's functions of the first kind
for n=1:2000;
     z(n)= n*0.01;
     J0(n)= besselj(0,z (n));
     J1(n)= besselj(1,z(n));
end

% plot Bessel's Functions of the First Kind
plot(z,J0, '-', z,J1, ':'); hold on
ylabel('Bessel's Functions of the First Kind')
xlabel('z')
legend('J_0','J_1', 2,'Location','NorthEast')
title('Bessel's Functions of the First Kind')

% compute Bessel's functions of the second kind
for n=50:2000;
     z(n)= n*0.01;
     Y0(n)= bessely(0,z(n));
     Y1(n)= bessely(1,z(n));
end

% plot Bessel's functions of the second kind
figure(2)
plot(z(50:2000),Y0(50:2000), '-', z(150:2000),Y1(150:2000), ':');
hold on
ylabel('Bessel's Functions of the Second Kind')
xlabel('z')
legend('Y_0','Y_1', 2,'Location','NorthEast')
title('Bessel's Functions of the Second Kind')

% compute modified Bessel's functions of the first kind
for n=1:2000;
     z(n)= n*0.01;
     I0(n)= besseli(0,z(n));
     I1(n)= besseli(1,z(n));
end

% plot modified Bessel's functions of the first kind
figure(3)
plot(z(1:300),I0(1:300), '-', z(1:300),I1(1:300), ':'); hold on
ylabel('Modified Bessel's Functions of the First Kind')
xlabel('z')
legend('I_0','I_1', 2,'Location','NorthWest')
title('Modified Bessel's Functions of the First Kind')
```

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```
% compute modified Bessel's functions of the second kind
for n=1:600;
     z(n)= n*0.001;
     K0(n)= besselk(0,z(n));
     K1(n)= besselk(1,z(n));
end

% plot modified Bessel's functions of the second kind
figure(4)
plot(z(1:350),K0(1:350), '-', z(72:350),K1(72:350), ':'); hold on
ylabel('Modified Bessel's Functions of the Second Kind')
xlabel('z')
legend('K_0','K_1', 2,'Location','NorthEast')
title('Modified Bessel's Functions of the Second Kind')
```

Figure 2.3a through d will appear on the screen when we run the code.

Dimensionless variables $c = (c - c_e)/(c_0 - c_e)$, $\xi = r/R$, $\eta = z/L$, $\tau = tD/R^2$, and $\ell = L/R$ may be introduced, then the partial differential equation, BCs, and IC, becomes

$$\frac{\partial c}{\partial \tau} = \frac{\partial^2 c}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial c}{\partial \xi} + \frac{1}{\ell^2}\frac{\partial^2 c}{\partial \eta^2}$$

BC1: $c(\tau,1,\eta) = 0$
BC2,3: $c(\tau,\zeta,1) = 0$ $\tau > 0$
BC4: $[dc/d\xi]_{\xi=0} = 0$
BC5: $[dc/d\eta]_{\eta=0} = 0$
IC: $c(0,\zeta,\eta) = 1$.

A new dependent variable may be defined to apply the method of the separation of variables:

$$c(\tau,\zeta,\eta) = \mathcal{R}(\tau,\zeta)\mathcal{Z}(\tau,\eta).$$

The dimensionless partial differential equation may be arranged as

$$\mathcal{R}\left(\frac{1}{\ell^2}\frac{\partial^2 \mathcal{Z}}{\partial \eta^2} - \frac{\partial Z}{\partial \tau}\right) + Z\left(\frac{\partial^2 \mathcal{R}}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial \mathcal{R}}{\partial \xi} - \frac{\partial \mathcal{R}}{\partial \tau}\right) = 0.$$

This equation is satisfied if

$$\frac{\partial^2 \mathcal{R}}{\partial \xi^2} + \frac{1}{\xi}\frac{\partial \mathcal{R}}{\partial \xi} - \frac{\partial \mathcal{R}}{\partial \tau} = 0$$

(unsteady state diffusion in radial direction) with the BCs and the IC as

$$\text{BC: } \mathcal{R}(\tau,1) = 0$$

$$\text{BC: } \left[\frac{d\mathcal{R}}{d\xi}\right]_{\xi=0} = 0$$

$$\text{IC: } \mathcal{R}(0,\zeta) = 1$$

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and

$$\frac{1}{\ell^2}\frac{\partial^2 Z}{\partial \eta^2} - \frac{\partial Z}{\partial \tau} = 0$$

(unsteady state diffusion in longitudinal direction)

$$\text{BC: } Z(\tau,1) = 0$$

$$\text{BC}: \left[\frac{dZ}{d\eta}\right]_{\eta=0} = 0$$

$$\text{IC: } Z(0,\eta) = 1.$$

We may use the method of the separation variables to solve the unsteady state diffusion in longitudinal direction: $Z(\tau,\eta) = f(\eta)\, g(\tau)$ and the equation is rewritten as

$$(1/\ell^2)(1/f)(\partial^2 f/\partial\eta^2) = (1/g)(\partial g/\partial\tau) = -C^2,$$

individual equations and their solutions are

Differential Equation	Solution
$\frac{dg}{d\tau} + C^2 g = 0$	$g = C_1 \exp(-C^2\tau)$ (see the previous examples)
$\frac{d^2 f}{d\eta^2} + C^2\ell^2 f = 0$	$f = C_2 \sin(C\ell\eta) + C_3 \cos(C\ell\eta)$ (see Table 2.6)

The solution to our problem should be symmetric, but the sin function is not symmetric; that is, $\sin(\alpha x) \neq (\sin - \alpha x)$, therefore $C_2 = 0$ and

$$Z(\tau,\eta) = C_m \exp(-C^2\tau)\cos(C\ell\eta),$$

where $C_m = C_1 C_3$.

The BC is $Z(\tau,1) = 0$; that is, $0 = C_4 \exp(-C^2\tau)\cos(C\ell)$ and satisfied when $C_m = \beta_m = [(2m-1)\pi/2l]$ and the final equation is

$$Z(\tau,\eta) = C_m \exp\{-(\beta_m^2\tau)\}\cos(\beta_m \ell\,\eta).$$

The IC is $Z(0,\tau)$ 1; that is, $1 = C_m\cos(\beta_m \ell\,\eta)$, which requires $C_m = (-1)^m(2/l\beta_m)$, then the solution becomes

$$Z(\tau,\eta) = \frac{2}{\ell}\sum_{m=1}^{\infty}\left[\frac{(-1)^{m+1}}{\beta_m}\right]\cos[\beta_m \ell\,\eta]\exp[-\beta_m^2\tau].$$

We may use the method of the separation of variables to solve the unsteady state diffusion in radial direction:

$$R(\tau,\zeta) = u(\zeta)v(\tau).$$

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After using similar procedures as in the previous examples we will get

$$v = C_4 \exp(-C^2\tau)$$

and

$$u = C_5 J_0(C\zeta) + C_6 Y_0(C\zeta)$$

BC: $[d\mathrm{R}/d\xi]_{\xi=0} = 0$ requires u = finite at $\zeta = 0$, but $Y_0(C\xi) \to -\infty$, therefore, $C_6 = 0$ and the solution becomes $\mathcal{R}(\tau,\zeta) = C_n \exp(-C^2\tau)\, J_0(C\zeta)$, where $C_n = C_4C_5$.

BC: $\mathcal{R}(\tau,1) = 0$ requires $0 = C_n \exp(-C^2\tau)\, J_0(C)$, therefore, $C = B_n$ = Eigen values of $J_0(\zeta)$ and the solution becomes

$$\mathrm{R}(\tau,\zeta) = \sum_{n=1}^{\infty} C_n \exp\left(-B_n^2\tau\right) J_0\left(B_n\zeta\right).$$

We may use the orthogonality principle to determine C_n as in the previous examples: $C_n = 2/B_nJ_1(B_n)$, then the solution is

$$\mathrm{R}(\tau,\zeta) = \sum_{n=1}^{\infty} \frac{2}{B_n J_1\left(B_n\right)} \exp\left(-B_n^2\tau\right) J_0\left(B_n\zeta\right),$$

and the overall solution to the problem is

$$\mathrm{c}(\tau,\xi,\eta) = \mathcal{Z}(\tau,\eta)\mathcal{R}(\tau,\xi) = \frac{c(\tau,\zeta,\eta) - c_e}{c_0 - c_e}$$

$$= \frac{4}{\ell} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{B_n J_1(B_n)\beta_m} J_0\left(B_n\zeta\right) \mathrm{Cos}\left(\beta_m \ell\, \eta\right) \exp\left[-\left(\beta_m^2 + B_n^2\right)\tau\right].$$

When we calculate the average moisture concentration (after performing averaging both in the radial and the axial directions) and rewrite this equation in terms of mass of water as (Ece and Cihan 1993)

$$\frac{m(t) - m_e}{m_0 - m_e} = \frac{2R^2}{\mathrm{L}^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{B_n^2\beta_m^2} \exp\left[-\left(\beta_m^2 + B_n^2\right)\frac{Dt}{R^2}\right].$$

MATLAB® code E.2.12 tests the validity of the final expression by comparing it with the experimental data (Figure E.2.12).

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MATLAB® CODE E.2.12

Command Window:

```
clear all
close all

% Enter the data
timeD1=[0 0.3 0.8 1.2 1.75 2.25 2.80 3.25 3.75 4.25 4.75 5.25 5.75];
% h
mData1=[1 0.84 0.72 0.62 0.54 0.49 0.43 0.4 0.36 0.33 0.32 0.29
0.27]; % (m-me)/(m0-me)
timeD2=[0 0.3 0.8 1.2 1.75 2.25 2.80 3.25 3.75]; % h
mData2=[1 0.84 0.65 0.52 0.44 0.37 0.31 0.28 0.24]; % (m-me)/(m0-me)

D = [3.1258e-8 5.0364e-8]; % m2/h
R = 0.00113; % m
L = 0.0065; % m
Bn=[2.405 5.520 8.654 11.792 14.93 18.07 21.212 24.353 27.494];

% plot the data
plot(timeD1,mData1,'*' ); hold on;
plot(timeD2,mData2,'o' ); hold on;
ylabel('(m-me)/(m0-me)')
xlabel('drying time (h)')
legend('with no tempering','with tempering',
2,'Location','NorthEast')

% model
for i=1:2; % effective diffusion coefficient
time(1) = 0;
    for j=1:1:70; % time
       time(j)=j*0.1;
        tau=(D(i))*(time(j))/(R^2);
        for n=1:1:9; % Bn
             for k=1:1:10; % beta
             beta(k)=(2*k-1)*pi*R/(4*L);
             s(n,k)=1/(((Bn(n))^2)*((beta(k))^2))* exp(-
((((Bn(n))^2)+(((beta(k))^2)))*tau));
        end
        s1sum=sum(s) ;
         end
         s2sum=sum(s1sum) ;
        mRatio(i,j)=(2*(R/L)^2)*s2sum ;
     end
end
plot(time,mRatio(1,:), '-',time,mRatio(2,:), ':');
grid on
```

Figures E.2.12 will appear on the screen when we run the code.

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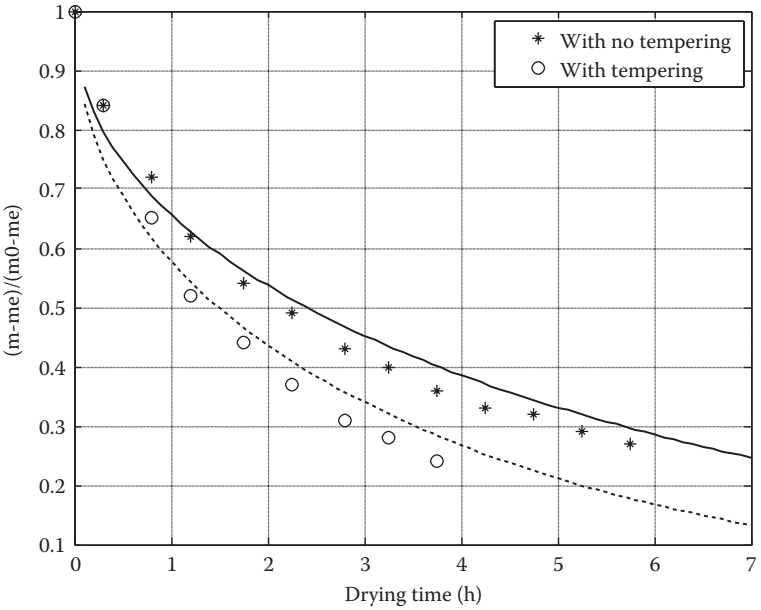


FIGURE E.2.12
Comparison of the model with the experimental data. (From Cihan, A. and Ece, M.C., *Journal of Food Engineering*, 49, 327–31, 2001.) In one of the experiments the initial drying period was 15 and the subsequent drying periods were 30 minutes, respectively. There were 60 minutes of tempering intervals between the drying periods, where the drying equipment was stopped and internal migration of the moisture was permitted without taking the data. The tempering periods were not included into the drying times shown in the horizontal axis of the figure.

Example 2.13: Salting of Semi-Hard Ripened Cheese

During production of semi-hard ripened white cheese (feta cheese), salting is one of the principle steps. Cheese blocks are dipped into brine during the salting process, where salt diffuses into the cheese. The equation of continuity in a rectangular coordinate system may describe this process:

$$\frac{\partial c_A}{\partial t} + \left(\frac{\partial N_{Ax}}{\partial x} + \frac{\partial N_{Ay}}{\partial y} + \frac{\partial N_{Az}}{\partial z} \right) = R_A. \tag{2.12}$$

When mass transfer is in the x direction only, i.e.,

$$\frac{dN_{Ay}}{dy} = \frac{dN_{Az}}{dz} = 0$$

and salt do not involve into any chemical reaction; that is, $R_A = 0$ Equation 2.12 is simplified as

$$\frac{\partial c_A}{\partial t} + \frac{\partial N_{Ax}}{\partial x} = 0.$$

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Salt flux in the x direction was expressed as

$$N_{AZ} = x_A\left(N_A + N_B\right) - D_{AB}\frac{dc_A}{dz}. \tag{2.10}$$

After assuming that the salt concentration in water is small (i.e., $x_A \cong 0$), dropping the subscripts and substituting the flux expression in the simplified form of the equation of continuity we will have

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}.$$

Salt molecules diffuses into the cheese through the aqueous phase entrapped in the porous solid. Some properties of the cheese (i.e., bound water), viscosity of the aqueous phase, friction and sieve effects of the pores, charged components in the aqueous, and the solid phases also affect this process; therefore, parameter D is actually an effective diffusion constant.

When the cheese blocks are in brine for brief periods, the BCs and the IC may be stated as

BC1: $c = c_1$ at $x = 0$ when $t > 0$
BC2: $c = c_0 = 0$ at $x \to \infty$ when $t > 0$
IC: $c = c_0 = 0$ at $x > 0$ when $t = 0$.

We may define the dimensionless concentration $c = (c - c_0)/(c_1 - c_0)$ and form a new variable $\eta = x/\sqrt{4Dt}$. We may anticipate that the solution will be in the form of $c = \phi(\eta)$. This is called the *method of the combination of variables*. There are many examples in the literature that this partial differential equation with the given boundary and the initial conditions may be solved with this substitution. In terms of the new variables, we will have $dc/dt = -(1/2)(\eta/t)\phi^{\bullet}$ and $d^2c/dx^2 = -(1/2)(\eta^2/x^2)\phi^{\bullet\bullet}$, where primes indicate differentiation with respect to η, then the partial differential equation becomes

$$\phi^{\bullet\bullet} + 2\eta\phi^{\bullet} = 0,$$

with the boundary conditions (BC)

BC1: $\eta = 0$ $\phi = 1$
BC2: $x \to \infty \to \phi = 0$.

If $\phi^{\bullet}$ is replaced with ψ, then we get a first-order separable equation $\psi^{\bullet} + 2\eta\psi = 0$ and the solution is $\phi^{\bullet} = \psi = C_1 e^{-\eta^2}$. Integrating once more gives $\phi = C_1\int_0^n e^{-\eta^2}d\eta + C_2$.

After using BC1 we will obtain $C_2 = 1$. Constant C_1 may be evaluated after using BC2: $C_1 = -1/\int_0^{\eta} e^{-\eta^2}d\eta = -2/\sqrt{\pi}$ then the solution becomes

$$\phi = 1 - \frac{2}{\sqrt{\pi}}\int_0^{\eta} e^{-\eta^2}d\eta.$$

The error function is defined as $erf(\eta) = \left(2/\sqrt{\pi}\right)\int_0^{\eta}\exp\left(-\eta^2\right)d\eta$ (See Tables 2.15, 2.16 and 2.17), then the final form of the solution is $(c - c_0)/(c_1 - c_0) = 1 - erf(x/2\sqrt{Dt})$ or $(c_1 - c_0)/(c_1 - c_0) = erf(x/2\sqrt{Dt})$.

MATLAB® code E.2.13 compares the model with experimentally determined salt concentration measurements (Figure E.2.13). It should be noticed that considering the cheese blocks as an infinite bodies may be valid during the initial stages of the brining process, but this assumption is not valid in the later stages of the experiments, where salt profiles also develop at the depths of the cheese.

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MATLAB® CODE E.2.13

Command Window:

```
clear all
close all

% Enter the data
distanceD=[0.007 0.017 0.026 0.033 0.045]; % m
cData=[3.3 1.9 1.0 0.3 0.15;3.0 0.9 0.15 0.01 0.0]; % kg/cm3
c1=4; % kg/cm3
c0=0; % kg/cm3

% plot the data
plot(distanceD,cData(1,: ),'*' ); hold on;
plot(distanceD,cData(2,: ),'o' ); hold on;
ylabel('c(t) (kg / m3)')
xlabel('x (m)')
legend('9 days','3 days',2,'Location','NorthEast')

% model
D=1.15e-6 ; % m2/h
deltaX=0.001;
for j=1:1:10;
        time(j)=j;
       x=0;
      for k=1:1:50;
     X(k)=x;
            z= X(k)/(2*sqrt(D*time(j)*24));
            c(j,k)=c1+(c0-c1)*erf(z);
            x=x+deltaX;
       end
end
plot(X,c(3,:), '-',X,c(9,:), ':'); hold on
grid on
```

Figure E.2.13 will appear on the screen when we run the code.

2.8 Chart Solutions to Unsteady State Conduction Problems

In most thermal processes solid foods are heated in a liquid medium (i.e., blanching of potatoes). The ratio of conductive resistance in a solid to convective resistance in a fluid is described with the Biot number (Bi = hR/k, Bi = hL/k, etc.). The Biot number may have values between 0 and ∞. When $k \to \infty$ ($Bi \to 0$) internal resistance to heat transfer is negligible; therefore, the solid may be assumed to be at uniform temperature and the heat transfer rate to the solid food may be expressed as

$$\rho c V \frac{dT}{dt} = hA(T_1 - T), \tag{2.37}$$

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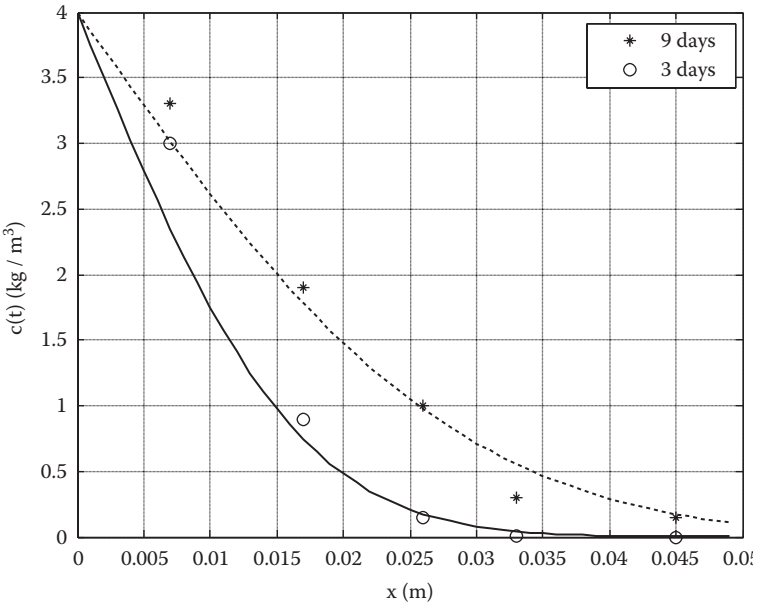


FIGURE E.2.13
Experimental and theoretical salt concentration profiles in white cheese. After 3 and 9 days of brining. (From Turhan, M. and Kaletunc, G., *Journal of Food Science*, 57, 1082–85, 1992.)

TABLE 2.16

Definition of Error Function and Its Important Properties

Error function *erf*(η) of the argument η	$erf(\eta) = \frac{2}{\sqrt{\pi}} \int_{\xi=0}^{\xi=\eta} \exp(-\xi^2) d\xi$
	MATLAB® function f = erf(eta) computes erf(eta)
Complementary error function *erfc*(η) of the argument η	$erfc(\eta) = 1 - erf(\eta)$
	$\frac{d[erf(\eta)]}{d\eta} = \frac{2}{\sqrt{\pi}} \exp(-\xi^2)$
	$erf(\infty) = 1$
	$erf(-\eta) = -erf(\eta)$

where ρ, *c*, *A*, and *V* are density, specific heat, effective heat transfer area, and volume of the food, respectively, *h* is convective heat transfer coefficient, *T* and T_1 are the food and the medium temperatures, respectively. When Bi → ∞ ($h \to \infty$) solid surface attains the temperature of the heating medium immediately with the contact of the phases. Under these conditions the external heat transfer resistance disappears and the temperature profile established only in the solid phase. Qualitative temperature profiles in a liquid/solid system are shown in Figure 2.4.

Chart solutions to the conduction problems are frequently used in bioprocess and food engineering analysis when both the internal and the external heat transfer resistances are not negligible in the following geometries:

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TABLE 2.17

Values of *erf*(η), *erfc*(η), and $2/\sqrt{\pi}\exp(-\eta^2)$

η	erf(η)	erfc(η)	$2/\sqrt{\pi}\exp(-h^2)$	η	erf(η)	erfc(η)	$2/\sqrt{\pi}\exp(-h^2)$
0	0	1.00	1.128	0.80	0.742	0.258	0.595
0.05	0.056	0.944	1.126	0.85	0.771	0.229	0.548
0.10	0.112	0.888	1.117	0.90	0.797	0.203	0.502
0.15	0.168	0.832	1.103	0.95	0.821	0.179	0.458
0.20	0.223	0.777	1.084	1.00	0.843	0.157	0.415
0.25	0.276	0.724	1.060	1.10	0.880	0.120	0.337
0.30	0.329	0.671	1.031	1.20	0.910	0.090	0.267
0.35	0.379	0.621	0.998	1.30	0.934	0.066	0.208
0.40	0.428	0.572	0.962	1.40	0.952	0.048	0.159
0.45	0.475	0.525	0.922	1.50	0.966	0.034	0.119
0.50	0.520	0.480	0.879	1.60	0.976	0.024	0.087
0.55	0.563	0.437	0.834	1.70	0.984	0.016	0.063
0.60	0.604	0.396	0.787	1.80	0.989	0.011	0.044
0.65	0.642	0.378	0.740	1.90	0.993	0.007	0.030
0.70	0.678	0.322	0.691	2.00	0.995	0.005	0.021
0.75	0.711	0.289	0.643				

Notes: For an extensive list of the mathematical functions given in Table 2.17 an interested reader may refer to *Handbook of Mathematical Functions,* Abrahamovitz, M. and Stegun, I. (editors). Dover Publications, New York, 1965). MATLAB® functions f = erf(eta) computes erf(eta), f = erfc(eta) computes erfc(eta). MATLAB® function eta = erfinv(f) returns the value of η for the given value of *f*.

i. Infinite plate of thickness 2*L*, for which $T = T(x,t)$ and x is measured from the plate centerline.
ii. Infinitely long cylinder with outside radius R, for which $T = T(r,t)$ and r is measured from the centerline.
iii. Sphere with radius R, for which $T = T(r,t)$ and r is measured from the center.

The boundary conditions for all three geometries are similar. The first boundary condition specifies the minimum in the temperature profile at the midplane location of the infinite plane, the centerline of the infinitely long cylinder, or the center of the sphere:

$$\left[\frac{dT}{dx}\right]_{x=0} = \left[\frac{dT}{dr}\right]_{r=0} = 0. \tag{2.38}$$

The second boundary condition requires that the heat transferred from the exterior surface of the solid is removed by a fluid with an ambient temperature T_1 and a heat transfer coefficient h. This boundary condition may be expressed mathematically for slab as

$$h(T_s - T_1) = -k\left[\frac{dT}{dx}\right]_s, \tag{2.39a}$$

and for sphere or cylinder as

$$h(T_s - T_1) = -k\left[\frac{dT}{dr}\right]_s, \tag{2.39b}$$

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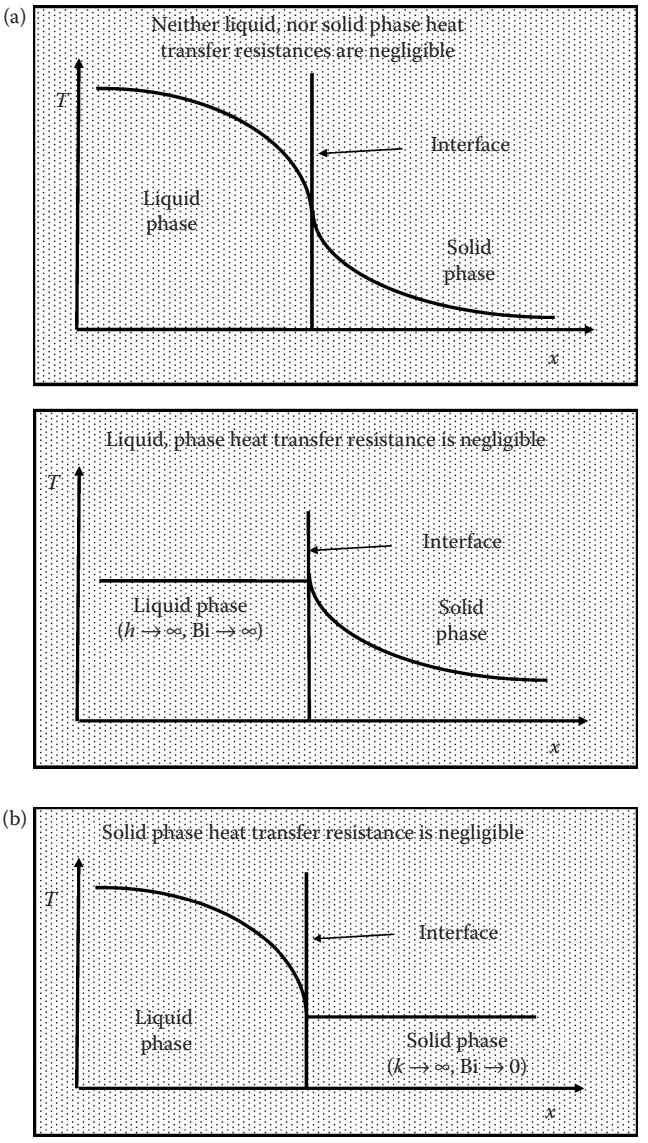


FIGURE 2.4
Qualitative temperature profiles in systems with different heat transfer resistances.

where subscript *s* indicates the quantity evaluated at the surface conditions. There is a second possible boundary condition to substitute Equation 2.39b if $h \to \infty$; that is, the thermal resistance of the convection layer is negligible and the surface temperature of the solid equals that of the surrounding fluid:

$$T_s = T_1. \tag{2.39c}$$

The initial conditions for these geometries may be

$$T = T_0 \text{ when } t = 0 \text{ for all } x \text{ or } r. \tag{2.40}$$

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Temperature distribution in any infinite slab, infinite cylinder, or sphere may be solved by using the separation of variables method for the solution of the appropriate partial differential equations, after employing the BC's given in Equations 2.38 and 2.39 and the IC given in Equation 2.40 in terms of the dimensionless temperature $Y = (T_1 - T)/(T_1 - T_0)$, Fourier number $\alpha t/L^2$ (or $\alpha t/R^2$) and the Biot number hL/k (or hR/k; Heisler 1947). Heisler charts are presented in Figures 2.5, 2.6, and 2.7.

The use of one-dimensional Heisler charts may be extended to two- and three-dimensional problems. The method involves using the product of the Y values from the one-dimensional charts. The basis for obtaining two- or three-dimensional solutions from one-dimensional charts is the manner in which partial differential equations may be separated into the product of two or three ordinary differential equations. When the external heat transfer resistance is negligible we may use the chart given in Example 4.35 to calculate the average temperature of the solids immersed in a heating medium.

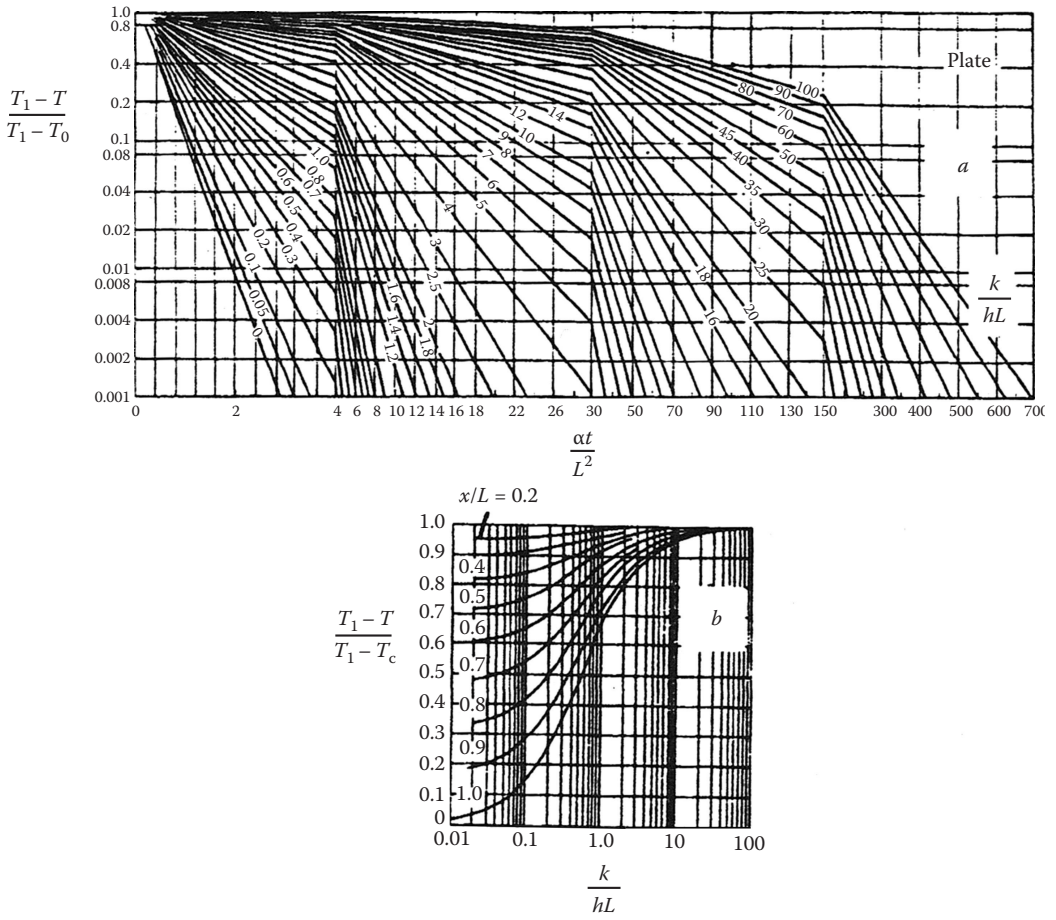


FIGURE 2.5
(a) Dimensionless midplane temperature for an infinite plane with thickness 2*L* and (b) dimensionless local temperature for an infinite plane with thickness 2*L* as a function of midplane temperature. (From Heisler, M. P., *Transactions of ASME*, 69, 227–36, 1947. © ASME, reproduced with permission.)

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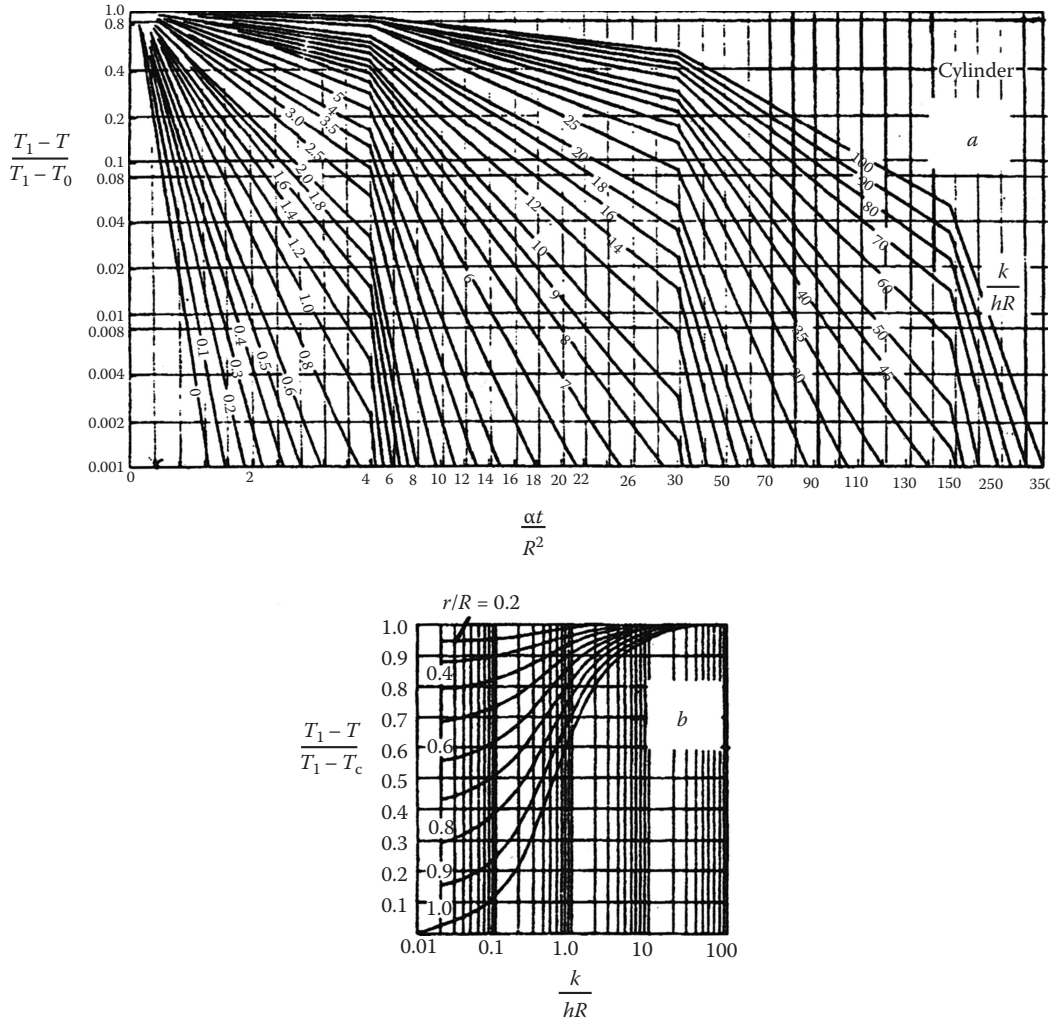


FIGURE 2.6
(a) Dimensionless axis temperature for an infinite cylinder with radius R and (b) dimensionless local temperature for an infinite cylinder with radius R as a function of axis temperature. (From Heisler, M. P., *Transactions of ASME*, 69, 227–36, 1947. © ASME, reproduced with permission.)

Example 2.14: Estimation of Processing Time and Local Temperatures During Thermal Processing of a Conduction Heating Food by Using Charts

A conduction heating food with $T_0 = 4°C$, $k = 0.63$ W/mK, $c_p = 4.19$ kJ/kgK, $\rho = 978$ kg/m^3 will be sterilized in 307×306 cans at retort temperature $T_1 = 110°C$. For complete sterilization, the critical point temperature must reach 100°C. The heat transfer coefficient between the can and the steam is $h_{outside} = 250$ W/m^{2}K. (i) Estimate the process time, (ii) estimate the temperature of the food at the end of the process at the point where $r = 0.5R$, $x = 0.5L$ (radius of the can = R, height of the can = $2L$).

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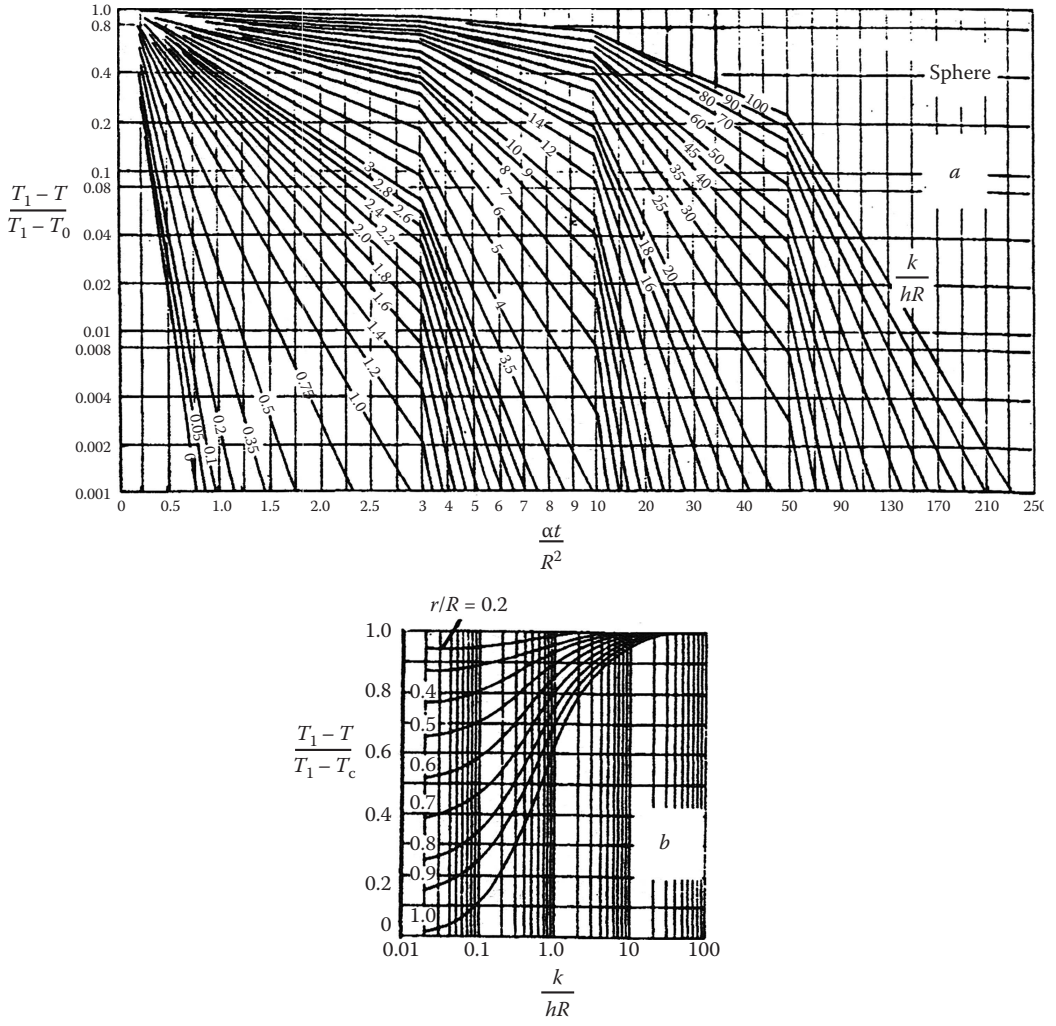


FIGURE 2.7
(a) Dimensionless center temperature for a sphere with radius R and (b) dimensionless local temperature for a sphere with radius R as a function of center temperature. (From Heisler, M. P., *Transactions of ASME*, 69, 227–36, 1947. © ASME, reproduced with permission.)

TABLE 2.18

Dimensionless Positions and Groups Used to Construct the Heisler Charts

Geometry	Position	Biot Number	Fourier Number
Infinite plate with thickness $2L$	x/L	hL/k	$\alpha t/L^2$
Infinite cylinder with radius R	r/R	hR/k	$\alpha t/R^2$
Sphere with radius R	r/R	hR/k	$\alpha t/R^2$

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Solution:

$$L=\left(\frac{1}{2}\right)\left(3+\frac{7}{16}\right)(2.54)=4.36\,cm,\ R=\left(\frac{1}{2}\right)\left(3+\frac{6}{16}\right)(2.54)=4.29\,\text{cm},\ \alpha=\frac{k}{\rho c_p}=9.25\times10^{-7}\,m^2/\text{min}.$$

i. Determination of the process time (solutions at the can center)
We will calculate the Biot number for the infinite slab and the infinite cylinder, we will estimate the process time, then calculate the Fourier numbers and use the charts to calculate Y_{slab} and $Y_{cylinder}$. Since $Y_{can}=Y_{slab}Y_{cylinder}$ we may calculate $Y_{can}=(T_1-T)/(T_1-T_0)$ and T. If $T=100°C$, the estimated process time is correct. We will repeat the trial and error solution until obtaining the correct processing time.

Geometry	Position	Inverse Biot Number	Fourier Number (t = 85 Minutes Estimated)	Y (from Charts)
Infinite slab (thickness = $2L$)	$\frac{x}{L}=0$	$\frac{k}{hL}=0.058$	$\frac{\alpha t}{L^2}0.041$	0.3 (Figure 2.5a)
Infinite cylinder (radius = R)	$\frac{r}{R}=0$	$\frac{k}{hR}=0.058$	$\frac{\alpha t}{R^2}0.041$	0.3 (Figure 2.6a)

$Y_{can}=Y_{slab}Y_{cylinder}=0.09$, $Y_{can}=T_1-T/T_1-T_0$, $0.09=110-T/110-4$ therefore $T=100.4°C$
100°C, therefore the processing time should be 85 minutes.

ii. Calculations at the point where $r=0.5R$, $x=0.5L$ at the end of the process

Geometry	Position	Inverse Biot Number	$\frac{T_1-T}{T_1-T_0}$ (from Charts)
Infinite slab (thickness = $2L$)	$\frac{x}{L}=0.5$	$\frac{k}{hL}=0.058$	0.74 (Figure 2.5b)
Infinite cylinder (radius = R)	$\frac{r}{R}=0.5$	$\frac{k}{hR}=0.058$	0.72 (Figure 2.6b)

$$\left[\frac{T_1-T}{T_1-T_c}\right]_{can}=\left[\frac{T_1-T}{T_1-T_c}\right]_{slab}\times\left[\frac{T_1-T}{T_1-T_c}\right]_{cylinder}=0.53,$$

$110-T/110-100=0.53$, therefore $T=104.7°C$.

iii. MATLAB® codes for production of the Heisler charts
MATLAB code E.2.14 evaluates the dimensionless temperature T_1-T/T_1-T_0 at the midplate of the slab as depicted in Figure E.2.14.

2.9 Interfacial Mass Transfer

Mass transfer usually occurs between two phases in most food and bioprocess engineering operations. Water transport from food materials to air during drying, diffusion of oxygen through the protective packaging to food materials during storage, and oxygen transfer from a bubble to broth during fermentation are among the common examples.

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MATLAB® CODE E.2.14

Command Window:

```
clear all
close all
clc

% THIS MATLAB CODE PRODUCES A PART THE HEISLER CHART AT THE CENTER
PLANE OF AN INFINITE SLAB

% InvBi= inverse Biot number
% InvBiMin=Minimum inverse Biot Number
% InvBiMax=Maximum inverse Biot Number
% InvBiStp=Inverse Biot Number step size
% FoMin= Minimum Fourier Number
% FoMax= Maximum Fourier Number

% choose the Biot Number range
InvBiMin = 0.1; InvBiMax = 1; InvBiStp= 0.1;

% we may choose the Fourier Number range as % 0-4, 4-30, 30-150,
150-700

FoMin= 0; FoMax= 4;
counter=0;
for b = (InvBiMin):(InvBiStp):(InvBiMax)
    Bi = 1/b;
 counter=counter+1;
if Bi >= 50
    Dt = 1.6;
elseif Bi >= 10
    Dt = 0.7;
elseif Bi >= 1
    Dt = 0.1;
elseif Bi >= 0.1
    Dt = 0.01;
elseif Bi >= 0.01
    Dt = 0.003;
end

G = 0; j = 0;
for i= 1:10000
    r = i / 1000;
    k(i) = r/cot(r);
    if (Bi - Dt) <= k(i)
        if k(i) <= (Bi + Dt)
            j = j + 1;
            G(j) = r;
        end
    end
    t(i) = r;
end

n = 1;
R(n) = G(1);
```

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```
for l = 2:j
    if G(l) > (1.2*G(l-1))
        n = n + 1;
        R(n) = G(l);
    end
end

% compute the model with the first 3 roots
for Fo = FoMin:FoMax
    sum = 0;
    for i = 1:3
         sum = sum+2*exp(-(R(i)^2)*(Fo))*(sin(R(i)) / (R(i) +
sin(R(i))*cos(R(i))));
    end

% Q=(T1-T)/(T1-T0)
k1= Fo+1;
    Q(counter,k1) = sum;
    f(counter,k1) = Fo;
end
end

% prepare a semilog plot
semilogy(f(1,1:5),Q(1,1:5), '-.*'), hold on
semilogy(f(2,1:5),Q(2,1:5), '-o'), hold on
semilogy(f(3,1:5),Q(3,1:5), ':p'), hold on
semilogy(f(4,1:5),Q(4,1:5), '-v'), hold on
semilogy(f(5,1:5),Q(5,1:5), ':^'), hold on
semilogy(f(6,1:5),Q(6,1:5), '-d'), hold on
semilogy(f(7,1:5),Q(7,1:5), ':+'), hold on
semilogy(f(8,1:5),Q(8,1:5), '->'), hold on
semilogy(f(9,1:5),Q(9,1:5), ':s'), hold on
semilogy(f(10,1:5),Q(10,1:5), '-.*'), hold on

% insert legend and define its location
legend( '1/Bi=0.1', '1/Bi=0.2', '1/Bi=0.3','1/Bi=0.4', '1/
Bi=0.5','1/Bi=0.6', '1/Bi=0.7','1/Bi=0.8', '1/Bi=0.9','1/
Bi=1.0','Location','SouthWest')

xlabel('Fourier Number')
ylabel('(T1-T)/(T1-T0)')
grid on
```

Figure E.2.14 will appear on the screen when we run the code.

A typical plot describing the variation of the mass fractions of the diffusing compound around the interface is shown in Figure 2.8.

During the interfacial mass transfer driving force is the concentration gradient within each phase, with no resistance to mass transfer at the interface. There is usually a concentration jump at the interface, but the interfacial concentrations are in local equilibrium, which may be described with Henry's Law or another equilibrium relation:

$$y_i = \mathcal{K} x_i, \tag{2.41}$$

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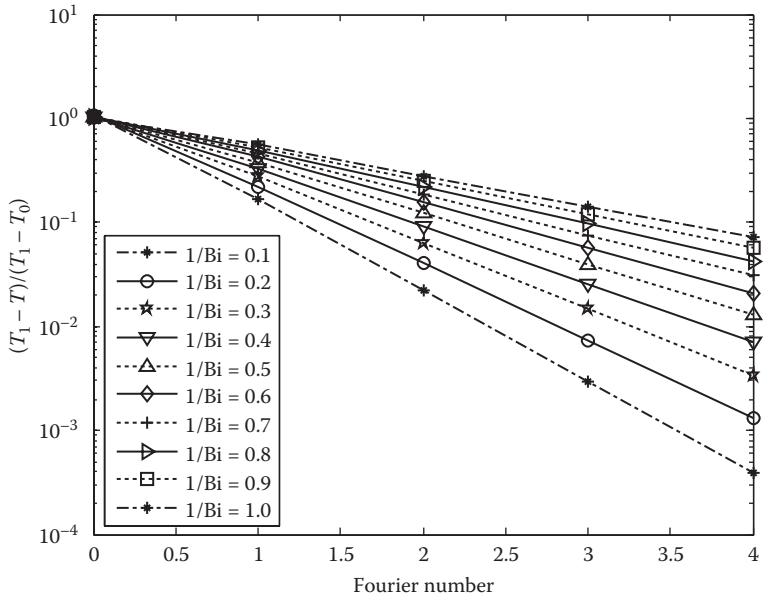


FIGURE E.2.14
Part of the Heisler chart as produced by the MATLAB® code E.2.14. This chart simulates the variation of the dimensionless temperature $T_1 - T/T_1 - T_0$ at the center plane of an infinite slab in the range of the Biot and the Fourier numbers employed in the code. The code may be modified to perform the same computation after choosing appropriate Bi and Fo ranges and substituting the following lines in accordance with the object.

Infinite slab:

```
k(i) = r /cot(r);
sum = sum + 2*exp(-(R(i)^2) * (Fo)) * (sin(R(i)) / (R(i) + sin(R(i)) *
cos(R(i))));
```

Infinite cylinder:

```
k(i) = r*bessel(1,r)/bessel(0,r);
 = sum + 2*(1/R(i))*exp(-R(i)^2*Fo)*bessel(1,R(i))/
((bessel(0,R(i)))^2 + (bessel(1,R(i)))^2);
```

Sphere:

```
k(i) = 1- r*cot(r);
sum = sum + 2*exp(-(R(i)^2)*(Fo))*(sin (R(i))-R(i)*cos(R(i)))/(R(i)-
sin(R(i))*cos(R(i)));
```

The legends of the figure should also be relevant with the chosen Biot numbers.

where y_i and x_i are mole fractions at the gas and liquid sides of the interface, respectively, and $\mathcal{K}$ is the partition coefficient;

$$y_i = \frac{\mathcal{H}}{P_{\text{tot}}} x_i, \tag{2.42}$$

where $\mathcal{H}$ is the Henry's Law constant and P_{tot} is the total pressure in the gas side. Although there is local equilibrium at the interface, this does not imply that the bulk average mole fractions of the two phases are in equilibrium. Interfacial mass transfer may be simulated with the following empirical equations:

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$$N_A = k_G\left(y_{A\infty} - y_{Ai}\right), \tag{2.43a}$$

$$N_A = k_L\left(x_{Ai} - x_{A\infty}\right), \tag{2.43b}$$

$$N_A = K_G\left(y_{A\infty} - y_A^*\right), \tag{2.43c}$$

$$N_A = K_L\left(x_A^* - x_{A\infty}\right), \tag{2.43d}$$

$$N_A = k_c\left(c_{Ai} - c_{A\infty}\right), \tag{2.43e}$$

$$N_A = K_c\left(c_A^* - c_{A\infty}\right), \tag{2.43f}$$

where $y_{A\infty}$ and $x_{A\infty}$ are the bulk mole fractions of species A far from the interface in the gas and the liquid phases, respectively; x_A^* is the mole fraction of species A in equilibrium with $y_{A\infty}$ and y_A^* is the mole fraction of species A in equilibrium with $x_{A\infty}$ (Figures 2.8 and 2.9). Equations 2.43e and 2.43f are essentially the same as Equations 2.43b and 2.43d, but

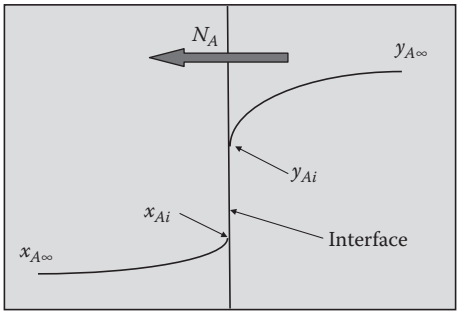


FIGURE 2.8
Variation of the mass fractions of a diffusing compound around the interface.

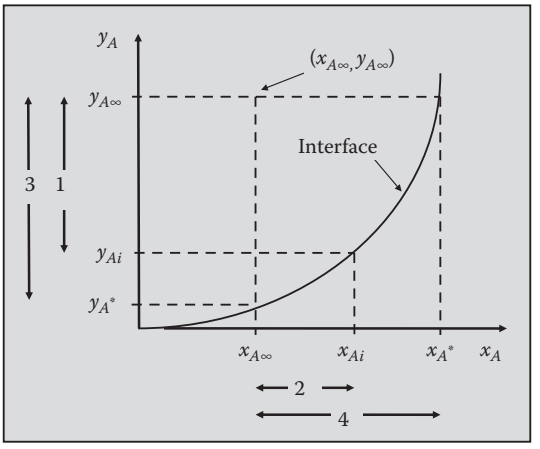


FIGURE 2.9
The equilibrium curve and the driving forces for Equations 2.43a through 2.43f. (1) $y_{A\infty} - y_{Ai}$: driving force in the gas phase, (2)$x_{Ai} - x_{A\infty}$: driving force in the liquid phase, (3) $y_{A\infty} - y^*$ overall gas phase driving force, and (4) $x_A^* - x_{A\infty}$: overall liquid phase driving force.

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written in terms of concentrations, instead of the mole fractions. Equations 2.43a through f are empirical equations, because they consider the mass transfer rate a constant fold of the driving force. Parameters k_G, k_L, K_G, K_L, k_c, and K_c are actually the proportionality constants. The equilibrium curve and the driving forces are shown in Figure 2.9.

2.10 Correlations for Parameters of the Transport Equations

Density, specific heat, thermal conductivity, viscosity, and diffusivity are the constants appearing in the transport Equations 2.4 through 2.7, 2.37, 2.39, and 2.43. The density, specific heat, thermal conductivity, and diffusivity are usually correlated to the food composition. Convective heat transfer coefficient h and mass transfer coefficient k are usually expressed in terms of the dimensionless numbers. Some examples to these correlations are presented here. Discussion of all the correlations available in the literature is beyond the scope of the book; more information may be found in the references.

2.10.1 Density of Dried Vegetables

A correlation relating the density of the bulk, sliced, and particle carrots, pears, potatoes, sweet potatoes, and garlic to the moisture content is presented as (Lozano, Rotstein, and Urbicain 1983)

$$\rho = h + \ell \frac{x}{x_0} + p\exp\left(q\frac{x}{x_0}\right), \tag{2.44}$$

where ρ = density (kg/m^3), x = moisture content (kg water/kg dry matter), x_0 = initial moisture content (kg water/kg dry matter); h, ℓ, p and q are constants. Values of these constants for two typical examples are

Foodstuff	Density	h	l	p	q
carrot	bulk	0.984	0	0.224	1.800
carrot	particle	1.497	–0.294	–0.253	39.793
garlic	bulk (sliced)	1.130	–0.567	0.187	–0.866
garlic	particle	2.694	0	–1.316	–1.1638

2.10.2 Specific Heat

Siebel or Choi and Okos equations may be used to predict the specific heat of the foods. Siebel's equation (ASHRAE 1965) may be stated above the freezing point as

$$c_{\text{unfrozen}} = 1674.72\omega_f + 837.36\ \omega_s + 4186.8\ \omega_w, \tag{2.45a}$$

and below the freezing point as

$$c_{\text{frozen}} = 1674.72\ \omega_f + 837.36\ \omega_s + 2093.4\ \omega_w, \tag{2.45b}$$

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where c = specific heat of the food (J/kg K), ω_f = mass fraction of fat, ω_s = mass fraction of nonfat solids, ω_w = mass fraction of water in the food.

Choi and Okos (1987) gives the correlations for the specific heat of the foods above the freezing point as

$$c = \omega_p c_p + \omega_f c_f + \omega_c c_c + \omega_{fi} c_{fi} + \omega_a c_a + \omega_w c_{waf}, \tag{2.46a}$$

where c, c_p, c_f, c_c, c_{fi}, c_a, and c_{wfa} are specific heats of the food, proteins, fat, carbohydrates, fibers, ash, and water (above the freezing point), respectively (all are in J/kg K); ω_p, ω_f, ω_c, ω_{fi}, ω_a, and ω_w represents the mass fractions of proteins, fat, carbohydrates, fiber, ash, and moisture, respectively. The following equations are used to predict the individual specific heats:

$$c_p = 2008.2 + 1208.9 \times 10^{-3}T - 1312.9 \times 10^{-6}T^2, \tag{2.46b}$$

$$c_f = 1984.2 + 1473.3 \times 10^{-3}T - 4800.8 \times 10^{-6}T^2, \tag{2.46c}$$

$$c_c = 1548.8 + 1962.5 \times 10^{-3}T - 5939.9 \times 10^{-6}T^2, \tag{2.46d}$$

$$c_{fi} = 1845.9 + 1930.6 \times 10^{-3}T - 4650.9 \times 10^{-6}T^2, \tag{2.46e}$$

$$c_a = 1092.6 + 1889.6 \times 10^{-3}T - 3681.7 \times 10^{-6}T^2, \tag{2.46f}$$

and

$$c_{waf} = 4176.2 - 9.0862 \times 10^{-5}T - 5473.1 \times 10^{-6}T^2. \tag{2.46g}$$

Siebel's equation assumes that all types of nonfat solids have the same specific heat and, all water is frozen below the freezing point, these may not always be correct and lead inaccurate results. Choi–Okos correlation generally predicts higher values than the Siebel's equation at high moisture contents. Siebel's equation has been found to agree closely with the experimental data when $\omega_w > 0.7$ and when no fat is present. Choi–Okos correlation is more accurate at low moisture contents and wider range of product composition, since it is based on published experimental values for a wide variety of foods. Siebel's equation is simpler than the Choi–Okos equation, therefore it is preferred in calculations where error tolerance is not too low (Toledo 2007).

2.10.3 Thermal Conductivity of Meat

Thermal conductivity is commonly related to the moisture content of nonfat meat when heat flow is nonperpendicular to the fibers as (Pham and Willix 1989)

$$k = 0.080 + 0.52x \ (0 < T < 60°\text{C}) \tag{2.47a}$$

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or

$$k = -0.28 + 1.9x - 0.0092T \ (-40 < T < -5°C), \tag{2.47b}$$

where x = moisture content (kg water/kg dry matter), k is thermal (W/mK). There are also correlations relating the thermal conductivity to structure (Pham and Willix 1989):

Model	Equation	
Parallel model	$k_{eff} = \sum_{i=1}^{n} v_i k_i$	(2.48)
Series model	$\frac{1}{k_{eff}} = \sum_{i=1}^{n} \frac{v_i}{k_i}$	(2.49)
Maxwell–Eucken model (used with food dispersions) water/ice or fat = continuous phase; other constituents = dispersed phase	$k_{eff} = k_c \frac{1-2rv_d}{1+rv_d}$ where $r = \frac{k_c - k_d}{2k_c + k_d}$	(2.50)
Levy's model (replace v_d in Maxwell–Eucken model with function F). Proposed to obtain the same numerical result when the continuous phase becomes the dispersed phase and vice versa =	$2F = \frac{2}{s} - 1 + v_d - \left[\left(\frac{2}{s} - 1 + v_d\right)^2 - \frac{8v_d}{s}\right]^{1/2}$ where $s = \frac{(k_d - k_c)^2}{(k_d - k_c)^2 + \frac{k_d k_c}{2}}$	
Hill–Leitman–Sunderland model (simulates heat transfer through a network in a continuous phase with simultaneous parallel and series conduction)	$k_{eff} = (2\phi - \phi^2)k_d + (1 - 4\phi + 3\phi^2)k_c + \frac{8(\phi - \phi^2)k_c k_d}{\phi k_c + (4 - \phi)k_d}$ where $\phi = 2 - \sqrt{4 - 2v_d}$	(2.51)

k_{eff} = effective thermal conductivity (W/mK).
k_c = thermal conductivity of the continuous phase (W/mK).
k_d = thermal conductivity of the dispersed phase (W/mK).
k_i = thermal conductivity of ith component (W/mK).
v_d = volume fraction of the dispersed phase.
v_i = volume fraction of ith component.

An interested reader is referred to Miles, van Beek, and Veerkamp (1983) for extensive coverage of the equations for thermal conductivity in foods.

2.10.4 Viscosity of Microbial Suspensions

Most foods and biological solutions contain suspended solids. Atkinson and Mavituna (1991) recommend using the following equations to predict viscosity of the microbial suspensions:

Model	Equation	
Kunitz equation	$\mu_m = \mu_1 \left\{\frac{1 + 0.5\phi_s}{(1 - \phi_s)^4}\right\}$ used when $\phi_s < 0.4$	(2.52)
Mori and Ototake equation	$\mu_m = \mu_1 \left\{\frac{1.56\phi_s}{0.52 - \phi_s}\right\}$ used when ϕ_s 0.1	(2.53)

(*Continued*)

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Model	Equation	
Mooney's correlation (used when experimental data are available to determine the adjustable parameter c)	$\ln\left(\frac{\mu_m}{\mu_1}\right) = 1 + \frac{2.5\phi_s}{1 - c\phi_s}$	(2.54)
Einstein equation (used with yeast suspensions at low volume fractions)	$\mu_m = \mu_l + (1 + \phi_s)$	(2.55)
Vand equation (used to estimate viscosity of yeast suspensions up to $\phi_s = 0.14$)	$\mu_m = \mu_l\left(1 + 2.5\phi_s + 7.25\phi_s^2\right)$	(2.56)

ϕ_s = fraction of the suspended solids.
μ_l = viscosity of the liquid phase.
μ_s = viscosity of the solid suspension.

2.10.5 Moisture Diffusivity in Granular Starch

There are some equations available for porous solids that relate the effective diffusivity to the diffusivities in each phase. These are empirical equations that include (Vagenas and Karathanos 1991):

Model	Equation	
Parallel model	$D_{eff} = (1 - \varepsilon)D_s + \varepsilon D_g$	(2.57)
Series model	$\frac{1}{D_{eff}} = \frac{(1-\varepsilon)}{D_s} + \frac{\varepsilon}{D_g}$	(2.58)
Random model	$D_{eff} = D_s^{1-\varepsilon} D_g^{\varepsilon}$	(2.59)
Mixed model	$\frac{1}{D_{eff}} = \frac{(1-f)}{(1-\varepsilon)D_s + \varepsilon D_g} + f\left[\frac{1-\varepsilon}{D_s} + \frac{\varepsilon}{D_g}\right]$	(2.60)
Topper model	$\frac{1}{D_{eff}} = \left[\frac{\left(1-\varepsilon^{3/4}\right)}{D_s}\right] + \frac{\varepsilon^{1/3}}{\varepsilon^{1/3}D_g + \left(1-\varepsilon^{1/3}\right)D_g}$	(2.61)
Bahren's model	$D_{eff} = D_s \frac{(p+1)+(p-1)\varepsilon}{(p+1)-(p-1)\varepsilon}$	(2.62)
Maxwell model	$D_{eff} = D_s \frac{D_g + 2D_s + 2\varepsilon\left(D_s - D_g\right)}{D_g + 2D_s + \varepsilon\left(D_s - D_g\right)}$	(2.63)

D = diffusivity in the solid.
D_{eff} = effective diffusivity.
D_g = diffusion in the gas phase.
f = constant.
$p = D_g / D_s$.
ε = porosity.

2.10.6 Convective Heat Transfer Coefficients during Heat Transfer to Canned Foods in Steritort

System	Correlation and Range of the Dimensionless Groups (Rao et al. 1985)	
Heat transfer to canned Newtonian liquids in steritort (Rao et al. 1985)	$Nu_D = 0.135\left(Gr\ \mathrm{Pr}\right)^{0.323} + 0.391 \times 10^{-3}$	(2.64a)
	$24 \le \mathrm{Nu}_D \le 272$	
	$0.4 \le \mathrm{Re}_D \le 458$	
	$2.8 \le \mathrm{Pr} \le 476$	
	$2.0 \times 10^4 \le Gr \le 2.9 \times 10^9$	
	$1.13 \le L/D \le 1.37$	

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Heat transfer to canned non-Newtonian liquids in steritort (Rao et al. 1985; see Section 2.11, Rheological models)	$Nu_D = 2.60(Gr^{\bullet}\ \mathrm{Pr}^{\bullet})^{0.205} + 7.15\times10^{-7}\left(\mathrm{Re}^{\bullet}\ \mathrm{Pr}^{\bullet}\ \frac{D}{L}\right)^{1.837}$ $24 \le \mathrm{Nu}_D \le 160$ $0.4 \le \mathrm{Re}^{\bullet}_D \le 96$ $205 \le \mathrm{Pr}^{\bullet} \le 5100$ $100 \le Gr^{\bullet}_D \le 5.2 * 10^5$ $1.13 \le L/D \le 1.37$	(2.64b)

D = can diameter (m).
g = gravitational acceleration (m/s^2).
$\mathrm{Gr} = gD^3\rho^2\beta\Delta T/\mu^2$ = Grashof number based on the can diameter (dimensionless).
$\mathrm{Gr}^{\bullet} = gD^3\rho^2\beta\Delta T/\mu_a^2$ = generalized Grashof number for the non-Newtonian fluids (based on the can diameter, dimensionless).
h = convective heat transfer coefficient (W/m^2 K).
k = thermal conductivity (W/m K).
K = consistency index of power law fluids (N s^n/m^2)) (defined in Equation 2.71).
L = length of the can (m).
n = flow behavior index of power law fluids (defined in Equation 2.71).
N = revolutions per second.
$\mathrm{Nu}_D = hD/k$ = Nusselt number (based on the can diameter, dimensionless).
$\mathrm{Pr} = c\mu/k$ = Prandl number (dimensionless).
$\mathrm{Pr}^{\bullet} = c\mu_a/k$ = generalized Prandl number for the non-Newtonian fluids (dimensionless).
$\mathrm{Re}_D = D^2N\rho/\mu$ = Reynolds number (based on the can diameter, dimensionless).
$\mathrm{Re}^{\bullet}_D = D^2N^{2-n}\rho/g^{n-1}K(3n+1/4n)^n$ = generalized Reynolds number for the non-Newtonian fluids (based on the can diameter, dimensionless).
β = coefficient of volumetric expansion (1/°C).
μ = viscosity (Pa/s).
$\mu_a = K8^{n-1}/N^{1-n}(3n + 1/4n)^4$ = apparent viscosity for the non-Newtonian liquids.
ρ = density (Kg/m^3).

2.10.7 Mass Transfer Coefficient *k* for Oxygen Transfer in Fermenters

Oxygen transfer from the gas phase (i.e., bubbles) to the fermentation broth is among the most important phenomena determining the biomass and product yield in the fermentation processes. Atkinson and Mavituna (1991) presented a detailed review of the correlations available in literature. Bailey and Ollis (1986) recommended the following correlations for oxygen transfer from the air bubbles to fermentation broth:

Model		Range of the Dimensionless Groups
$\mathrm{Sh} = 1.01\ \mathrm{Pe}^{1/3}$	(2.65)	Re << 1, Pe >> 1
$\mathrm{Sh} = 2.0 + 0.60\ \mathrm{Re}^{1/2}\mathrm{Sc}^{1/3}$	(2.66)	Re >> 1
$\mathrm{Sh} = 0.31\ \mathrm{Gr}^{1/3}\mathrm{Sc}^{1/2}$	(2.67)	d_b < 2.5 mm
$\mathrm{Sh} = 0.42\ \mathrm{Gr}^{1/3}\mathrm{Sc}1^{/2}$	(2.68)	d_b > 2.5 mm

d_b = bubble diameter (m).
D = molecular diffusivity of oxygen in fermentation broth (m^2/s).
g = gravitational acceleration (m/s^2).
Gr = Grashoff number = $d_b^3\rho_c(\rho_c - \rho_g)g/\mu_c^2$ (dimensionless).
Pe = Peclet number = $d_p v/D$ (dimensionless).
Re = Reynolds number = $d_p v\rho_c/\mu$ (dimensionless).
Sc = Schmidt number = $\mu_c d_p/D$ (dimensionless).
Sh = Sherwood number = $\mu_c/\rho_c D$ (dimensionless).
v = approaching velocity far away from the bubble (m/s).
μ_c = viscosity of the continuous phase (N s/m^2).
ρ_c = density of the continuous phase (kg/m^3).
ρ_g = density of the gas phase (kg/m^3).

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Example 2.15: Drying Behavior of Frozen Beef

Meat is stored refrigerated, as well as in a frozen state, or aged at refrigeration temperatures for 1 or 2 weeks to permit tenderization. When a refrigerated or frozen meat slab is stored without an adequate moisture barrier, it loses weight by evaporation of water or sublimation of ice. Equation 2.43d describes interfacial mass transfer (Tutuncu, Özilgen, and Ungan 1990):

$$N_A = \mathcal{K}_L(x^* - x). \tag{2.43d}$$

Total mass flux N_A was expressed calculated as

$$N_A = \frac{1}{A} V \frac{dx}{dt},$$

where A = interfacial area, $V = Ah$ = volume of the beef slab, h = thickness of the slab, x = average fraction of water in the beef. After combining these expressions we obtain

$$\frac{dx}{dt} = -K\left(x - x^*\right),$$

where $K = \mathcal{K}/h$. The water content of lean beef is very high (about 76%), and the equilibrium water content may be assumed negligible. The term "equilibrium water content" refers to water or ice content of beef in equilibrium with the ambient air. Since drying rates are very slow at the refrigeration or freezing temperatures, numerical values of x do not change much and remain always substantially greater than x^*, thus the mass transfer equation may be rewritten as

$$\frac{dx}{dt} = -Kx.$$

Upon integration we will obtain (Tutuncu, Özilgen, and Ungan 1990)

$$\ln(x) = \ln(x_0) - Kt.$$

This is an equation in line with independent variable t, dependent variable $\ln(x)$, intercept (with $1/T = 0$ axis) $\ln(x_0)$, and slope K. MATLAB® code E.2.15.a compares this equation with the experimental data obtained under different conditions as depicted in Figure E.2.15.1.

The effect of temperature on the overall mass transfer coefficient, K, was described by the Arrhenius expression:

$$K = K_0 \exp\left(-\frac{E_a}{RT}\right),$$

where K_0 = preexponential constant, E_a = activation energy, R = gas constant, and T = absolute temperature. The Arrhenius expression may be linearized as

$$\ln(K) = \ln(K_0) - \frac{E_a}{R}\frac{1}{T},$$

when $\ln(K)$ is plotted versus $1/T$, $\ln(K_0)$ is the intercept with $1/T = 0$ axis, and E_a/R is the slope. MATLAB® code E.2.15.b compares the linearized Arrhenius equation with the experimental data given in Figure E.2.15.2.

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MATLAB® CODE E.2.15a

Command Window:

```
clear all
close all

% enter the data
lnXdataGB= [1.08 1.05 1.03 1.03 1.01 1.0 0.98 0.97 0.92 0.94 0.91
0.89 0.88 0.87 0.84 0.82 0.80 0.79 0.78 0.77 0.77 0.76]; %ground
beef
tDataGB= [0 35 50 55 76 80 99 103 120 125 144 148 164 168 198 202
240 247 261 264 284 292]; % ground beef

lnXdata= [1.1 1.09 0.99 0.98 0.98 0.95 0.93 0.92 0.90 0.89 0.85
0.84 0.80 0.79 0.78 0.77 0.76 0.72 ;1.1 1.09 0.98 0.97 0.97 0.94
0.92 0.90 0.87 0.84 0.80 0.78 0.76 0.75 0.71 0.70 0.69 0.62]; %
beef
tData= [0 20 40 48 58 64 88 100 120 138 145 160 164 182 192 205 218
230]; % beef

% plot the data
plot(tDataGB, lnXdataGB,'d' ); hold on;
plot(tData, lnXdata(1, :),'*' ); hold on;
plot(tData, lnXdata(2, :),'o' ); hold on;

ylabel('ln(x)')
xlabel('t (h)')
legend('ground beef','meat was cut in parallel direction to the
fibers','meat was cut in perpendicular direction to the fibers',2,'
Location','SouthWest')

% MODELING (n=1 ground beef; n=2 meat is cut perpendicular to the
fibers; n=3 meat is cut parallel to the fibers)

for n=1:3;
% determine the model coefficients,
 if n==1;
     lnXdata1=lnXdataGB;
     tData1=tDataGB;
else
     n1=n-1;
    lnXdata1=lnXdata(n1,:);
    tData1=tData;
end;
  f1= polyfit(tData1,lnXdata1,1);
   fp1= polyval(f1, tData1);
    K= - f1(1);
    lnX0=f1(2);

% determine the correlation coefficient and standard error
for j=1:1:size(tData1);
      lnXmodel=lnX0-K*tData1;
      d1 = (lnXdata1-lnXmodel);
      d2=d1*d1';
end;
```

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```
Se= sqrt(mean(d2));
   rmatrix=corrcoef(lnXdata1,tData1);
  r=rmatrix(1,2);
  fprintf('\nwhen n= %.2g mass transfer model is ln(x)= %.2g -%2gt
and r= %2g se= %2g \n',n, lnX0, K, r, Se)

% plot the model
plot(tData1, lnXmodel,':' ); hold on;
end;
grid on
```

When we run the code the following lines and Figure E.2.15.1 will appear on the screen:

```
when n= 1 mass transfer model is ln(x)= 1.1 -0.00118441t and r=
-0.991723 se= 0.0609219
when n= 2 mass transfer model is ln(x)= 1.1 -0.00153456t and r=
-0.984418 se= 0.0807688
when n= 3 mass transfer model is ln(x)= 1.1 -0.00192371t and r=
-0.990561 se= 0.0784387
```

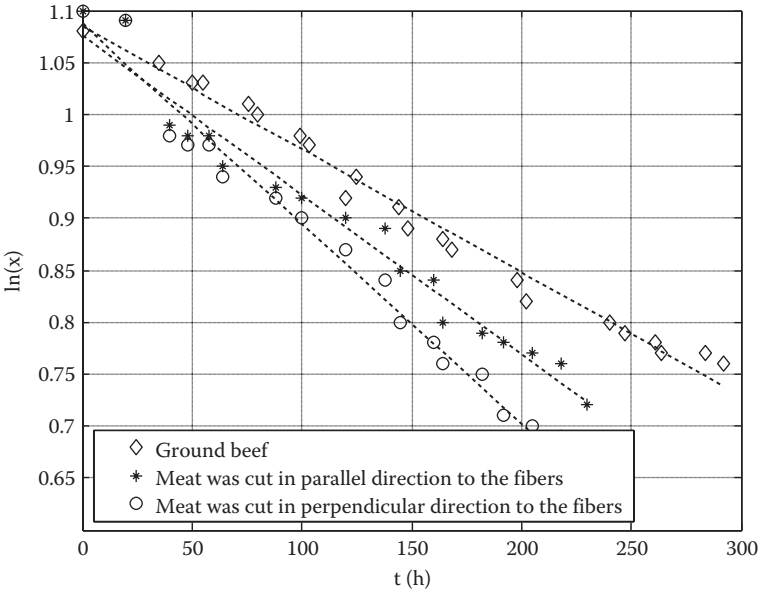


FIGURE E.2.15.1
Comparison of the drying model with the data at –5°C. Thickness of the infinite slabs were 20 mm. (From Tutuncu, M. A., Özilgen, M., and Ungan, S., *Canadian Institute of Food Science and Technology Journal*, 23, 76–78, 1990.) The model shows that the moisture loss is the highest when the meat is cut in perpendicular direction to the fibers. The smallest moisture loss rates were observed with the ground beef, where the distorted meat structure creates obstacles to transport water.

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MATLAB® CODE E.2.15b

Command Window:

```
clear all
close all
format compact
% enter the data
R = 8.314;
T = [8 5 -5 -20]; % C
lnKdata=[-5.2 -5.5 -6 -9.2];
[Ea,lnK0,Se,r]=ARRHENIUS(T,lnKdata);
EaR=Ea/R;
% print the model, correlation coefficient and the standard error
fprintf('\nArrhenius relation is ln(K)= %.2g -%2g/T and r= %2g se=
%2g \n', lnK0, EaR, r, Se)

% plot the model
invT= 1./(T+273);
lnKmodel=lnK0-EaR*invT;
plot(invT, lnKmodel,'k:', 'LineWidth',2 );
```

M-file 1:

```
function [Ea,lnK0,Se,r]=ARRHENIUS(T,lnKdata)
R = 8.314;
% plot the data
for i = 1:length(T)
 invT(i)= 1./(T(i)+273);
end
plot(invT,lnKdata,'k*','LineWidth',2); hold on;
ylabel('ln(K)')
xlabel('T (1/K)')
grid on

% determine the model coefficients,
f1= polyfit(invT,lnKdata,1);
fp1= polyval(f1, invT);
EaR= - f1(1);
Ea=EaR*R;
lnK0=f1(2);

% determine the correlation coefficient and standard error
for j=1:length(T);
 lnKmodel=lnK0-EaR*invT;
 d1 = (lnKdata-lnKmodel);
 d2=d1*d1';
end;
Se= sqrt(mean(d2));
rmatrix=corrcoef(lnKdata,invT);
r=rmatrix(1,2);
```

When we run the code the following line and Figure E.2.15.2 will appear on the screen:

```
Arrhenius relation is ln(K)= 31 -10048.2/T and r= -0.968029 se=
0.802188
```

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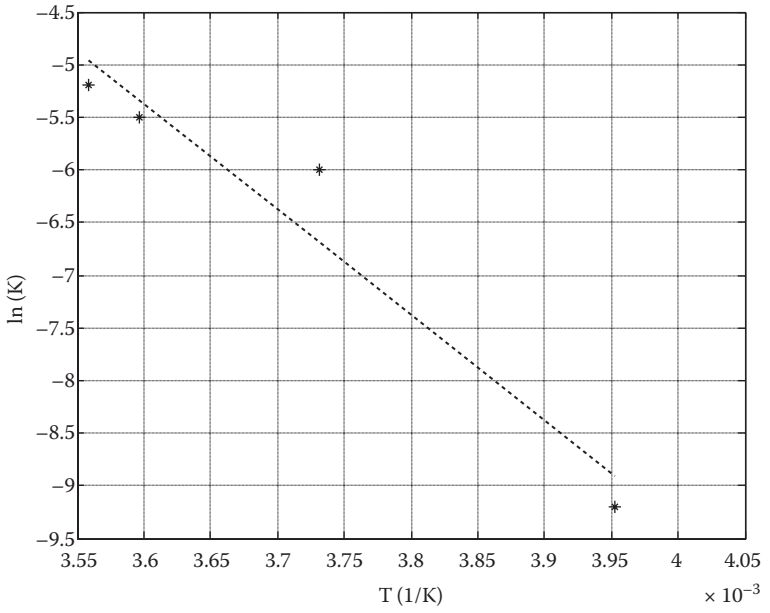


FIGURE E.2.15.2
Arrhenius plot for the mass transfer coefficient *K*. Thickness of the infinite slabs were 10 mm. (From Tutuncu, M. A., Özilgen, M., and Ungan, S., *Canadian Institute of Food Science and Technology Journal,* 23, 76–78, 1990.)

Example 2.16: Theoretical Expressions for Interfacial Mass Transfer Coefficients

Theoretical expressions may be obtained for interfacial mass transfer coefficients under limited conditions. Total mass flux N_A was expressed empirically as

$$N_A = k_c(c_{Ai} - c_{A\infty}). \tag{2.43e}$$

Where c_{Ai} = concentration of A at the interface and $C_{A\infty}$ = concentration of A away from the interface, k_c = mass transfer coefficient. In stationary systems *film model*s are used, which assume that the concentration profile development is confined within an imaginary thin film with thickness = δ, through which mass transfer occurs under steady state conditions. We may use the following BCs with such systems:

BC1: $c_A = c_{Ai}$ at $x = 0$ when $t > 0$
BC2: $c_A = C_{A\infty}$ at $x = \delta$ when $t > 0$.

In agitated systems, *penetration and surface renewal models* are used and based on unsteady state mass transfer to pockets of liquid exposed to the interface ($x = 0$) for a short time, then swept away and remixed with the bulk of the liquid. We may use the following IC and BCs with such systems:

IC: $c_A = C_{A\infty}$ for all x when $t = 0$
BC1: $c_A = c_{Ai}$ at $x = 0$ when $t > 0$
BC2: $c_A = C_{A\infty}$ as x when $t > 0$.

Obtain an expression for k_c in terms of diffusivity of A and the contact time t.

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Solution: The equation of continuity in rectangular coordinate system is

$$\frac{\partial c_A}{\partial t}+\left(\frac{\partial N_A}{\partial x}+\frac{\partial N_A}{\partial y}+\frac{\partial N_A}{\partial z}\right)=R_A. \tag{2.12}$$

When mass transfer is in x direction only; that is, $(\partial N_{Ay}/\partial y) = (\partial N_{Az}/\partial z) = 0$ and there are no chemical reactions (i.e., $R_A = 0$) Equation 2.12 is simplified as

$$\frac{\partial c_A}{\partial t}+\frac{\partial N_A}{\partial x}=0.$$

Flux in the x direction was

$$N_{Ax}=x_A\left(N_A+N_B\right)-D_{AB}\frac{dc_A}{dx}. \tag{2.10}$$

After assuming that the concentration of A in water is small (i.e., x_A 0) the flux expression will be

$$N_A=-D_A\frac{dc_A}{dx}.$$

We may substitute the flux expression in the simplified form of the equation of continuity to obtain

$$\frac{\partial c_A}{\partial t}=D\frac{\partial^2 c_A}{\partial x^2}.$$

i. Film model: since the steady state conditions prevail $dc_A/dt = 0$ and we will have $(\partial c_A/\partial t) = 0$. After integrating this expression twice we will obtain the concentration profile $c_A = K_1x + K_2$. The BCs require $K_1 = (c_{A\infty} - c_{Ai})/\delta$, $K_2 = c_{Ai}$, therefore the concentration profile along the film is $c_A = (c_{A\infty} - c_{Ai})(\delta/x) + c_{Ai}$. Flux through the interface is

$$N_A=-D_A\left[\frac{dc_A}{dx}\right]_{x=0}.$$

Therefore, $N_A = (D_A/\delta)(c_{Ai} - c_{A\infty})$. Comparing this equation with $N_A = k_c(c_{Ai} - c_{A\infty})$ requires $k_c = D_A/\delta$.

ii. Penetration and surface renewal models: solution of this partial differential equation with the method of combination of variables was previously given in Example 2.13:

$$c_A(t)=\left(c_{Ai}-c_{A\infty}\right)erfc\left(x/2\sqrt{D_At}\right)+c_{A\infty},$$

therefore

$$\frac{dc_A}{dx}=\frac{\left(c_{Ai}-c_{A\infty}\right)}{2\sqrt{D_At}}\exp\left(-\frac{x}{2D_At}\right).$$

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Flux through the interface is: $N_A = -D_A[dc_A/dx]_{x=0}$.
Therefore

$$N_A = \sqrt{\frac{D_A}{\pi t}}\left[\frac{dc_A}{dx}\right]_{x=0}.$$

Comparing this equation with $N_A = k_c\left(c_{Ai} - c_{A\infty}\right)$ requires $k_c = \sqrt{D_A/\pi t}$.

2.11 Rheological Modeling

Most of the rheological models are empirical in nature. A simple classification of the rheological models has been presented in Figure 2.10.

Since the raw materials are highly variable, maintaining uniform consistency of the processed foodstuffs is one of the major challenges in the industry and rheological measurements are among the powerful tools for quality assurance (Race 1991). Flow behavior of orange juice, salad dressing or ketchup, and the spreadability of mayonnaise affect consumer preference, therefore characterizing (i.e., modeling) rheological behavior of such products is important for the manufacturers. Rheological behavior of fermentation media affects the heat and oxygen transfer, in turn contributing significantly to the bioprocess design and economics. Extensive review of the rheological models used in bioprocesses has been given by Atkinson and Mavituna (1991).

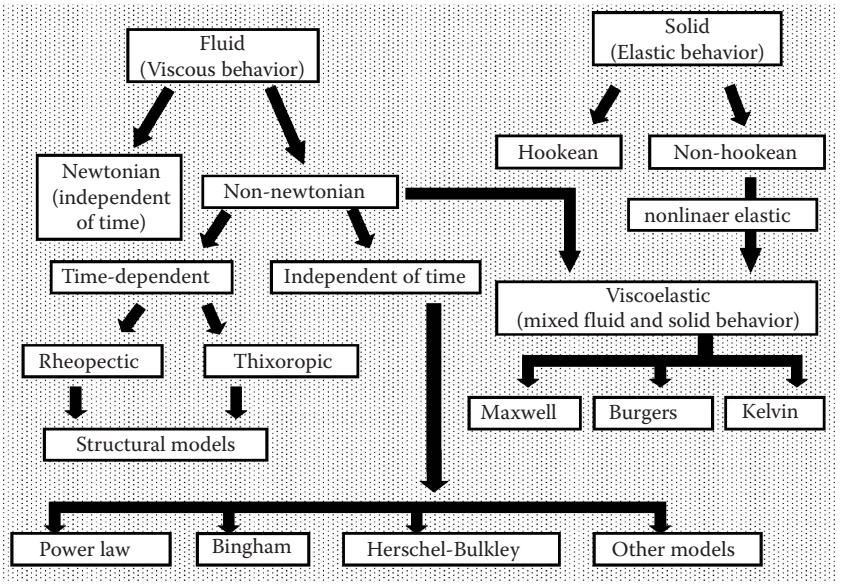


FIGURE 2.10
Steffe's classification of rheological and viscoelastic behavior of fluids and solids. (From Steffe, J. F., *Rheological Methods in Food Process Engineering*, Freeman Press, East Lansing, MI, 1996.)

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Rheological models are empirical and valid only within the range of the experimental work that their constants have determined. The Herschel–Bulkley model is among the most general models:

$$\sigma = K\dot{\gamma}^n + \sigma_0, \tag{2.69}$$

where σ = shear stress (Pa), $\dot{\gamma}$ = shear rate = $d\gamma/dt$ (s^{-1}), K = consistency index (Pa s^n), and σ_0 = yield stress (Pa). The yield stress may be defined as the minimum shear stress required to initiate flow. Special cases of the Herschel–Bulkley model may be described as

Special Case	Model	
$n = 1$	Bingam plastic: $\sigma = K\dot{\gamma} + \sigma_0$	(2.70)
$\sigma_0 = 0$	Power law: $\sigma = K\dot{\gamma}^n$ Pseudoplastic: $n < 1$ Dilatant: $n > 1$	(2.71)
$\sigma_0 = 0$, $n = 1$	Newtonian: $\sigma = \mu\dot{\gamma}$ (flow behavior index K is substituted with viscosity μ)	(2.72)

Rheological behavior of serum samples of low-pulp concentrated orange juice (Vitali and Rao 1984), applesauce and applesauce serum (Rao et al. 1986), apple juice-bentonite suspensions (Dik and Özilgen 1994) and tomato juice concentrates (Tanglertpaibul and Rao 1987) were described by the power law model. The Casson model is widely used to describe the rheological behavior of liquid foods, for example, cocoa and hot chocolate (Steffe 1996); yogurt (Parnell-Clunies, Kakuda, and Deman 1986); and raisin suspensions (Pekyardimci and Özilgen 1994). Rheological behavior of microbial suspensions were also modeled with the power law and the Casson equations Atkinson and Mavituna (1991).

The Casson equation relates the shear rate to the shear stress as

$$\sqrt{\sigma} = K\sqrt{\dot{\gamma}} + \sqrt{\sigma_0}. \tag{2.73}$$

A modified form of the Casson equation is called the Mizrahi and Berk equation and expressed as

$$\sqrt{\sigma} = K\dot{\gamma}^n + \sqrt{\sigma_0}. \tag{2.74}$$

Constants of the rheological models are generally evaluated by curve fitting and the yield stress is determined by extrapolation to zero shear rate. Such a model may represent the relation between the shear stress and the shear rate within the range of the experiments, but the shear rate may not represent the actual physical properties of the fluid. A detailed discussion of the relations between the fluid properties and the yield stress has been discussed by many authors (i.e., Qui and Rao 1988). Michaels and Bolger (1962) proposed a structural model for flow behavior of kaolin suspensions. This model considers small clusters of particles (and enclosed water) as the basic flow units of the flocculated suspensions. At low shear rates, those flow units group into aggregates to form a "network" extending through the container. The network may give a finite yield stress to the suspension at low shear rates. Hunter and Nicol (1968) improved this theory to correlate the rheological behavior of kaolinite sol with its surface properties. Metz, Kossen, and

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van Suijdam (1979) and Berkman-Dik, Özilgen, and Bozoglu (1992) suggested that this concept may be useful for studying the rheological behavior of the mold suspensions. The network concept may also describe the physical structure of the food or biological dispersions.

Temperature effects on the consistency index K of Equation 2.71 was described with the Arrhenius expression with many fluids; that is, tomato concentrates (Harper and El-Sahrigi 1965), concentrated orange juice (Vitali and Rao 1984), apple juice bentonite suspensions (Dik and Özilgen 1994):

$$K = K_0 e^{E/RT}, \tag{2.75}$$

where K_0 was the preexponential coefficient, R was the gas constant, and E was the activation energy. Consistency index K of Equation 2.71 may also be related to the solids concentration of the medium with an exponential (i.e., Equation 2.76; Vitali and Rao 1984) or a power type expression (i.e., Equation 2.77; Dik, Katnas, and Özilgen 1996):

$$K = K_0 \exp(\alpha_1 c), \tag{2.76}$$

$$K = K_0 + K_1 c_1^{\alpha 1} + K_2 c_2^{\alpha 2} + K_3 c_3^{\alpha 3}, \tag{2.77}$$

where α_i and K_i are constants; c and c_i are solids concentration.

Apparent viscosity is defined as the ratio of the shear stress to the shear rate:

$$\mu_{app} = \frac{\sigma}{\dot{\gamma}}. \tag{2.78}$$

Temperature effects on apparent viscosity may also be described with the Arrhenius expression (Vitali and Rao 1984)

$$\mu_{app} = \mu_0 e^{E/RT}, \tag{2.79}$$

where μ_0 is a preexponential constant. The concentration dependence of the apparent viscosity may be expressed as (Harper and El-Sahrigi 1965)

$$\mu_{app} = \kappa c^{\alpha} \tag{2.80}$$

or (Vitali and Rao 1984)

$$\mu_{app} = \kappa \exp(\beta c), \tag{2.81}$$

where α, β, and κ are constants and c is concentration.

Time dependent rheological models are observed when shear stress–shear rate relation varies with time under shear. Thixotropic and rheopectic materials exhibit, respectively, decreasing and increasing shear stress (and apparent viscosity) over time at a fixed shear rate. In other words, thixotropy is time-dependent thinning and rheopecty is time-dependent thickening.

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Example 2.17: Viscosity Model for Tomato Paste

Tomato paste is a dispersion of solid particles (pulp) in an aqueous medium (serum). Viscosity is among the quality attributes that determine the overall quality and consumer acceptability of the tomato paste. Flow properties are decisive in control and optimization of the unit operations. A constant viscosity range was observed with the tomato paste at low shear rates, but there was a power law decrease in viscosity at higher shear rates. The Carreau model fits well to this behavior (Valencia et al. 2003):

$$\frac{\eta}{\eta_o} = \frac{1}{\left[1+\left(\dot{\gamma}/\dot{\gamma}_c\right)\right]^s}, \tag{E.2.17}$$

Where η is viscosity, $\dot{\gamma}$ is the shear rate, η_o is the viscosity before the onset of decrease, and $\dot{\gamma}_c$ is the critical shear rate for the onset of the shear thinning region and *s* is a parameter with the slope of this region. MATLAB® code E.2.17 compares Equation E.2.17 as depicted in Figure E.2.17.

MATLAB® CODE E.2.17

Command Window:

```
clear all
close all

% enter the data
gammaPrimeData=[1.1e-5 2e-5 3e-5 5e-5 9.5e-5 1.1e-4 8.5e-4 1.1e-3
4.5e-3 2e-2 1.8e0 1.1e1]; % shear rate data (1/s)
etaData=[1.03e7 1.02e7 1e7 9.5e6 7e6 4e6 1.5e6 1.01e6 2e5 8e4 4.5e2
1.2e2]; % viscosity data (Pa s)
% plot the data
loglog(gammaPrimeData, etaData, '*'); hold on;
grid on;

% enter the constants of the model
gammaCprime=4.0e-5; % (1/s)
etaO=1.1e7; % (Pa s)
s=0.45;

% plot the model
for n=1:8
gammaPrime(n)=(1e-6)*10^n;
eta(n)=etaO*(1/(1+( gammaPrime(n)/gammaCprime)));
end

loglog(gammaPrime, eta, '-'); hold on;
xlabel('Shear Rate (1/s)')
ylabel('viscosity (Pa s) ')
```

When we run the code, Figure E.2.17 will appear on the screen.

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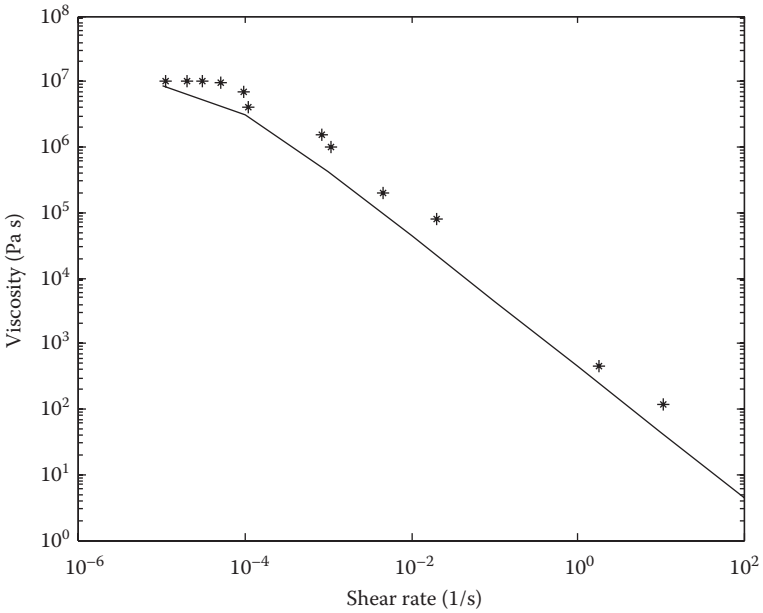


FIGURE E.2.17
Viscous flow curve for tomato paste sample with breaking temperature = 65°C and 2.2 mm screen size. (Data and model constants adapted from Valencia, C., Sanchez, M. C., Ciruelos, A., Latorre, A., Madiedo, J. M., and Gallegos, C., *Food Research International*, 36, 911–19, 2003.)

Example 2.18: Rheological Behavior of the Orange Juice Concentrate

Equation 2.71 may be linearized as $\log(\sigma) = \log(K) + n\log(\dot{\gamma})$. MATLAB® code E.2.18.a compares two sets of stress–strain data obtained with the power law model.

Experimental data obtained by (Vitali and Rao 1984) shows that $n \cong 0.78$. Parameter K was determined with orange juice at 65°Brix at different temperatures as

T (°C)	K(Ns^n/m^2)
–18.8	24.45
–14.5	15.59
–9.9	8.80
–5.4	6.49
–0.8	4.74
9.5	2.06
19.4	1.25
29.2	0.68

MATLAB code E.2.18.b shows that temperature effects on parameter K may be described with the Arrhenius equation

$$K = K_0 \exp\left\{-\frac{E_a}{RT}\right\} \tag{3.5}$$

as depicted in Figure E.2.18.2.

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MATLAB® CODE E.2.18a

Command Window:

```
clear all
close all
format compact

% enter the data
ShearStressData1= [7 10 13 19 23 30 45 50 66 70 75 85 80 90 100 110
110 120 125 130 150 160 180 200 220 250 300 330 390 400 500 600]; %
-18.8 oC
ShearRateData1= [0.21 0.31 0.4 0.6 1.0 2.5 3 3.3 3.3 4.0 4.0 4.7
4.7 5.1 5.8 5.9 7.9 8.0 8.2 8.3 9.9 10 13 15 18 22 25 30 35 40 55
65]; % -18.8 oC
ShearStressData2= [4.2 4.7 5.2 6.0 6.5 7.2 8.0 10 13 14 15 22 30 40
44 49 59 64 74 82 95 110 130 140 160 190 210 240 290 320 350 470];%
9.5 oC
ShearRateData2= [2 3.5 2.7 3.2 3.7 4.6 5.3 6.2 7.3 9.1 10 13 17 22
27 44 50 78 90 110 160 190 220 250 300 350 420 490 570 600 700
900];% 9.5 oC

% plot the data
loglog(ShearRateData1, ShearStressData1, '*', ShearRateData2,
ShearStressData2, 'd'); hold on;
xlabel('Shear Rate (1/s)')
ylabel('Shear Stress (N/m2) ')
legend('-18.8 oC','9.5 oC', 2,'Location','SouthEast')
grid on

% modeling at -18.8 oC
ShearStressVersusShearRate(-18.8, ShearRateData1, ShearStressData1)

% modeling at 9.5 oC
ShearStressVersusShearRate(9.5, ShearRateData2, ShearStressData2)
```

M-file 1:

```
function ShearStressVersusShearRate(T, ShearRateData,
ShearStressData)
N=1;
X=log(ShearRateData);
Y=log(ShearStressData);
[A1 B1 S R]=LineFitting(X,Y,N);
fprintf('\n\nat -18.8 oC\n')
logK=A1
n=B1
StandardError=S;
CorrelationCoefficient=R;
fprintf('\n at %.2gC the model is log(Sigma)= %.2g + %2g*log(gamma)
with r= %2g Se= %2g \n',T,logK, n, CorrelationCoefficient,
StandardError)

% plot the model
logSSM=logK+n.*log(ShearRateData);
ShearStressModel=exp(logSSM);
loglog(ShearRateData, ShearStressModel, '-'); hold on;
```

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M-file 2:

```
function [A B Se r]=LineFitting(xData,yData,N)

% function LineFitting determines the constans of a linear model
and evaluates the standard error and the correlation coefficient

% determine the model coefficients
coeff=polyfit(xData,yData,N);
% coeff=coefficients of the polynomial of degree N
yData= polyval(coeff,xData);
B=coeff(1); % slope
A=coeff(2); % intercept with xData=0 axis

% determine the correlation coefficient and standard error
for j=1:1:size(xData);
      yModel=A+B*xData;
      d1=yData(j)-yModel;
end;
   d2=d1.^2;
   Se=sqrt(mean(d2));
   rmatrix=corrcoef(yData,xData);
  r=rmatrix(1,2);
```

When we run the code the following lines and Figure E.2.18.1 will appear on the screen:

```
at -18.8 oC
logK =
    3.1781
n =
    0.7726

 at -19C the model is log(Sigma)= 3.2 + 0.772551*log(gamma) with r=
1 Se= 2.82009

at -18.8 oC
logK =
    0.9872
n =
    0.7386

 at 9.5C the model is log(Sigma)= 0.99 + 0.738575*log(gamma) with
r= 1 Se= 2.69823
```

Concentration effects on apparent viscosity may be described with Equation 2.81:

$$\mu_{app} = \kappa \exp(\beta c). \tag{2.81}$$

Equation 2.81 may be linearized as:

$$\log(\mu_{app}) = \log(\kappa) + \beta c. \tag{2.82}$$

MATLAB code E.2.18.c evaluates the constants κ and c and compares the model with two sets of data as shown in Figure E.2.18.3.

The common mechanical feature of solids is that they can support appreciable levels of shear stress and therefore do not flow under their own weight or small external loads. The viscoelastic behavior of materials may be characterized with mathematical models that describe their stress–strain, stress-relaxation, and creep curves. In a creep test, material is subject to a constant stress and the corresponding strain is measured as a function of time $\gamma(t)$. Massless mechanical models, composed

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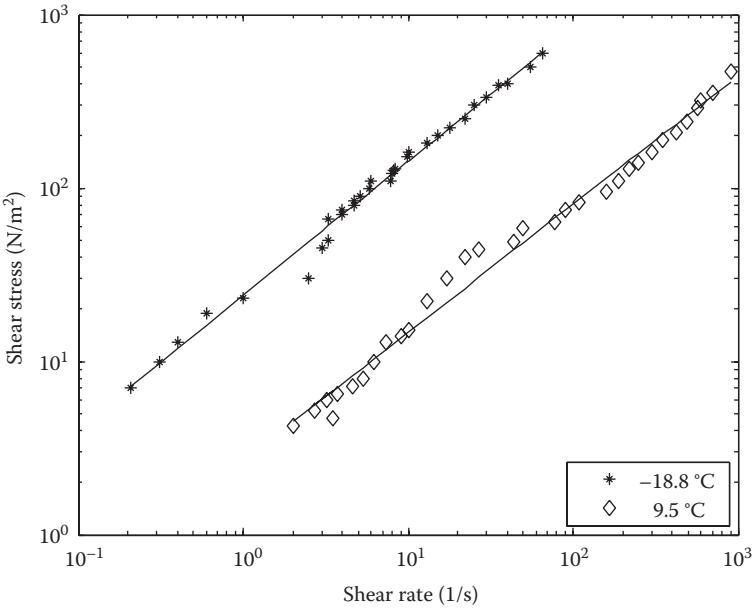


FIGURE E.2.18.1
Comparison of Equation 2.71 with the data obtained with orange juice at 65°Brix was compared between –18.8°C and 9.5°C. (Adapted from Vitali, A. A. and Rao, M. A., *Journal of Food Science*, 49, 882–88, 1984.)

MATLAB® CODE E.2.18b

Command Window:

```
clear all
close all
format compact

% enter the data
R = 8.314;
T = [-18.8 -14.5 -9.9 -5.4 -0.8 9.5 19.4 29.2]; % C
Kdata=[24.45 15.59 8.80 6.49 4.74 2.06 1.25 0.68];
lnKdata=log(Kdata);
[Ea,lnK0,Se,r]=ARRHENIUS(T,lnKdata);
EaR=Ea/R;
% print the model, correlation coefficient and the standard error
fprintf('\nArrhenius relation is ln(K)= %.2g -%2g/T and r= %2g se=
%2g \n', lnK0, EaR, r, Se)

% plot the model
invT= 1./(T+273);
lnKmodel=lnK0-EaR.*invT;
plot(invT, lnKmodel,'k:' , 'LineWidth',2);
grid on
```

When we run the code the following line and Figure E.2.18.2 will appear on the screen:

```
Arrhenius relation is ln(K)= -19 -5625.09/T and r= 0.996742 se=
0.265275
```

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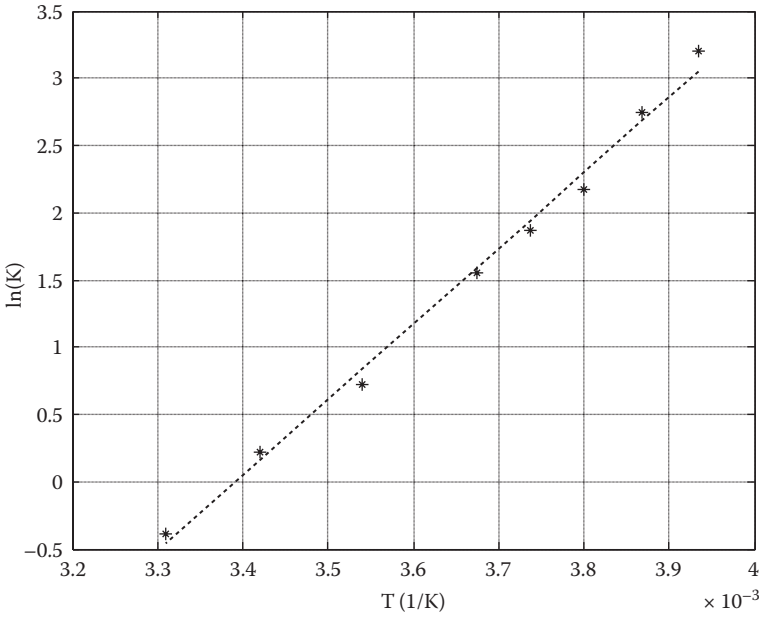


FIGURE E.2.18.2
Comparison of Equation 3.5 with the rheological data obtained with orange juice at 65°Brix and $\dot{\gamma} = 100 s^{-1}$. (Adapted from Vitali, A. A. and Rao, M. A., *Journal of Food Science,* 49, 882–88, 1984.)

MATLAB® CODE E.2.18c

Command Window:

```
clear all
close all
format compact
format short g

% enter the data
ConcentrationData= [51 56.5 58 61.5 65]; % oBrix
ApparentViscosityData1= [0.15 0.40 0.50 0.70 1.0]; % -5.4 oC
ApparentViscosityData2= [0.06 0.10 0.15 0.20 0.27]; % 19.5 oC

% plot the data
semilogy(ConcentrationData, ApparentViscosityData1, '*'); hold on;
semilogy(ConcentrationData, ApparentViscosityData2, 'd'); hold on;
ylabel('Apparent Viscosity (Pa s)')
xlabel('Concentration (oBrix) ')
legend('-5.4 oC','19.5 oC', 2,'Location','SouthEast')
grid on

% modeling at T=-5.4 oC
T=-5.4;
CEOV(T,ConcentrationData,ApparentViscosityData1);

% modeling at T=19.5 oC
T=19.5;
CEOV(T,ConcentrationData,ApparentViscosityData2);
```

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M-file:

```
function CEOV(T,ConcentrationData,ApparentViscosityData)
% Concentration Effects on Apparent Viscosity
T=-5.4;
N=1;
Y=log(ApparentViscosityData);
X=ConcentrationData;
[A1 B1 S R]=LineFitting(X,Y,N);
logKappa=A1;
Beta=B1;
StandardError=S;
CorrelationCoefficient=R;
fprintf('\n at %.2g oC the model is log(Apparent Viscosity)=%.2g+
%2g*Concentration with r=%.3g Se=%.3g\n',T,logKappa, Beta,
CorrelationCoefficient, StandardError)
% plot the model
lnModelApparentViscosity=logKappa+Beta.*ConcentrationData;
ModelApparentViscosity=exp(lnModelApparentViscosity);
semilogy(ConcentrationData,ModelApparentViscosity ,':' );

The following lines and Figure E.2.18.3 will appear on the screen
after running the code:

at -5.4 oC the model is log(Apparent Viscosity)=-8.6+
0.133851*Concentration with r=1 Se=1.18

at -5.4 oC the model is log(Apparent Viscosity)=-8.4+
0.110315*Concentration with r=1 Se=0.969
```

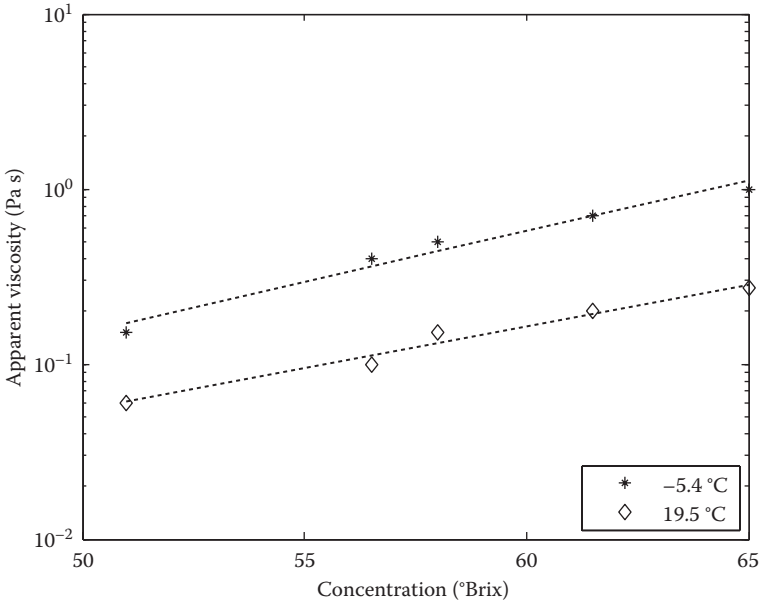


FIGURE E.2.18.3
Comparison of Equation 2.81 with the rheological data obtained with orange juice at 65°Brix and $\dot{\gamma} = 100 s^{-1}$. (Adapted from Vitali, A. A. and Rao, M. A., *Journal of Food Science,* 49, 882–88, 1984.)

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of springs and dashpots, are useful in conceptualizing rheological behavior. The spring is an ideal solid element obeying Hooke's Law; and the dashpot is the ideal fluid element obeying Newton's Law. Springs and dashpots can be connected in various ways to portray the behavior of viscoelastic materials; however, a particular combination of elements is not unique because many different combinations may be used to model the same set of experimental data. The most common mechanical analogs of rheological behavior are the Maxwell and Kelvin–Voigt models (Steffe 1996):

Basic Models		
i) Elastic (spring) model	$\sigma = G\gamma$	(2.83)
ii) Viscous (dashpot) model	$\sigma = \mu\dot{\gamma}$	(2.84)
Combination Models		
Maxwell model	$\dot{\gamma} = \frac{\dot{\sigma}}{G} + \frac{\sigma}{\mu}$	(2.85)
Kelvin–Voigt model	$\sigma = G\gamma + \mu\dot{\gamma}$	(2.86)
Burgers model	$\gamma = \frac{\sigma_0}{G_1} + \frac{\sigma_0}{G_2}\left[1 - \exp\left(-\frac{G_2 t}{\mu_2}\right)\right] + \frac{\sigma_0 t}{\mu_3}$	(2.87)

where $\dot{\gamma} = d\sigma/dt$.

Most food materials exhibit nonlinear viscoelasticity and rheological memory. In special cases there are also specific modes of behavior characterized by discontinuities in the stress–strain relationships; that is, a bio-yield point in some fruits, stress generation in muscle tissues during rigor mortis, and so on. To account for nonlinearity the linear models may be modified (Peleg 1983):

$$\sigma = C_1\gamma + C_2\dot{\gamma} + C_3\dot{\gamma}\gamma \text{ (modified Kelvin–Voigt model)}, \tag{2.87}$$

$$\sigma = C_1 + C_2\dot{\gamma} + C_3\dot{\gamma}^2 + C_4\dot{\gamma}^3 + \ldots \text{ (Green–Rivlin model)}. \tag{2.88}$$

The Maxwell model described in Figure 2.11 is composed of a spring and a dashpot in series. The spring and the dashpot experience the same stress, but the total strain is the sum of the individual strains:

$$\gamma = \gamma_{\text{spring}} + \gamma_{\text{dashpot}}, \tag{E.2.19.1}$$

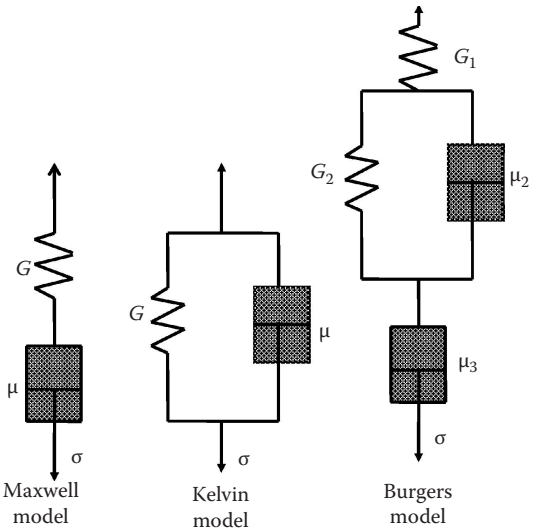


FIGURE 2.11
Maxwell, Kelvin–Voight, and Burgers models.

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differentiating this equation with respect to time yields

$$\dot{\gamma} = \dot{\gamma}_{spring} + \dot{\gamma}_{dashpot}. \tag{E.2.19.2}$$

Since $\sigma = G\ \gamma_{spring}$ with the spring and $\sigma = G\dot{\gamma}_{dashpot}$ with the dashpot; and $\gamma_{spring} = \sigma/G$ and $\dot{\gamma}_{dashpot} = \sigma/\mu$ we will have:

$$\dot{\gamma} = \frac{1}{G}\frac{d\sigma}{dt} + \frac{\sigma}{\mu}$$

or

$$\sigma + \tau_{ret}\frac{d\sigma}{dt} = \mu\dot{\gamma},$$

where $\tau_{ret} = \mu/G$ time takes out a molecule to be stretched when deformed.

Under constant stress σ_0 this equation becomes

$$\frac{d\gamma}{dt} = \frac{\sigma_0}{\mu}.$$

The initial strain in the system is given as

$$\text{IC: } \gamma = \sigma_0/G \text{ at } t = 0.$$

The spring responds to the stress immediately, while the dashpot delays; therefore, we observe the response of the spring (i.e., the first element in the IC). The solution to the differential equation with the given IC is

$$\gamma = \frac{\sigma_0}{G} + \frac{\sigma_0}{\mu}t. \tag{E.2.19.3}$$

The Kevin–Voigt model was described in Figure 2.11 is composed of a spring and a dashpot in parallel. The spring and the dashpot are strained equally, but the total stress is the sum of the individual stresses:

$$\sigma + G\gamma = \mu\dot{\gamma}, \tag{2.86}$$

which may be rewritten under constant stress σ_0 as

$$\frac{d\gamma}{dt} + \frac{\gamma}{\tau_{ret}} = \frac{\sigma_0}{\mu},$$

where τ_{ret} = retardation time (unique for the material in question). The system was not strained initially:

$$\text{IC: } \gamma = 0 \text{ at } t = 0.$$

The solution of the differential equation with the given IC is

$$\gamma = \frac{\sigma_0}{G}\left(1 - \exp\left(-\frac{t}{\tau_{ret}}\right)\right). \tag{E.2.19.4}$$

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The Burger model described in Figure 2.11 is composed of a Maxwell and a Kevin–Voigt element in series. The total strain is the sum of the individual Maxwell and Kevin–Voigt element strains:

$$\gamma = \frac{\sigma_0}{G_1} + \frac{\sigma_0}{G_2}\left(1 - \exp\left(-\frac{t}{\mu_2}\right)\right) + \frac{\sigma_0}{\mu_3}t. \tag{E.2.19.5}$$

Example 2.19: Application of the Burger Model to Study Creep Properties of the Rice Gel

Xu et al. (2008) reported that when rice gels are subject to stress, first the linkages between the structural units stretch elastically as described by the first term, σ_0/G_1, of the Burger model. If the stress is removed during the elastic stretching stage, the sample recovers its original structure. The second term, $(\sigma_0/G_2)(1 - \exp(-t/\mu_2))$, of the Burger model represents the stage where the links between the structural elements of the gel rupture. At the third stage of the process, the number of the broken linkages reach such a level that some of the linear molecules undergo displacement with respect to the others, resulting in viscous flow of the gel as described by the third term of the Burgers equation as $(\sigma_0/\mu_3)t$. MATLAB® code E.2.19 describes an evaluation of the parameters of the Burger model and compares the model with the data as depicted in Figure E.2.19.

Xu et al. (2008) stated that parameter K_1 and K_4 correspond to the intersection of deformation curve with $t = 0$ axis, and the plateau attained at the end of the process, respectively. Parameter K_2 is related with the slope of the final section of the curve. The regression analysis was preferred in this example, but other options may lead to more meaningful conclusions in the structural studies. An interested

MATLAB® CODE E.2.19

Command Window:

```
clear all
close all
format compact

% enter the data
tData=[0 0.5 2.5 5 8.6 13.7 17 20.6 26 28.3 33.4 39.4 42.9 48.5
52.3 56.6 66 71 77 81.4 86 92 97.7 102.9 106 118 120 ]; % s
DfrmtnD=[12 25 39 41 43 44 45 46 48 48.5 49 50 50.5 51 51.5 52 53
54 55 56 56.5 57.5 58 58.3 58.5 59.9 60]; % percent deformation
data

% plot the data
plot(tData, DfrmtnD, '*'); hold on
ylabel('Deformation (%)')
xlabel('time (s)')
grid on

% Evaluate the constants of the Burger Model
tModel=[0:1:120];
[COEFF,resid,J]=nlinfit(tData, DfrmtnD, 'Burger', [9 24 1e-1 4] );
DfrmtnModel=COEFF(1)+COEFF(2)*(1-exp(-tModel/
COEFF(3)))+COEFF(4)*tModel;
plot(tModel,DfrmtnModel, ':'); hold on
legend('data', 'model', 2,'Location','SouthEast')
fprintf('\n WITH THE BURGER MODEL COEFF(1)=%.2g, COEFF(2)=%.2g,
COEFF(3)=%.2g, COEFF(4)=%.2g %\n',COEFF(1), COEFF(2), COEFF(3),
COEFF(4))
```

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M-file:

```
function DfrmtnM=Burger(coeff, tData)
% introduce the constants and coefficients and the independent
variable
K1=coeff(1);
K2=coeff(2);
mu2=coeff(3);
K3=coeff(4);

% model:
DfrmtnM=K1+K2*(1-exp(-tData/mu2))+K3*tData;
```

The following lines and Figure E.2.19 will appear on the screen when we run the code:

```
WITH THE BURGER MODEL COEFF(1)=13, COEFF(2)=30, COEFF(3)=1.1,
COEFF(4)=0.15
```

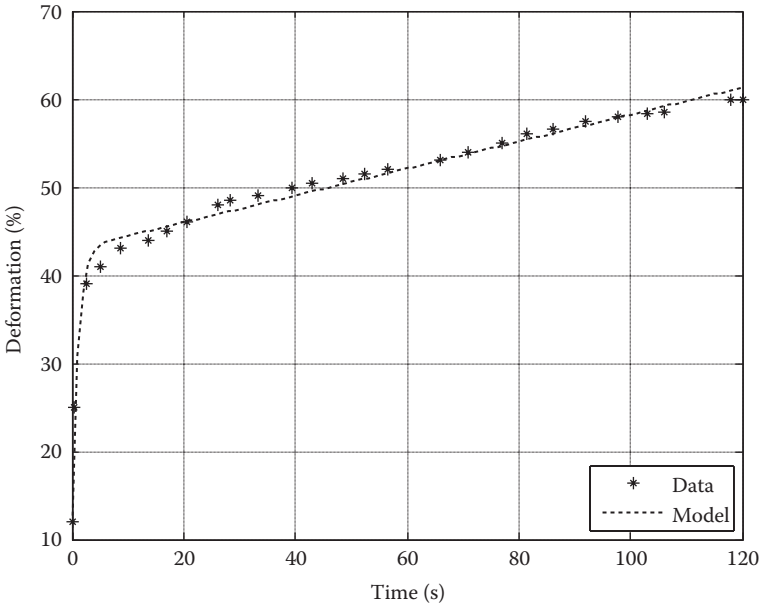


FIGURE E.2.19
Comparison of the Burger model with experimental data. The initial guess of the parameters and the data pertain to sample "*Liangyou 103*." (Adapted from Xu, Y. L., Xiong, S. B., Li, Y. B., and Zhao, S. M., *Journal of Food Engineering*, 86, 10–16, 2008.)

reader is strongly recommended to refer to Xu et al. (2008) for a detailed discussion about the relation between the material properties of the sample and the numerical values of the coefficients.

Example 2.20: Viscoelastic Behavior of Processed Cheese

The generalized Maxwell model is the most general linear viscoelasticity model, which suggests that the relaxation occurs at a distribution of time due to molecular segments of different lengths with shorter ones contributing less than the longer ones. The model includes as many spring-dashpot (Maxwell) elements as needed to represent the distribution. Dimitreli and Thomareis

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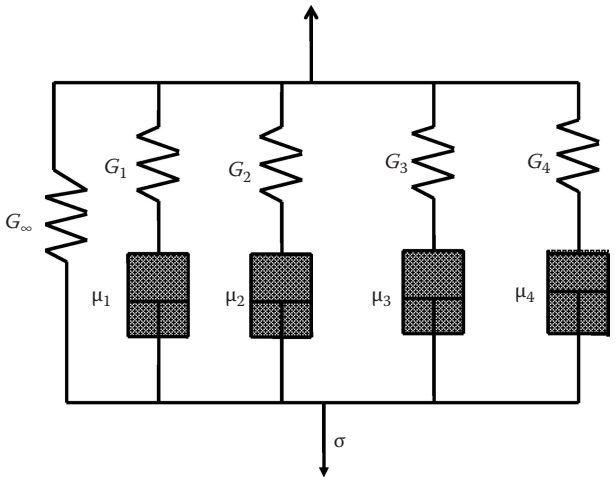


FIGURE E.2.20.1
Schematic description of the modules involved in the generalized Maxwell model.

(2007) suggested that one purely elastic and four Maxwellian parallel elements were needed to represent the viscoelastic behavior of the processed cheese as depicted in Figure E.2.20.1. The relaxation curve is expressed as

$$E(t) = E_\infty + \sum_{i=1}^{4} E_i \exp\left(-\frac{t}{\tau_i}\right). \tag{E.2.20.1}$$

Where $E(t)$ is the elastic modulus at time t, E_∞ is the equilibrium modulus of the pure elastic element; E_i's and t_i's are the elastic modulus and relaxation times of the ith element, respectively. Coefficients of viscosity, η_i, of each dashpot element are calculated as

$$\eta_i = E_i \tau_i. \tag{E.2.20.2}$$

MATLAB® code E.2.20 describes the evaluation of the model constants and compares the model with the data as shown in Figure E.20.2.

MATLAB® CODE E.2.20

Command Window:

```
clear all
close all
format compact

% enter the data
tData=[0:10:800]; % (s)
RelaxtnD=[0.1541 0.0825 0.0701 0.0625 0.0575 0.0540 0.0514 0.0493
0.0477 0.0462 0.0449 0.0438 0.0428 0.0418 0.0409 0.0401 0.0394 0.0387
0.0380 0.0374 0.0368 0.0363 0.0358 0.0353 0.0348 0.0344 0.0340 0.0336
0.0333 0.0329 0.0326 0.0323 0.0320 0.0317 0.0315 0.0312 0.0310 0.0308
0.0305 0.0303 0.0301 0.0299 0.0297 0.0295 0.0294 0.0292 0.0290 0.0289
0.0287 0.0285 0.0284 0.0282 0.0281 0.0280 0.0278 0.0277 0.0276 0.0274
0.0273 0.0272 0.0271 0.0269 0.0268 0.0267 0.0266 0.0265 0.0264 0.0262
0.0261 0.0260 0.0259 0.0258 0.0257 0.0256 0.0255 0.0254 0.0253 0.0252
0.0251 0.0250]; % F (N)
```

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```
% plot the data
plot(tData(1:80), RelaxtnD(1:80), '-'); hold on
ylabel('Force (N)')
xlabel('time (s)')
grid on

% Evaluate the constants of the Generalized Maxwell Model
[COEFF,resid,J]=nlinfit(tData(1:80), RelaxtnD(1:80),
'RelaxationModel', [13e-3 21e-3 26e-3 40e-3 53e-3 1200 120 1.8 0.24]
);
C(1:5)=1000*COEFF(1:5);
C(6:9)=COEFF(6:9)/60;
fprintf('\n Einf=%.2g, E1=%.2g, E2=%.2g, E3=%.2g, E4=%.2g,
tau1=%.2g, tau2=%.2g, tau3=%.2g, tau4=%.2g',C(1), C(2), C(3), C(4),
C(5), C(6), C(7), C(8), C(9) )

% compute the viscosities

for i=1:4
eta(i)=COEFF(i+1)*COEFF(i+5); % (Pa s)
end

fprintf('\n eta1=%.2g (Pa s), eta2=%.2g (Pa s), eta3=%.2g (Pa s)
eta4=%.2g (Pa s)' ,eta(1), eta(2), eta(3), eta(4))
```

M-file:

```
function RelaxtnM=RelaxationModel(Coeff, tModel)

% model
RelaxtnM=Coeff(1)+Coeff(2)*(exp(-tModel/Coeff(6)))+ Coeff(3)*(exp(-
tModel/Coeff(7))) +Coeff(4)*(exp(-tModel/Coeff(8))) +Coeff(5)*(exp(-
tModel/Coeff(9)));
```

The following lines and Figure E.2.20 will appear on the screen when we run the code:

```
Einf=13, E1=23, E2=27, E3=41, E4=51, tau1=22, tau2=2, tau3=0.29,
tau4=0.004

eta1=30 (Pa s), eta2=3.1 (Pa s), eta3=0.71 (Pa s) eta4=0.012 (Pa s)
```

Example 2.21: Viscoelastic Characteristics of Yams

The viscoelastic properties of solids may be demonstrated by relaxation curves. In physical sciences, relaxation usually means the return of a perturbed system to equilibrium. In viscoelasticity studies a good mathematical model must be sensitive to physical changes and have physically meaningful constants. The fracture stress, σ, for a symmetrical beam with a rectangular cross section is calculated as

$$\sigma = \frac{3FL}{2bh^2}. \tag{E.2.21.1}$$

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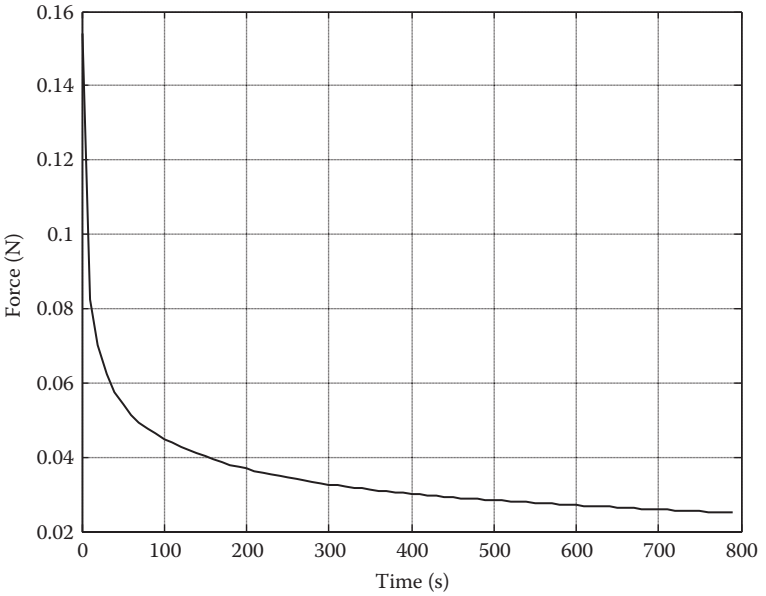


FIGURE E.2.20.2
Stress relaxation curve. (Data and initial values of the constants of the model adapted from Dimitreli, G. and Thomareis, A., *Journal of Food Engineering*, 79, 1364–73, 2007.)

Where F is the force applied to the beam, b and h are the dimensions of the cross section, and L is the length. The decaying parameter $Y_{(t)}$ is

$$Y(t) = \frac{F_0 - F_t}{F_0}. \tag{E.2.21.2}$$

Where F_t is the force recorded after 1 minute at relaxation. A typical function for $Y(t)$ is

$$Y(t) = \frac{abt}{1+bt}, \tag{E.2.21.3}$$

where a and b are constants. Equation E.2.21.3 is referred to as the *Peleg Equation* in the literature. When $a = 0$ the material is regarded as ideal elastic where the stress does not relax at all. Parameter $a = 1$ when the stress level reaches to zero and this is a property of the liquids. The constant b is the representative of the rate at which the stress relaxes. When $t = 1/b$ stress relaxes to level $a/2$. Equation E.2.21.3 gives a straight line when plotted as

$$\frac{1}{Y(t)} = \frac{1}{ab} + \frac{t}{a}. \tag{E.2.21.4}$$

MATLAB® code E.2.21 plots $1/Y(t)$ versus t and determines the parameters a and b from experimental data and compares the model with the data (Figure E.2.21).

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MATLAB® CODE E.2.21

Command Window:

```
clear all
close all
format compact

% enter the data
tData=[25:25:475]; % t (s)
t_Y=[170 200 240 300 400 450 500 550 600 650 710 760 810 880 950
1000 1090 1130 1170]; % t/Y (s)

% plot the data
plot(tData, t_Y, 'o'); hold on
ylabel('t/Y(s)')
xlabel('time (s)')
grid on

% fit a polynomial empirical model to the data
N=1; % degree of the fitted polynomial determine N
c = polyfit(tData, t_Y,N) % best fitting line to the data
t_Ymodel=polyval(c,tData);
plot(tData, t_Ymodel, '-'); hold on

% compute the constants of the model
a=1/c(1)
b=1/(c(2)*a)
```

The following lines and Figure E.2.21 will appear on the screen when we run the code:

```
c =
    2.2821   90.5263
a =
   0.4382
b =
   0.0252
```

2.12 Engineering Bernoulli Equation

First law of thermodynamics was already expressed as

$$\left[m^{\bullet}(u+e_p+k+P\nu)\right]_{\text{in}}-\left[m^{\bullet}(u+e_p+k+P\nu)\right]_{\text{out}}+Q-W=\frac{d}{dt}\left[m_{\text{acc}}(u+e_p+k)_{\text{acc}}\right] \quad \text{(E.1.5)}$$

After ignoring the influences of heat transfer and internal energy changes, Equation E.1.5 becomes the mechanical energy balance. Under steady state conditions, on a unit mass basis and for an incompressible fluid Equation E.1.5 is commonly written as (Heldman and Singh 2009)

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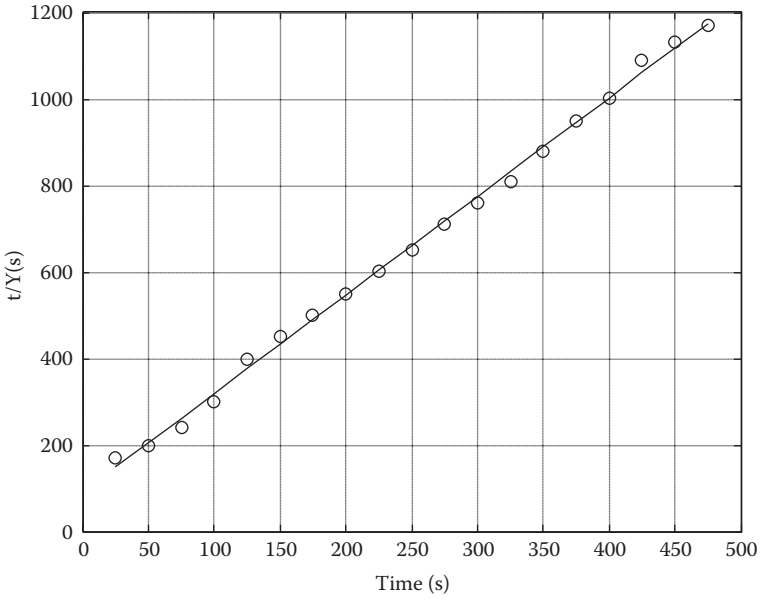


FIGURE E.2.21
Comparison of Equation E.2.21.4 with the data obtained with Pico de Botella yams. (Adapted from Alvis, A., Villamiel, M., and Rada-Mendoza, M., *Journal of Texture Studies,* 41, 92–99, 2010.)

$$gh_1 + \frac{P_1}{\rho} + \frac{\bar{v}_1^{-2}}{2\alpha} - W = gh_2 + \frac{P_2}{\rho} + \frac{\bar{v}_2^{-2}}{2\alpha} - \sum F, \tag{2.89}$$

where subscripts refer to points 1 and 2 in a fluid handling system, Z is the elevation from a reference, g is the gravitational acceleration, P is the pressure; ρ and $\bar{v}$ are the density and the average velocity of the liquid, respectively, α is the kinetic energy correction factor, W is the work output per unit mass of the liquid, and ΣF is frictional loss of energy per unit mass of the liquid. The gh and $\bar{v}_1^2/2$ terms are the potential and the kinetic energy per unit mass of the liquid. The term P/ρ is the pressure energy; that is, the ability of doing pressure volume work by the unit mass of liquid. Equation 2.89 may be used for modeling flow in foods or pipeline design.

Example 2.22: Shrinkage and Whey Expulsion in Rennet Curd

The casein micelles of milk have hydrophobic cores and hydrophilic external layers. During renetting, casein macropeptide residues are removed and the hydrophobic core is exposed. The paracasein micelles form a network, which apply pressure on whey and forces it to synerese.

Syneresis is observed with newly cut curd during cheese making and is critical to the yields, texture, moisture content, flavor, and quality of the final cheese. The surfaces of the undisturbed gel are not permeable for water since they stick on the vessel walls and are covered with lipids at the milk/air interfaces. Expulsion of whey from the rennet curd is coupled with a rearrangement of the network (Figure E.2.22.1). Pump work done by unit thickness of the network for expelling water is (Özilgen and Kauten 1994)

$$W = PA\frac{dZ}{Z_i}, \tag{E.2.22.1}$$

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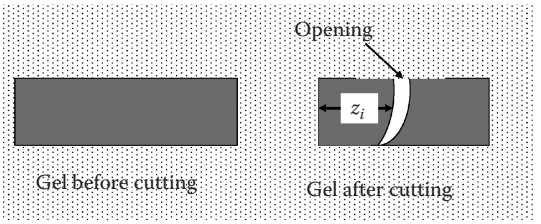


FIGURE E.2.22.1
Schematic drawing of the of the rennet curd before and after cutting. Distance z_i was measured for all the levels (from bottom to top) along the surface of the opening.

where A = cross-sectional area of the curd, P is the force applied by the network on the entrapped whey, and dZ/Z_i is the change of the curd thickness (dZ) per unit initial thickness (Z_i) of the curd. Equation 2.89 was stated for unit mass of water as

$$gh_1 + \frac{P_1}{\rho} + \frac{\bar{v}_1^2}{2\alpha} - W = gh_2 + \frac{P_2}{\rho} + \frac{\bar{v}_2^2}{2\alpha} - \sum F, \tag{2.89}$$

since the elevation of the curd is the same everywhere (i.e., $gh_1 = gh_2$), the pressure drop along the curd is negligible (i.e., $P_1 = P_2$), and when $\alpha = 1$ for expulsion of the differential amount of water dM, Equation 2.89 becomes

$$-PA\frac{dZ}{Z_i} = dM\left(\frac{\bar{v}_2^2}{2\alpha} - \frac{\bar{v}_1^2}{2\alpha}\right) + dM\sum F. \tag{E.2.22.2}$$

Total resistance to flow in the curd may be expressed as

$$\sum F = K(z_i - z)\bar{v}_2^2, \tag{E.2.22.3}$$

where $z_i - z$ is the distance over which differential amount of water dM is pumped and K is a constant. After substituting this expression for ΣF and $\bar{v}_1^2$, the final form of the Bernoulli equation was integrated to obtain an expression for the amount of water removed from the curd as a function of distance from the cut surface (Özilgen and Kauten 1994)

$$M = M_i + \frac{C}{K}\ln\left[1 + 2K\left(z_i - z\right)\right], \tag{E.2.22.4}$$

where $C = PA/\bar{v}_2^2 z_i$. Profiles of the remaining water are calculated by subtracting this equation from the constant initial water content. The intensity of the NMR signal, S, along the curd is proportional with the amount of entrapped water and expressed as

$$S = S_i + \frac{C}{K}\ln\left[1 + 2K(z_i - z)\right], \tag{E.2.22.5}$$

where S_i is the intensity of the NMR signal on the cutting surface, $\Delta z = z_i - z$, C and K are constants. MATLAB® code E.2.22 plots Equation E.2.22.5 and compares the signal intensity with the experimental data (Figure E.2.22).

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MATLAB® CODE E.2.22

Command Window:

```
clear all
close all
format compact

% enter the data
deltaZdata=[30.5 31 32 32.5 33 34 34.7 35.5 36 37 37.5 38.2 39 40];
% distance from the cut
Sdata=[3.1 3.3 3.9 4 4.1 4.7 4.4 4.7 4.6 4.9 5.5 5.7 5.8 5.9]; %
signal intensity
% plot the data
plot(deltaZdata,Sdata,'s'); hold on

% call the nonlinear least squares data fitting function nlinfit
[COEFF,resid,J]=nlinfit(deltaZdata, Sdata, 'shrinkage', [7 0.21
0.09]);

Si=COEFF(1)
C=COEFF(2)
K=COEFF(3)

deltaZmodel(1)=1;
S(1)=COEFF(1)

for i=2:40
    deltaZmodel(i)=deltaZmodel(i-1)+1;
    S(i)=Si+(C/K)*(log(1+2*K*deltaZmodel(i)));
 end

plot(deltaZmodel(30:40),S(30:40),'-'); hold on % plot the model
xlabel('z_i-z (mm)');
ylabel('S_i');
```

M-file:

```
function Smodel=Shrinkage(coeff,deltaZmodel)
Smodel= coeff(1)+(coeff(2)/coeff(3))*log(1+2*coeff(3)*deltaZmodel);
% model:
```

When we run the code, the following lines and Figure E.2.22.2 will appear on the screen:

```
S =
  -19.6389
Si =
  -19.6389
C =
    1.2046
K =
    0.1056
```

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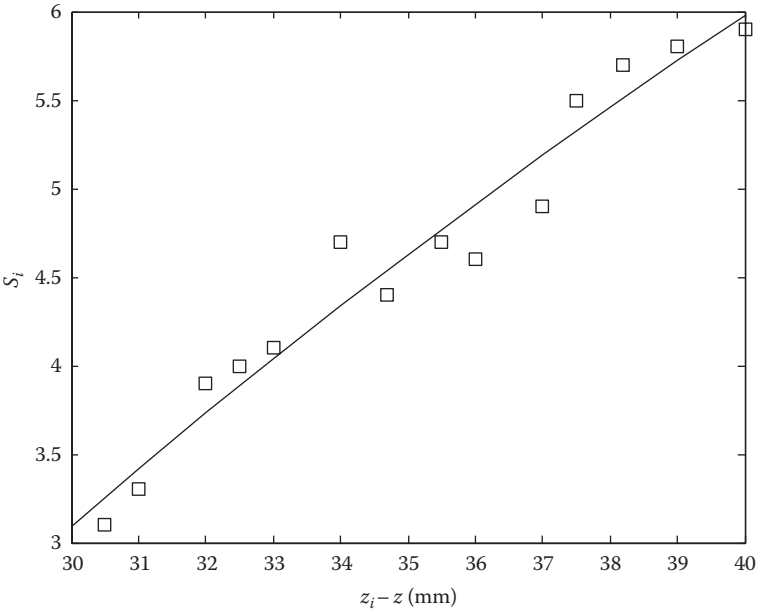


FIGURE E.2.22.2
Comparison of the model with the data 136 minutes after cutting the curd. (Adapted from Özilgen, M. and Kauten, R. J., *Process Biochemistry*, 29, 373–79, 1994.)

In Equation 2.89, energy losses due to friction were shown with Σ*F*, which include losses in straight pipe, valves, and fittings and may be expressed as

$$\sum F = \frac{2f\overline{v}^2 L}{D} + \sum_{i=1}^{m}\left[\frac{f\overline{v}^2}{2}\right]_m, \tag{2.90}$$

where f = Fanning friction factor, L = pipe length, D = inner diameter of the pipe, k_f = friction loss coefficient (unique for any particular valve or fitting), and m is the number of the fittings in the flow system. Different values of $\overline{v}$, k_f, and f may be required when the pumping system includes pipes having different diameters.

A procedure was outlined by Steffe and Morgan (1986) to calculate the energy losses for non-Newtonian fluids under laminar flow conditions. We may calculate f from

$$f = \frac{16}{\psi \mathrm{Re}}, \tag{2.91}$$

where

$$\mathrm{Re} = \frac{D^n\left(\overline{v}^{n-2}\right)\rho}{8^{n-1}K}\left(\frac{4n}{1+3n}\right)^n, \tag{2.92}$$

$$\psi = \left(1+3n\right)^n\left(1-\xi_0\right)^{n+1}\left[\frac{\left(1-\xi_0\right)^2}{1+3n} + \frac{2\xi_0\left(1-\xi_0\right)}{1+2n} + \frac{\xi_0^2}{1+n}\right], \tag{2.93}$$

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and

$$\xi_0 = \frac{2\tau_0}{f\rho\bar{v}^2}.$$

For power law and Newtonian liquids $\zeta_0 = 0$ and $\psi = 1$, therefore f may be calculated easily using Equations 2.91 and 2.92. The Reynold's number is also given as

$$\mathrm{Re} = 2\mathrm{He}\left(\frac{n}{1+3n}\right)^2\left(\frac{\psi}{\xi_0}\right)^{2/n-1}, \tag{2.94}$$

where He is the Hedstrom number defined as

$$\mathrm{He} = \frac{D^2\rho}{K}\left(\frac{\tau_0}{K}\right)^{(2/n)-1}. \tag{2.95}$$

To calculate the friction factor for Herschel–Bulkley fluids, ζ_0 is estimated through an iteration of Equation 2.94 using Equations 2.92, 2.93, and 2.94, then f can be calculated using Equations 2.91 and 2.92. The kinetic energy correction factor α is 2 in turbulent flow. When the flow is laminar, α may be calculated from the Osorio–Steffe equation (1984):

$$\alpha = \frac{2\left(1+3n+2n^2+2n^2\zeta_0+2n\zeta_0+2n^2\zeta_0^2\right)^3\left(2+3n\right)\left(3+5n\right)\left(3+4n\right)}{\left(1+2n\right)^2\left(1+3n\right)^2\left[18+nf_1\left(\zeta_0\right)+n^2f_2\left(\zeta_0\right)+n^3f_3\left(\zeta_0\right)+n^4f_4\left(\zeta_0\right)+n^5f_5\left(\zeta_0\right)\right]}, \tag{2.96}$$

where

$$f_1\left(\zeta_0\right) = 105+66\zeta_0,$$

$$f_2\left(\zeta_0\right) = 243+306\zeta_0+85\zeta_0^2,$$

$$f_3\left(\zeta_0\right) = 279+522\zeta_0+350\zeta_0^2,$$

$$f_4\left(\zeta_0\right) = 159+390\zeta_0+477\zeta_0^2,$$

$$f_5\left(\zeta_0\right) = 36+108\zeta_0+216\zeta_0^2.$$

Non-Newtonian foods rarely flow under turbulent conditions; however, it is recommended checking the flow behavior using the Hanks and Ricks (1974) diagram (Figure 2.12), which gives the value of the critical number, Re_c, where laminar flow ends. MATLAB® code 2.2 produces a plot and the empirical correlations, which may be used to estimate the critical Reynold's numbers as a function of the flow behavior index and the Hedstrom number.

Example 2.23: Pump Power Requirement With a Herschel-Bulkley Fluid

A Herschel–Bulkley fluid $\tau_0 = 150$ Pa, $K = 5.20$ Pa s, $n = 0.45$, $\rho = 1300$ kg/m^3) is pumped in the following system (inside a diameter of the steel pipe was 4.1×10^{-2} m before the pump and 5.3×10^{-2} m after the pump) with the flow rate of 3×10^{-3} m^3/s (Figure E.2.23). Friction loss factors for elbows

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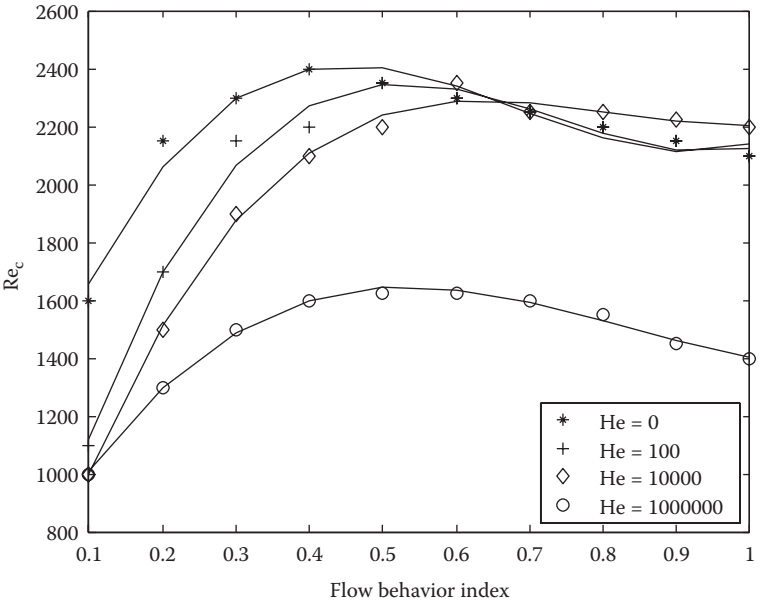


FIGURE 2.12
Variation of the critical Reynolds number with the flow behavior index at different Hedstrom numbers. The following empirical correlations were fit to the values adapted from Hanks, R. W. and Ricks, B. L., *Journal of Hydronautics*, 8, no. 4, 163–66, 1974:

When He = 0 $Re_c = 10^4[0.5779n^3 - 1.1903n^2 + 0.7214n + 0.1047]$
When He = 10^2 $Re_c = 10^4[0.6410n^3 - 1.4138n^2 + 0.9552n + 0.0300]$
When He = 10^4 $Re_c = 10^4[0.4186n^3 - 1.0221n^2 + 0.7936n + 0.0302]$
When He = 10^6 $Re_c = 10^3[0.25155n^3 - 6.3287n^2 + 4.6071n + 0.6067]$.

MATLAB® CODE 2.2

Command Window:

```
clear all
close all
format compact

% enter the data
n=[0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0]
He=[0 1e2 1e4 1e6];
Re=[1600 2150 2300 2400 2350 2300 2250 2200 2150 2100; 1100 1700 2150
2200 2350 2300 2250 2200 2150 2100; 1000 1500 1900 2100 2200 2350
2250 2250 2225 2200; 1000 1300 1500 1600 1625 1625 1600 1550 1450
1400];

% plot the data

plot(n,Re(1,:), '*', n,Re(2,:), '+', n,Re(3,:), 'd', n,Re(4,:), 'o');
hold on
ylabel('Re_c')
```

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```
xlabel('Flow Behavior Index')
legend('He=0','He=100', 'He=10000' ,'He=1000000',
'Location','SouthEast')

% find the best fitting empirical equations for each curve
N=3
f1 = polyfit(n,Re(1,:),N)
ReModel1 = polyval(f1,n);
f2 = polyfit(n,Re(2,:),N)
ReModel2 = polyval(f2,n);
f3 = polyfit(n,Re(3,:),N)
ReModel3 = polyval(f3,n);
f4 = polyfit(n,Re(4,:),N)
ReModel4 = polyval(f4,n);

% plot the model
plot(n, ReModel1,n,ReModel2,n,ReModel3,n,ReModel4);
```

The following lines and Figure 2.12. will appear on the screen when we run the code.

```
f1 =
  1.0e+004 *
    0.5779 -1.1903 0.7214 0.1047
f2 =
  1.0e+004 *
    0.6410 -1.4138 0.9552 0.0300
f3 =
  1.0e+004 *
    0.4186 -1.0221 0.7936 0.0302
f4 =
  1.0e+003 *
    2.5155 -6.3287 4.6071 0.6067
```

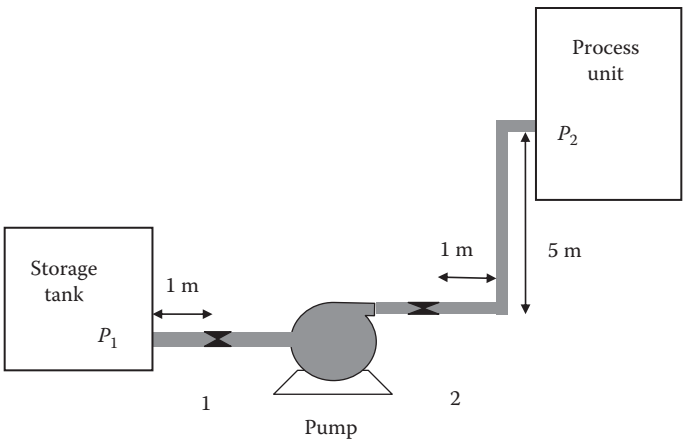


FIGURE E.2.23
Schematic drawing of the flow system.

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and the valves were $k_f = 0.45$ and $k_f = 0.90$, respectively. Calculate the power requirement for the pump. You may neglect sudden contraction and sudden expansion friction losses at the exit of the storage tank and at the entrance of the process unit. Compute the pump work requirement when the flow rate increases by 50%.

MATLAB® code E.2.3 computes the solution.

MATLAB® CODE E.2.23

Command Window:

```
clear all
close all
format compact

% enter the data
n=0.45;
K=5.20; % (Pa s)
rho=1300; % (kg/m3)
tau0=150; % Pa
F=3e-3; % flow rate (m3/s)
d=[4.1e-2 5.3e-2]; % d(1): before the pump, d(2): after the pump (m)
L(1)=1; % pipe length before the pump (m)
L(2)=1+5; % pipe length after the pump (m)
kf=[0.45 0.90]; % friction loss factors for elbows and valves,
respectively
P=[1.2e5 1.4e5]; % pressure in the storage tank and the process
unit (Pa)
for i=1:2
      % compute the velocities, Re and He numbers
      v(i)=F/(pi.*(d(i)/2)^2); % velocity (m/s)
       Re(i)=(((d(i)^n))*(v(i)^(2-n))*rho/((8^(n-1))*K))*((4*n/
(1+3*n))^n);
        He(i)=((d(i)^2)*rho/K)*(tau0/K)^((2/n)-1);

    % trial and error solution to determine zeta0 values
        PSI1(i)=Re(i)/(2*He(i)*(n/(1+3*n))^2);
         z(1)=1e-2;

     for j=2:60
            z(j)=z(1)*j;
            psi1(i)=(PSI1(i)^(1/((2/n)-1)))*z(j);
            psi2(j)=((1+3*n)^n)*((1-z(j))^(n+1))*((((1-z(j))^2)/
(1+3*n))+((2*z(j)*(1-z(j)))/(1+2*n))+((z(j)^2)/(1+n)))^2;
              error= psi1(i)-psi2(j);

                if abs(error)<=0.01;
                     zeta0(i)=z(j);
                 end

       end

      psi(i)=(PSI1(i)^(1/((2/n)-1)))*zeta0(i);
      f(i)=16/(psi(i)*Re(i));

% compute alpha
     f1(i)=105+66*zeta0(i);
     f2(i)=243+306*zeta0(i)+85*zeta0(i)^2;
     f3(i)=279+522*zeta0(i)+350*zeta0(i)^2;
```

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```
     f4(i)=159+390*zeta0(i)+477*zeta0(i)^2;
      f5(i)=36+108*zeta0(i)+216*zeta0(i)^2;

numerator1(i)=2*((1+3*n+2*(n^2)+2*(n^2)*zeta0(i)+2*n*zeta0(i)+2*(n^
2)*(zeta0(i))^2)^3);
     numerator2(i)=(2+3*n)*(3+5*n)*(3+4*n);
     denominator1(i)=((1+2*n)^2)*((1+3*n)^2);
     denominator2(i)=(18+n*f1(i)+(n^2)*f2(i)+(n^3)*f3(i)+(n^4)*f4(i)+
(n^5)*f5(i));
     alpha(i)=(numerator1(i)/denominator1(i))*(numerator2(i)/
denominator2(i));

% compute the total friction

sigmaF(i)=(2*f(i)*(v(i)^2)*L(i)/d(i))+(kf(1)*(v(i)^2)/2)+
(kf(2)*(v(i)^2)/2);

end

zeta0
psi
f
alpha
sigmaF

% compute the pump work requirement
W=-(((P(2)/rho)+ v(1)^2/(2*alpha(2)))+sigmaF(1)+sigmaF(2)-((P(1)/
rho)+ v(1)^2/(2*alpha(1)))) % (J/kg)
```

The following lines will appear on the screen after running the code:

```
zeta0 =
    0.3400    0.4300
psi =
    0.2063    0.1845
f =
    0.1315    0.2902
alpha =
    1.3858    1.4478
sigmaF =
   36.5942   122.7589
W =
 -174.6580
```

When we increase the flow rate by 50% the following lines will appear on the screen:

```
zeta0 =
    0.3000    0.3800
psi =
    0.2185    0.1957
f =
    0.0662    0.1460
alpha =
    1.3603    1.4126
sigmaF =
   45.3652  140.3074
W =
 -200.8990
```

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2.13 Laplace Transformations in Mathematical Modeling

Most food and bioprocess engineering problems are solved in time domain. Transformation into Laplace domain (Tables 2.19 and 2.20) converts an ordinary differential equation into an algebraic equation, or a partial differential equation into an ordinary differential equation and makes it easier to obtain the solution. The procedure of using the Laplace transformations is described in Figure 2.13.

Example 2.24: Solution of a Linear Ordinary Differential Equation With Laplace Transformations

An ordinary differential equation

$$\frac{d^2x(t)}{dt^2}+\frac{dx(t)}{dt}+0.125x(t)=1, \tag{E.2.24.1}$$

with the initial conditions

$$x(0)=0 \tag{E.2.24.2}$$

and

$$\frac{dx(0)}{dt}=0 \tag{E.2.24.3}$$

TABLE 2.19

Laplace Transformation and Its Important Properties

Laplace transformation $\mathcal{L}[f(t)]$ of a function $f(t)$

$$\mathcal{L}\left[f(t)\right]=\int_0^\infty e^{-st}f(t)dt$$

comments:

i) If the integral on the right-hand side of the definition can not be calculated, the Laplace transform of the function $f(t)$ would not be available.

ii) The Laplace transform involves no information for the behavior of $f(t)$ when $t<0$.

The Laplace transform is linear

$$\mathcal{L}\left[\alpha f_1(t)+\beta f_2(t)\right]=\alpha\mathcal{L}\left[f_1(t)\right]+\beta\mathcal{L}\left[f_2(t)\right]$$

Shifting theorem $\mathcal{L}\left[e^{-\alpha t}f(t)\right]=\int_0^\infty e^{-(s+\alpha)}f(t)dt=f(s+\alpha)$

Heaviside's expansion theorem 1: (used when $Q(s)$ has a higher degree than $P(s)$)

$$\mathcal{L}^{-1}\left\{\frac{P(s)}{Q(s)}\right\}=\sum_{m=1}^{\infty}\frac{P(s_m)}{Q^{\bullet}(s_m)}\exp\{s_m t\}\quad \text{where } s_m=\text{roots of } Q(s)=0\quad Q^{\bullet}(s)=\frac{dQ}{ds}$$

Heaviside's expansion theorem 2: (used when $Q(s)=(s-s_1)^{m_1}(s-s_2)^{m_2}.....(s-s_n)^{m_n}$ and degree of $P(s)$ is less than $\left\{\sum_{j=1}^{n}m_j\right\}-1$)

$$\mathcal{L}^{-1}\left\{\frac{P(s)}{Q(s)}\right\}=\sum_{k=1}^{n}\sum_{j=1}^{m_k}\frac{\phi_{kj}(s_k)}{(m_k-j)!(j-1)!}t^{m_k-j}\exp\{s_k t\}$$

where $\phi_{kj}(s)=\frac{d^{j-1}}{ds^{j-1}}\left[\frac{P(s)}{Q_k(s)}\right]$ and $Q_{ks}=\frac{Q_s}{(s-s_k)^{m_k}}$

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TABLE 2.20

Laplace Transforms of Simple Functions

Step function:
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = 1,\ L\{f(t)\} = 1/s$
Ramp function:
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = t,\ L\{f(t)\} = 1/s^2$
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = t^n,\ L\{f(t)\} = n!/s^n + 1$
Exponential function:
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = e^{-\alpha t},\ L\{f(t)\} = 1/s + \alpha$
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = t^n e^{-\alpha t},\ L\{f(t)\} = n!/(s+\alpha)^{n+1}$
Sine function:
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = \sin(\kappa t),\ L\{f(t)\} = \kappa/s^2 + \kappa^2$
Cosine function:
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = \cos(\kappa t),\ L\{f(t)\} = s/s^2 + \kappa^2$
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = e^{-\alpha t}\sin(\kappa t)\ L\{f(t)\} = \kappa/(s+\alpha)^2 + \kappa^2$
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = e^{-\alpha t}\cos(\kappa t)\ L\{f(t)\} = s + \alpha/(s+\alpha)^2 + \kappa^2$
Hyperbolic sine function:
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = \sinh(\kappa t),\ L\{f(t)\} = \kappa/s^2 - \kappa^2$
Hyperbolic cosine function:
When $t < 0\ f(t) = 0$, when $t \geq 0\ f(t) = \cosh(\kappa t),\ L\{f(t)\} = s/s^2 - \kappa^2$
Unit impulse
When $t < 0\ f(t) = 0, f(t) = \delta(t) = 0$, when $t > 0\ f(t) = 0, L\{f(t)\} = 1$
When $t < 0\ f(t) = 0$, when $t > 0$ Laplace transform of the derivative $df(t)/dt$ is $L\{f(t)\} = sf(s) - f(0)$
When $t < 0\ f(t) = 0$, when $t > 0$ Laplace transform of the higher order derivative $d^n f(t)/dt^n$ is

$$L\{f(t)\} = s^n f(s) - s^{n-1} f(0) - s^{n-2}\left(\frac{df(t)}{dt}\right)_{t=0} - s^{n-3}\left(\frac{d^2 f(t)}{dt^2}\right)_{t=0} - \ldots. - \left(\frac{d^{n-1} f(t)}{dt^{n-1}}\right)_{t=0}$$

When $t < 0\ f(t) = 0$, when $t > 0$ Laplace transform of the integral $\int_0^t f(t)dt$ is $L\{f(t)\} = 1/sf(s)$
When $t < 0\ f(t) = 0$, when $t > 0$ Laplace transform of the complimentary error function $erfc(k/2\sqrt{t})$ is $L\{f(t)\} = 1/s\exp(-k\sqrt{s})$ where $k \geq 0$

Notice: You may compute Laplace transforms by using the symbolic toolbox of MATLAB®. If you want to compute the Laplace transform of $x(t) = t$, run the following MATLAB code:

```
syms f t
format compact
f = t;
laplace(f)
```

the following will appear in the screen:

```
ans =
1/s^2
```

are converted into the Laplace domain with transformation of the individual terms as:

$$\mathcal{L}\left\{\frac{d^2x(t)}{dt^2}\right\} = s^2x(s) + sx(s) + 0.125x(s) = \frac{1}{s}, \tag{E.2.24.4}$$

$$\mathcal{L}\left\{\frac{dx(t)}{dt}\right\} = sx(s) - x(0) = sx(s), \tag{E.2.24.5}$$

$$\mathcal{L}\{x\} = x(s), \tag{E.2.24.6}$$

$$\mathcal{L}\{1\} = \frac{1}{s}. \tag{E.2.24.7}$$

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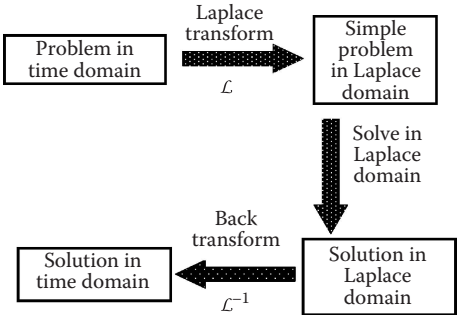


FIGURE 2.13
Schematic description of problem solving by using Laplace transformation.

After substituting the transformation Equations E.2.24.4 through E.2.24.7 in Equation E.2.24.1 we will obtain the Laplace transformation of the original ordinary differential equation as

$$s^2x(s)+sx(s)+0.125x(s)=\frac{1}{s}. \tag{E.2.24.8}$$

Equation E.2.24.8 may be rearranged as

$$x(s)=\frac{1}{\left(s^2+s+0.125\right)s}. \tag{E.2.24.9}$$

We may apply the partial fractions as

$$\frac{1}{\left(s^2+s+0.125\right)s}=\frac{A}{s}+\frac{B}{s^2+s+0.125}. \tag{E.2.24.10}$$

It should be noticed that the second term has a polynomial at the denominator and its numerator is also a polynomial such that
(power of the numerator) = (power of the denominator) – 1.
Equation E.2.24.10 requires

$$A(s^2 + s + 0.125) + (Bs + C)s = 1. \tag{E.2.24.11}$$

Equation E.2.24.11 may be rearranged as

$$(A + B)s^2 + (A + C)s + 0.125A = 1. \tag{E.2.24.12}$$

Coefficients of the equal powers of s should be the same on both sides of Equation E.2.24.12, therefore

$$A = 8, \tag{E.2.24.13}$$

$$A + C = 0, \tag{E.2.24.14}$$

and

$$A + B = 0. \tag{E.2.24.15}$$

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Equations E.2.24.13 through E.2.24.15 requires $B = -8$ and $C = -8$, then Equation E.2.24.9 may be rewritten as

$$x(s) = 8\left\{\frac{1}{s}\frac{s+1}{s^2+s+0.125}\right\}. \tag{E.2.24.15}$$

We should transform Equation E.2.23.15 into the time domain to obtain the solution to the problem:

$$\mathcal{L}^{1}\left\{\frac{1}{s}\right\} = 1. \tag{E.2.24.16}$$

We may apply the Heaviside's expansion theorem (Table 2.19) to obtain the back transform of the second term:

$$\mathcal{L}^{-1}\left\{\frac{P(s)}{Q(s)}\right\} = \sum_{m=1}^{\infty}\frac{P(s_m)}{Q^{\bullet}(s_m)}\exp\{s_m t\}, \tag{E.2.24.17}$$

$$P(s) = s + 1, \tag{E.2.24.18}$$

$$Q(s) = s^2 + s + 0.125, \tag{E.2.24.19}$$

$$Q'(s) = 2s + 1.$$

The roots of $Q(s) = s^2 + s + 0.125 = 0$ are $s_{1,2} = -1 \pm \sqrt{1-(4)(1)(0.125)}/(2)(1)$, therefore, $s_1 = -0.854$ and $s_2 = -0.146$:

$$\mathcal{L}^{-1}\left\{\frac{P(s)}{Q(s)}\right\} = \sum_{m=1}^{\infty}\frac{P(s_m)}{Q^{\bullet}(s_m)}\exp\{s_m t\} = \frac{s_1+1}{2s_1+1}\exp(s_1 t) + \frac{s_2+1}{2s_2+1}\exp(s_2 t)$$

$$= -0.206\exp(-0.854t) + 1.206\exp(-0.146t). \tag{E.2.24.20}$$

Example 2.25 : Diffusion of Salt Into Semi-Hard White Cheese

In Example 2.13 diffusion of salt into semi-hard white cheese was described with the following partial differential equation boundary and initial conditions:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}$$

BC1: $c = c_1$ at $x = 0$ when $t > 0$
BC2: $c = c_0 = 0$ at $x \to \infty$ when $t > 0$
IC: $c = c_0 = 0$ at $x > 0$ when $t = 0$.

We used the method of a combination of variables to solve this problem. The Laplace transformations may also be used to obtain the solution. The transform of each term into the Laplace domain is

$$\mathcal{L}\left\{\frac{d^2 c}{dx^2}\right\} = D\frac{d^2 c(s)}{dx^2},$$

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$$\frac{d^2c(s)}{dx^2} = sc(s) - c_0,$$

and that of the partial differential equation is

$$D\frac{d^2c(s)}{dx^2} = sc(s) - c_0,$$

and may be rearranged as

$$\frac{d^2c(s)}{dx^2} - \frac{s}{D}c(s) - \frac{c_0}{D} = 0.$$

The boundary conditions are transformed into the Laplace domain as

BC1: $c(s) = c_1/s$ at $x = 0$
BC2: $c(s) = c_0/s$ at x .

This is a second order nonhomogeneous ordinary differential equation with constant coefficients. Its solution may be obtained by using Table 2.6 as

$$c(s) = K_1\exp\left(-\sqrt{s/D}x\right) + K_2\exp\left(\sqrt{s/D}x\right) + \frac{c_0}{s}.$$

BC2 requires $c(s)$ = finite at $x \to \infty$, but $\exp\left(-\sqrt{s/D}x\right) \to \infty$, therefore $K_2 = 0$. We may use the may BC1 to evaluate $K_1 = (c_1 - c_0)/s$, then the solution is

$$c(s) = \frac{c_1 - c_0}{s}\exp\left\{-\sqrt{sD}x\right\} + \frac{c_0}{s}.$$

We may use Table 2.19 to make back transformations as

$$\mathcal{L}^{-1}\left\{\frac{c_0}{s}\right\} = c_0,$$

and

$$\mathcal{L}^{-1}\left\{\frac{1}{s}\exp\left\{-\sqrt{sD}x\right\}\right\} = erfc\left(\frac{x}{2\sqrt{Dt}}\right).$$

The back transformation of the solution is

$$c(t) = (c_1 - c_0)erfc\left(\frac{x}{2\sqrt{Dt}}\right) + c_0,$$

upon rearrangement we obtain

$$\frac{c_1 - c}{c_1 - c_0} = erfc\left(\frac{x}{2\sqrt{Dt}}\right).$$

This is the same solution as we obtained in Example 2.13.

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Example 2.26: Temperature Profiles in a Steak During Frying

In Example 2.8, a steak was dipped into vegetable oil for frying, where heat transfer was simulated with the following partial differential equation, BCs, and the IC:

$$\frac{\partial^2 T}{\partial z^2} - \frac{1}{\alpha}\frac{\partial T}{\partial t} = 0$$

BC1: $T = T_1$ at $z = -L$ when $t > 0$ ($2L$ = thickness of the steak)
BC2: $T = T_1$ at $z = L$ when $t > 0$
BC3: $dT/dz = 0$ at $z = 0$ when $t > 0$
BC4: $T = T_1$ for all z when $t \to \infty$
IC: $T = T_0$ when $t = 0$ for all z.

We may transform the partial differential equation and the BCs into Laplace domain:

$$\frac{d^2 T(s)}{dz^2} - \frac{s}{\alpha}T(s) + \frac{T_0}{\alpha} = 0$$

BC1: $T(s) = T_1/s$ at $z = -L$
BC2: $T(s) = T_1/s$ at $z = L$
BC3: $dT(s)/dz = 0$ at $z = 0$.

The solution of the ordinary differential equation may be obtained by using Table 2.6:

$$T(s) = K_1 \exp\left(\sqrt{\frac{s}{\alpha}}z\right) + K_2 \exp\left(-\sqrt{\frac{s}{\alpha}}z\right) + \frac{T_0}{s}.$$

After using BCs 2 and 3 we will find

$$K_1 = K_2 = \frac{(T_1 - T_0)/s}{\exp\left(\sqrt{\frac{s}{\alpha}}L\right) + \exp\left(-\sqrt{\frac{s}{\alpha}}L\right)},$$

then the solution will be

$$T(s) = \frac{T_1 - T_0}{s}\frac{\exp\left(\sqrt{\frac{s}{\alpha}}z\right) + \exp\left(-\sqrt{\frac{s}{\alpha}}z\right)}{\exp\left(\sqrt{\frac{s}{\alpha}}L\right) + \exp\left(-\sqrt{\frac{s}{\alpha}}L\right)} + \frac{T_0}{s}.$$

After using the identity $\cosh(u) = (e^u + e^{-u})/2$ we will obtain

$$T(s) = \frac{T_1 - T_0}{s}\frac{\cosh\left(\sqrt{\frac{s}{\alpha}}z\right)}{\cosh\left(\sqrt{\frac{s}{\alpha}}L\right)} + \frac{T_0}{s}.$$

We may use Heaviside's Theorem 1 (Table 2.17) to obtain the back transform:

$$\mathcal{L}^{-1}\left\{\frac{P(s)}{Q(s)}\right\} = \sum_{m=1}^{\infty}\frac{P(s_m)}{Q^{\bullet}(s_m)}\exp\{s_m t\}.$$

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We may also use the identity $\cosh(u) = \cos(iu)$, then we will have

$$P(s) = \cosh\left(\sqrt{\frac{s}{\alpha}}z\right) = \cos\left(i\sqrt{\frac{s}{\alpha}}z\right),$$

$$Q(s) = s\cosh\left(\sqrt{\frac{s}{\alpha}}L\right) = s\cos\left(i\sqrt{\frac{s}{\alpha}}L\right),$$

$Q(s) = 0$ when $s_{m1} = 0$ and $s_{m2} = -\left(n+\frac{1}{2}\right)^2\left(\frac{\pi}{L}\right)^2\alpha$,

$$\begin{aligned} Q^{\bullet}(s) &= \cosh\left(\sqrt{\frac{s}{\alpha}}L\right) + \frac{1}{2}\left(\sqrt{\frac{s}{\alpha}}L\right)\sinh\left(\sqrt{\frac{s}{\alpha}}L\right) \\ &= \cos\left(i\sqrt{\frac{s}{\alpha}}L\right) + \frac{1}{2}\sqrt{\frac{s}{\alpha}}L\sin\left(i\sqrt{\frac{s}{\alpha}}L\right)\sum_{m=1}^{\infty}\frac{P(s_m)}{Q^{\bullet}(s_m)}\exp\{s_m t\} = \frac{\cos(0)}{\cos(0)+0} = \exp(0) \\ &\quad + \sum_{n=0}^{\infty}(-1)^n\frac{\cos\left[-\left(n+\frac{1}{2}\right)\pi\frac{z}{L}\right]}{\cos\left[-\left(n+\frac{1}{2}\right)\pi\right] + \frac{1}{2}\left(n+\frac{1}{2}\right)\pi\sin\left[-\left(n+\frac{1}{2}\right)\pi\right]}\exp\left\{-\left(n+\frac{1}{2}\right)^2\left(\frac{\pi}{L}\right)^2\alpha t\right\} \end{aligned}$$

after substituting $\cos(-\beta) = \cos(\beta)$, $\sin(-\beta) = -\sin(\beta)$, and $\sin\{[n + (1/2)]\pi\} = (-1)^n$ we will have

$$\begin{aligned} &\sum_{m=1}^{\infty}\frac{P(s_m)}{Q^{\bullet}(s_m)}\exp\{s_m t\} \\ &= 1 - 2\sum_{n=0}^{\infty}(-1)^n\frac{\cos\left[-\left(n+\frac{1}{2}\right)\pi\frac{z}{L}\right]}{\cos\left[-\left(n+\frac{1}{2}\right)\pi\right] + \frac{1}{2}\left(n+\frac{1}{2}\right)\pi\sin\left[-\left(n+\frac{1}{2}\right)\pi\right]}\exp\left\{-\left(n+\frac{1}{2}\right)^2\left(\frac{\pi}{L}\right)^2\alpha t\right\} \end{aligned}$$

We also have $\mathcal{L}^{-1}\{T(s)\} = T$ and $\mathcal{L}^{-1}\{T/s\} = T_0$. After substituting the back transformations we will have

$$\frac{T - T_1}{T_0 - T_1} = 2\sum_{n=0}^{\infty}(-1)^n\frac{\cos\left[\left(n+\frac{1}{2}\right)\pi\frac{z}{L}\right]}{\left(n+\frac{1}{2}\right)\pi}\exp\left\{-\left(n+\frac{1}{2}\right)\pi^2\alpha t/L^2\right\}.$$

This is the same solution as we had in Example 2.8.

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2.14 Numerical Methods in Mathematical Modeling

There are numerous food and bioprocess engineering problems involving ordinary or partial differential equations that may not be solved with the analytical solution techniques. The numerical solution techniques are usually easier than the analytical techniques and may be preferred when computers are available. The analytical solutions are usually represented as continuous functions within the range of the independent variables. A differential equation may be transformed into a numerical form using the differentiation formulas given in Table 2.21. The numerical solutions are presented as an array of numbers with some space between them. There is usually no error involved in the analytical solution techniques, but the numerical methods are subject to inherent error of the preferred technique (Table 2.21).

Numerical differentiation is usually subject to a larger error than numerical integration; therefore, modeling techniques requiring integration are preferred over the ones involving differentiation. There are truncation, roundoff, and propagation errors involved in the

TABLE 2.21

Numerical Differentiation and Integration Formulas and Order of Magnitude of the Involved Error

i) First order differentiation:

		Error
Forward difference	$\frac{df(x)}{dx} = \frac{f(x+h)-f(x)}{h}$	$O(h)$
Central difference	$\frac{df(x)}{dx} = \frac{f(x+h)-f(x-h)}{2h}$	$O(h^2)$
Backward difference	$\frac{df(x)}{dx} = \frac{f(x)-f(x-h)}{h}$	$O(h)$
Four point	$\frac{df(x)}{dx} = \frac{1}{12h}\{f(x-2h)-8f(x-h)+8f(x+h)-f(x+2h)\}$	$O(h^4)$

ii) Second order differentiation:

		Error
Forward difference	$\frac{d^2f(x)}{dx^2} = \frac{f(x+2h)-f(x+h)-f(x)}{h^2}$	$O(h)$
Central difference	$\frac{d^2f(x)}{dx^2} = \frac{f(x+h)-2f(x)+f(x-h)}{h^2}$	$O(h^2)$
Backward difference	$\frac{d^2f(x)}{dx^2} = \frac{f(x)-2f(x-h)+f(x-2h)}{h^2}$	$O(h)$

iii) Integration formulas: $A = \int_{x_0}^{x_n} f(x)dx$

		Error
Trapezoidal rule	$A = \frac{h}{2}[f_0 + 2f_1 + 2f_2 + ... + 2f_{n-1} + f_n]$	$O(h^3)$
	where $f_n = f_0 + nh$	
Simpson's rule	$A = \frac{h}{3}[f_0 + 4f_1 + 2f_2 + 4f_3 + ... + 2f_{n-2} + 4f_{n-1} + f_n]$	$O(h^4)$

Note: You may use MATLAB® function quad for numerical integration with Simpson's rule.

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application of the numerical methods. The truncation error arises when an infinite series expansion of a function is approximated with a limited number of terms. The roundoff error is introduced when the computer rounds the number up or down to predetermined significant figures. The propagation error is caused by the inherent nature of the numerical techniques, where insignificant errors of individual steps of calculation builds up to large amounts.

Ordinary differential equations may be written in canonical form as

$$\frac{dy_1}{dx} = f_1(y_1, y_2, \ldots, y_n, x), \tag{2.97a}$$

$$\frac{dy_2}{dx} = f_1(y_1, y_2, \ldots, y_n, x), \tag{2.97b}$$

$$\frac{dy_n}{dx} = f_n(y_1, y_2, \ldots, y_n, x). \tag{2.97n}$$

With the initial conditions at x_0:

$$y_1(x_0) = y_{1,0}, \tag{2.98a}$$

$$y_2(x_0) = y_{2,0}, \tag{2.98b}$$

$$y_n(x_0) = y_{n,0}. \tag{2.98n}$$

These equations may be solved by the techniques outlined in Table 2.22. Most ordinary differential equations may be converted into canonical forms with appropriate transformations.

TABLE 2.22

Solutions to Ordinary Differential Equations in Canonical Form and Order of Magnitude of the Involved Error

Method	Calculation Procedure	Error
Euler's method	$y_{i+1} = y_i + k_1$	$O(h^2)$
Modified Euler's method	$y_{i+1} = y_i + \frac{1}{2}(k_1 + k_2)$	$O(h^2)$
Second-order Runge–Kutta method	$y_{i+1} = y_i + k_3$	$O(h^2)$
Fourth-order Runge–Kutta method	$y_{i+1} = y_i + \frac{1}{6}(k_1 + 2k_3 + 2k_4 + k_5)$	$O(h^4)$
	where	
	$\frac{dy}{dt} = f(x, y)$	
	$h = x_{i+1} - x_i$	
	$k_1 = hf(x_i, y_i)$	
	$k_2 = hf(x_i + h, y_i + k_1)$	
	$k_3 = hf\left(x_i + \frac{1}{2}h, y_i + \frac{1}{2}k_1\right)$	
	$k_4 = hf\left(x_i + \frac{1}{2}h, y_i + \frac{1}{2}k_3\right)$	
	$k_5 = hf(x_i + h, y_i + k_4)$	

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Example 2.27: Canonical Form of a Third-Order, Nonlinear Heterogeneous Ordinary Differential Equation

Transform the following third-order nonlinear heterogeneous ordinary differential equation into canonical form

$$\frac{d^3z}{dt^3}+3z\frac{d^2z}{dt^2}-7\frac{dz}{dt}+3z=e^{-t}.$$

Solution: We may rewrite this equation as

$$\frac{d^3z}{dt^3}=e^{-t}-3z+7\frac{dz}{dt}-3z\frac{d^2z}{dt^2},$$

then substitute
$y_1=e^{-t}$; therefore, $dy_1/dt=e^{-t}=-y_1$,
$z=y_2$,

$$\frac{dz}{dt}=\frac{dy_2}{dt}=y_3,$$

$$\frac{d^2z}{dt^2}=\frac{dy_3}{dt}=y_4,$$

$$\frac{d^3z}{dt^3}=\frac{dy_4}{dt}.$$

The set of the canonical equations will be

$$\frac{dy_1}{dt}=-y_1,$$

$$\frac{dy_2}{dt}=y_3,$$

$$\frac{dy_3}{dt}=y_4,$$

$$\frac{dy_4}{dt}=y_1-3y_2+7y_3-3y_2y_4.$$

These are an autonomous set of ordinary differential equations. If we know the initial conditions $y_1(t_0)=y_{1,0}$, $y_2(t_0)=y_{2,0}$, $y_3(t_0)=y_{3,0}$, and $y_4(t_0)=y_{4,0}$ we can easily solve them by using the techniques outlined in Table 2.22.

Example 2.28: Drying Behavior of Honey–Starch Mixtures

Two consecutive falling rate periods were observed during the drying of thin films of honey–starch mixture at 70°C. Variation of the moisture contents of these films were simulated after using Equation 2.43f (Yener, Ungan, and Özilgen 1987):

$$\frac{dc}{dt}=\mathcal{K}_c\left(c^*-c\right).$$

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In the first falling rate period, the drying rate constant was $K_c = k_0 c + k_1$, and in the second falling rate period $K_c = k_2$. With 10% honey + 90% starch mixture, the constants were: $k_0 = 17.33$ (h kg moisture/kg dry solids)$^{-1}$, $k_1 = -0.36$ h^{-1}, $k_2 = 0.116$ h^{-1} where other parameters were $c_0 = 0.078$ kg moisture/kg dry solids and $c^* = 0.015$ kg moisture/kg dry solids. The first falling rate prevailed for 4 hours. Constant weight was attained after 30 hours of drying. Calculate the model moisture contents (c) as a function of time with a fourth-order Runge–Kutta method after writing a MATLAB® code. Compare the results with the experimental data $c$data (kg moisture/kg dry solids) and $t$data (h).

Solution: A fourth-order Runge–Kutta method was outlined in Table 2.22 as

$$c_{i+1} = c_i + \frac{1}{6}(k_1 + 2k_3 + 2k_4 + k_5),$$

where

$$k_1 = hf(x_i, y_i),$$

$$k_2 = hf\left(x_i + h, y_i + k_1\right),$$

$$k_3 = hf\left(x_i + \frac{1}{2}h, y_i + \frac{1}{2}k_1\right),$$

$$k_4 = hf\left(x_i + \frac{1}{2}h, y_i + \frac{1}{2}k_3\right),$$

$$k_5 = hf\left(x_i + h, y_i + k_4\right).$$

The first falling rate expression is

$$\frac{dc}{dt} = -17.33c^2 + 0.62c - 5.4 * 10^{-3} \qquad (0\ t\ 4 \text{ hours})$$

The second falling rate is

$$\frac{dc}{dt} = 0.0017 - 0.116c \qquad (4\ t\ 30 \text{ hours})$$

MATLAB® code E.2.28 computes and plots the moisture content as a function of time (Figure E.2.28).

The problem solved in Example 2.28 is called an *initial value problem,* since the solution was propagated starting from the readily available IC. There are also cases where BCs (i.e., the final values of the dependent variable) are available. Such problems are called the *boundary value problems*. A boundary value problem may be converted into an initial value problem by using a *shooting method* as exemplified with the following equations:

$$\frac{dy_1}{dt} = f_1(t, y_1, y_2), \qquad (2.99)$$

$$\frac{dy_2}{dt} = f_2(t, y_1, y_2), \qquad (2.100)$$

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MATLAB® CODE E.2.28

Command Window:

```
clear all
close all
clc

% enter the data
tData=[0 0.17 0.33 0.50 0.67 0.83 1 1.17 1.33 1.50 1.67 1.83 2 3 4 5 6
7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30];

% water content data
cData=[0.078 0.077 0.068 0.062 0.056 0.053 0.050 0.048 0.045 0.044
0.043 0.040 0.039 0.028 0.030 0.028 0.027 0.025 0.024 0.023 0.022
0.021 0.020 0.020 0.019 0.018 0.018 0.018 0.017 0.017 0.017 0.017
0.017 0.017 0.016 0.016 0.016 0.016 0.016 0.016 0.015];

% First falling rate period model
c0 = 0.078;
t0 = 0;
t(1)=0;
k1_0 = -17.33*(c0^2) + 0.62*c0 - 0.0054;
k3_0 = -17.33*(c0 + (1/2)*(k1_0))^2 + 0.62*(c0 + (1/2)*(k1_0))
- 0.0054;
k4_0 = -17.33*(c0 + (1/2)*(k3_0))^2 + 0.62*(c0 + (1/2)*(k3_0))
- 0.0054;
k5_0 = -17.33*(c0 + k4_0)^2 + (c0 + k4_0)*0,62 - 0.0054;
c(1) = c0 + (1/6)*(k1_0+2*k3_0+2*k4_0+k5_0);
for (i=1:3)
    t(i+1)=i;
    k1(i) = -17.33*(c(i)^2) + 0.62*c(i) - 0.0054;
    k3(i) = -17.33*(c(i) + 1/2*(k1(i)))^2 + 0.62*(c(i) +
1/2*(k1(i))) - 0.0054;
    k4(i) = -17.33*(c(i) + 1/2*(k3(i)))^2 + 0.62*(c(i) +
1/2*(k3(i))) - 0.0054;
    k5(i) = -17.33*(c(i) + k4(i))^2 + 0.62*(c(i) + k4(i)) -0.0054;
    c(i+1) = c(i) + (1/6)*(k1(i)+2*k3(i)+2*k4(i)+k5(i));
end

% Second falling rate period model
% c = [c0,c]
%c4=c(5);
% k1_4 = -0.116*c(4) + 0.0017;
% k3_4 = -0.116*(c0 + (1/2)*(k1_4)) + 0.0017;
% k4_4 = -0.116*(c0 + (1/2)*(k3_4)) + 0.0017;
% k5_4 = -0.116*(c0 + k4_0) + 0.0017;
% c(5) = c0 + (1/6)*(k1_4 + 2*k3_4 + 2*k4_4 + k5_4);

for (i=4:29)
    t(i)=i;
    k1(i) = -0.116*c(i) + 0.0017;
    k3(i) = -0.116*(c(i) + 1/2*(k1(i))) + 0.0017;
    k4(i) = -0.116*(c(i) + 1/2*(k3(i))) + 0.0017;
    k5(i) = -0.116*(c(i) + k4(i)) + 0.0017;
    c(i+1) = c(i) + (1/6)*(k1(i)+2*k3(i)+2*k4(i)+k5(i));
end
```

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```
t(i+1)=i+1;
t(i+2)=i+2;
c = [c0,c];
c = c';
plot(t,c,'-'); hold on
plot(tData,cData, '*') ; hold on
xlabel('time (h)');
ylabel('cA');
```

When we run the code Figure E.2.28 will appear on the screen.

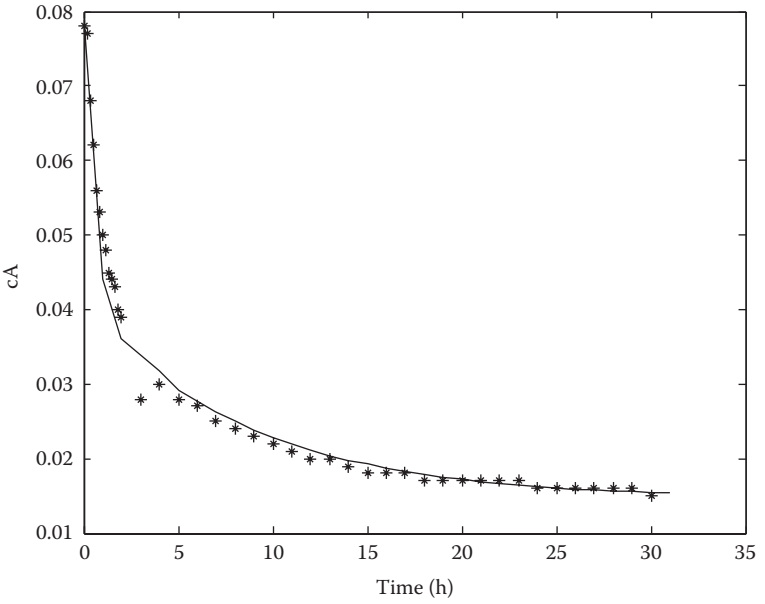


FIGURE E.2.28
Variation of the moisture content of the honey-starch mixture with time. (From Yener, E., Ungan, S., and Özilgen, M., *Journal of Food Science,* 52, 1054–58, 1987.)

with initial (IC) and boundary conditions (BC)

$$\text{IC: } y_1(t_0) = y_{1.0} \tag{2.101}$$

$$\text{BC: } y_2(t_f) = y_{2.f}. \tag{2.102}$$

We guess the initial condition for y_2

$$y_2(t_0) = \gamma. \tag{2.103}$$

Since the value of $y_2(t_0)$ was a guess, the trajectory of y_2 may not satisfy the BC and cause an error $\varepsilon(\gamma)$:

$$\varepsilon(\gamma) = y_2(t_f,\gamma) - y_{2,f}, \tag{2.104}$$

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where $y_2(t_f,\gamma)$ = the calculated value of y_2 at t_f. The desirable objective at the BC was $y_2(t_f,\gamma) = y_{2,f}$. If the error $\varepsilon(\gamma)$ is unacceptable, a new value may be assigned for γ as

$$\gamma_{new} = \gamma_{old} + \Delta\gamma. \tag{2.105}$$

Parameter $\Delta\gamma$ is chosen intuitively. The Newton method may be outlined as

i. The ordinary differential Equations 2.99 and 2.100 are solved with IC Equations 2.101 and 2.103.
ii. Error $\varepsilon(\gamma)$ is calculated by using Equation 2.105.
iii. If $|\varepsilon(\gamma)| > \varepsilon_p$ the correction $\Delta\gamma$ to be applied to γ using Equation 2.105 where ε_p is the predetermined error.
v. Steps i and iii are repeated until

$$\left|\varepsilon(\gamma)\right| \le \varepsilon_p. \tag{2.106}$$

Even when the truncation and roundoff errors are negligible, numerical methods are subject to instabilities arising from the differences between the analytical and the numerical solutions. Any numerical method that has a finite general stability bound is said to be conditionally stable. The solution to the differential equation

$$\frac{dy}{dt} = \lambda y \tag{2.107}$$

with the Euler's method is

$$y_{n+1} = y_n + \Delta h y_n. \tag{2.108}$$

Equation 2.108 may be rearranged as

$$y_{n+1} - (1 + \Delta h)y_n = 0. \tag{2.109}$$

We may assume a trial solution as $y_n = C\mu^n$ and $y_{n+1} = C\mu^{n+1}$, then substitute in Equation 2.109:

$$C\mu^{n+1} - (1 + \lambda h)C\mu^n = 0. \tag{2.110}$$

Equation 2.110 yields that

$$\mu = 1 + \lambda h, \tag{2.111}$$

and the solution is

$$y_n = C(1 + \lambda h)^n. \tag{2.112}$$

As n increases without bound, the solution remains stable if

$$\lim_{n \to \infty} y_n = 0. \tag{2.113}$$

Equation 2.113 may be achieved only when $-2 \le \lambda h \le 0$ and $\lambda < 0$. After following a similar approach, it may be shown that $\mu = (1 - \lambda h)/(1 + \lambda h/2)$ with the modified Euler's method and

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the solution is stable when $\lambda < 0$. We may also show that $\mu = 1 + \lambda h + (1/2)\lambda^2 h^2$ with the second and $\mu = 1 + \lambda h + (1/2)\lambda^2 h^2 + (1/6)\lambda^3 h^3 + (1/24)\lambda^4 h^4$ with the fourth-order Runge-Kutta methods. Therefore the stability boundaries are $-2 \le \lambda h \le 0$ with the second- and $-2,785 \le \lambda h \le 0$ with the fourth-order Runge–Kutta methods. An interested reader may refer to Costantinides and Mostoufi (1999) for details.

The *finite difference method* replaces the derivatives in the differential equations with finite difference approximations (Table 2.21) and converts the differential equation into a large set of simultaneous nonlinear algebraic equations. This method may be demonstrated with the following differential equations:

$$\frac{dy_1}{dt} = f_1(t, y_1, y_2), \tag{2.114}$$

$$\frac{dy_2}{dt} = f_2(t, y_1, y_2), \tag{2.115}$$

$$\text{BC1: } y_1(t_0) = y_{1,0}, \tag{2.116}$$

$$\text{BC2: } y_2(t_f) = y_{2,f}. \tag{2.117}$$

After replacing the derivatives with the forward difference numerical differentiation formula (Table 2.21) we will have

$$y_{1,i+1} - y_{1,i} = h\, f_1(t, y_{1,i}, y_{2,i}), \tag{2.118}$$

$$y_{2,i+1} - y_{2,i} = h\, f_1(t, y_{1,i}, y_{2,i}), \tag{2.119}$$

$$\text{BC1: } y_1(t_0) = y_{1,0}, \tag{2.120}$$

$$\text{BC2: } y_2(t_f) = y_{2,f}. \tag{2.121}$$

The solution interval will be divided into n segments of equal length and resulting equations will be written for $i = 1,2, \ldots, n-1$. They will form a set of $2n$ simultaneous nonlinear algebraic equations in $2n + 2$ variables (there are $n + 1$ variables in each equation, including $y_{1,0}$; $y_{1,n}$; $y_{2,0}$ and $y_{2,n}$). The boundary conditions will provide values for two of these variables $y_1(t_0) = y_{1,0}$ and $y_2(t_f) = y_{2,n}$, then the system of $2n$ equations in $2n$ unknowns will be solved.

In food and bioprocess modeling the finite difference method is very popular especially to solve partial differential equations. Table 2.23 may be used to convert the partial differential equations into the finite difference equations.

Example 2.29: Drying Behavior of an Apple Slice

A $5 \times 4.9 \times 2.0$ cm apple slice was placed in a sample holder and dried in a tunnel drier. Only the top and the bottom faces were exposed to air flow. The variation of the moisture content along the slice may be described with equation of continuity in rectangular coordinates (McCarthy, Perez, and Özilgen 1991):

$$\frac{\partial c}{\partial t} + \left(\frac{\partial N_x}{\partial x} + \frac{\partial N_y}{\partial y} + \frac{\partial N_z}{\partial z} \right) = R. \tag{2.12}$$

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TABLE 2.23

Numerical Partial Differentiation Formulas

i) First order partial derivative:

		Error
Forward difference	$\left[\frac{\partial u}{\partial x}\right]_{i,j,k} = \frac{1}{h}\left(u_{i+1,j,k} - u_{i,j,k}\right)$	$O(h)$
central difference	$\left[\frac{\partial u}{\partial x}\right]_{i,j,k} = \frac{1}{2h}\left(u_{i+1,j,k} - u_{i-1,j,k}\right)$	$O(h^2)$
Backward difference	$\left[\frac{\partial u}{\partial x}\right]_{i,j,k} = \frac{1}{h}\left(u_{i,j,k} - u_{i-1,j,k}\right)$	$O(h)$

ii) Second order partial derivative:

		Error
Forward difference	$\left[\frac{\partial^2 u}{\partial x^2}\right]_{i,j,k} = \frac{1}{h^2}\left(u_{i+2,j,k} - 2u_{i+1,j,k} + u_{i,j,k}\right)$	$O(h)$
Central difference	$\left[\frac{\partial^2 u}{\partial x^2}\right]_{i,j,k} = \frac{1}{h^2}\left(u_{i+1,j,k} - 2u_{i,j,k} + u_{i-1,j,k}\right)$	$O(h^2)$
Backward difference	$\left[\frac{\partial^2 u}{\partial x^2}\right]_{i,j,k} = \frac{1}{h^2}\left(u_{i,j,k} - 2u_{i-1,j,k} + u_{i-2,j,k}\right)$	$O(h)$

iii) Second order mixed partial derivative:

		Error
Forward difference	$\left[\frac{\partial^2 u}{\partial x \partial y}\right]_{i,j,k} = \frac{1}{hk}\left(u_{i+1,j+1,k} - u_{i,j+1,k} - u_{i+1,j,k} + u_{i,j,k}\right)$	$O(h+k)$
Central difference	$\left[\frac{\partial^2 u}{\partial x \partial y}\right]_{i,j,k} = \frac{1}{4hk}\left(u_{i+1,j+1,k} - u_{i-1,j+1,k} - u_{i+1,j-1,k} + u_{i-1,j-1,k}\right)$	$O(h^2+k^2)$
Backward difference	$\left[\frac{\partial^2 u}{\partial x \partial y}\right]_{i,j,k} = \frac{1}{hk}\left(u_{i,j,k} - u_{i,j-1,k} - u_{i-1,j,k} + u_{i-1,j-1,k}\right)$	$O(h+k)$

Since there is no flux in y and z directions and water does not involve into any chemical reactions, Equation 2.12 will be simplified:

$$\frac{\partial c}{\partial t} + \frac{\partial N_x}{\partial x} = 0. \tag{E.2.29.1}$$

Parameter N_x and water flux in x direction were defined as

$$N_x = x_w\left(N_x + N_s\right) - D\frac{dc}{dz}, \tag{2.10}$$

where $N_s = 0$ (flux of the solids) and $x_w = c/c + c_s$ (c_s = solid content of the apple = 0.3284 g solids/cm^3).

Equation E.2.30.1 is rearranged after substituting Equation 2.10 in Equation E.2.29.1:

$$\frac{\partial c}{\partial t} = \frac{D}{c_s}\left[\frac{\partial c}{\partial x}\right]^2 + D\left(\frac{c}{c_s} + 1\right)\frac{\partial^2 c}{\partial c^2}. \tag{E.2.29.2}$$

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The origin of the coordinate system (i.e., $x = 0$) was located on the apple–air interface. The IC and the BCs are

$$\text{IC: } c = c_0 = 0.627 \text{ g/cm}^3 \text{ at } t = 0 \text{ for all } x, \tag{E.2.29.3}$$

$$\text{BC1: } c = c_e \text{ at } t\ 0 \text{ for } x = 0 \tag{E.2.29.4}$$

(c_e = equilibrium moisture content = 0.054 g/cm^3),

$$\text{BC2: } \frac{dc}{dx} = 0 \text{ at } t \geq 0 \text{ for } x = L \tag{E.2.29.5}$$

($2L$ = 5 cm = thickness of the apple slab).

Equation E.2.29.2 was converted into a finite difference equation by using the forward difference formulas:

Partial Derivative	Finite Difference Equivalent
$\partial c/\partial t$	$1/\Delta t(c_{i,j+1} - c_{i,j})$
$\partial c/\partial x$	$1/\Delta x(c_{i+1,j} - c_{i,j})$
$\partial^2 c/\partial x^2$	$1/\Delta x^2(c_{i+1,j} - 2c_{i,j} + c_{i-1,j})$

After substituting the finite difference equivalents, Equation E.2.29.2 becomes (McCarthy, Perez, and Özilgen 1991)

$$\frac{c_{i,j+1} - c_{i,j}}{\Delta t} = \left(\frac{D}{c_s}\right)\frac{c_{i+1,j}^2 - 2c_{i+1,j}c_{i,j} + c_{i,j}^2}{(\Delta x)^2} + D\left(\frac{c_{i,j}}{c_s} + 1\right)\frac{c_{i+1,j} - 2c_{i,j} + c_{i-1,j}}{(\Delta x)^2}. \tag{E.2.29.6}$$

Equation E.2.29.6 may be rearranged as (McCarthy, Perez, and Özilgen 1991)

$$c_{i,j+1} = c_{i,j} + \Delta t\left[\left(\frac{D}{c_s}\right)\frac{c_{i+1,j}^2 - 2c_{i+1,j}c_{i,j} + c_{i,j}^2}{(\Delta x)^2} + D\left(\frac{c_{i,j}}{c_s} + 1\right)\frac{c_{i+1,j} - 2c_{i,j} + c_{i-1,j}}{(\Delta x)^2}\right]. \tag{E.2.29.7}$$

All the parameters on the right-hand side are known when $t = 0$. After assigning a numerical value for D, it will be possible to determine $c_{i,j+1}$. for all i's. The same procedure may be repeated for all j's to simulate the drying process over the entire drying period. MATLAB® code E.2.29 solves the equations and compares the model with the experimental data (Figures E.2.29.1 through E.2.29.3):

Example 2.30: Temperature Profiles Along a Spherical Potato Tuber During Blanching

Calculate the temperature profile along a spherical potato tuber ($\alpha = 0.19\ 10^{-6}$ m^2/s, $k = 0.554$ W/mK, radius = 4.1 cm, $T_0 = 18°C$) 5 and 15 minutes after dipping in blanching water ($T_w = 100°C$) with the convective heat transfer coefficient $h = 70$ W/m^{2}K.

Solution: The equation of energy in the spherical coordinates is

$$\frac{\partial T}{\partial t} + v_r\frac{\partial T}{\partial r} + \frac{v_\theta}{r}\frac{\partial T}{\partial \theta} + \frac{v_\phi}{r\sin\theta}\frac{\partial T}{\partial \phi} = \frac{\dot{\psi}_G}{\rho c} + \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\alpha\frac{\partial T}{\partial r}\right) + \frac{1}{r^2\sin\theta}\frac{\partial}{\partial \theta}\left(\alpha\sin\theta\frac{\partial T}{\partial \theta}\right)$$
$$+ \frac{1}{r^2\sin^2\theta}\frac{\partial}{\partial \phi}\left(\alpha\frac{\partial T}{\partial \phi}\right). \tag{2.18}$$

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MATLAB® CODE E.2.29

Command Window:

```
clear all
close all

% This code may simulate the moisture profiles along the apple slab
180, 570 and 810 minutes after the beginning of the drying process.
% Enter y=1 to obtain the profile at t=180 min
% Enter y=2 to obtain the profile at t=570 min
% Enter y=3 to obtain the profile at t=810 min

y=3

% Enter the moisture content and time data at different times
distanceD(:,1) = [1 4.5 7 10 13.5 17 19.5 22.5 25];
Ce(:,1) = [0.475 0.64 0.629 0.625 0.625 0.625 0.59 0.595 0.620];
distanceD(:,2) = [1 4.5 7 10 13.5 17 19.5 22.5 25];
Ce(:,2) = [0.21 0.55 0.61 0.625 0.630 0.625 0.59 0.595 0.620];
distanceD(:,3) = [1 4.5 7 10 13.5 17 19.5 22.5 25];
Ce(:,3) = [0.25 0.50 0.58 0.59 0.630 0.629 0.59 0.595 0.620];

l=30;                          % length (mm)
t=[180 570 810];               % time (min)

% Define constants
D = 8.3e-11; dx = 0.001; dt = 2; Cs = 0.3284;

% Define boundary conditions and initial condition (BC1, BC2 and IC)
C(1,1) = 0.054; len(1) = 0;
for i = 2:l
    C(1,i) = 0.627;
    distance(i) = i-1;
end

% Solve with finite difference method
for j = 2:(t(y)*60/dt)
    C(j,l) = 0.627;
    C(j,1) = 0.054;
    for i = 2:l-1
        C(j,i) = C(j-1,i)+dt*((D/Cs)*((C(j-1,i+1)^2-2*C(j-
1,i+1)*C(j-1,i)+C(j-1,i)^2)/(dx^2))+(D*((C(j-1,i)/Cs)+1)*(C(j-
1,i+1)-2*C(j-1,i)+C(j-1,i-1))/(dx^2)));
    end
end

% Plot the results
figure; hold on;
ylabel('Water Content (g/cm3)');
xlabel('Distance from The Interface (mm)');
plot(distanceD(:,y), Ce(:,y), '*');
plot(distance, C(j,:));
```

When we run the code after entering y = 1, y = 2, and y = 3 we will obtain Figures E.2.29.1, E.2.29.2, and E.2.29.3, respectively.

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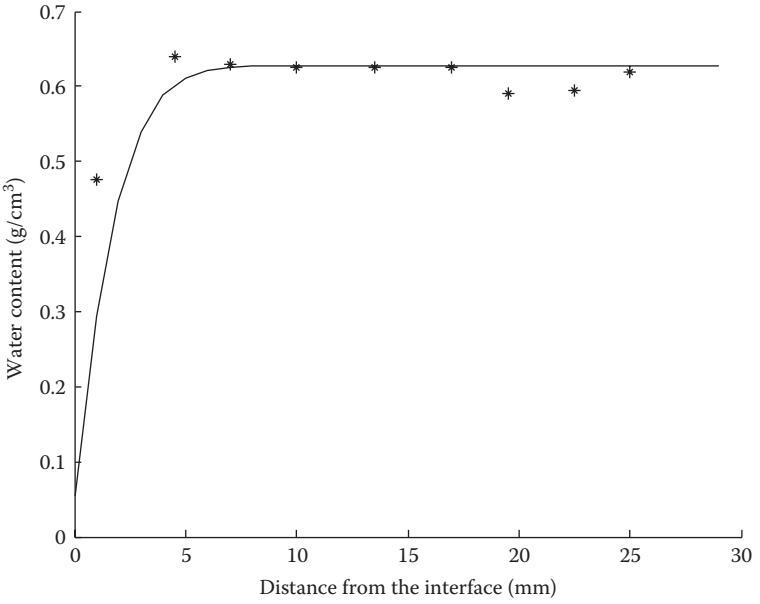


FIGURE E.2.29.1
Moisture profile along the apple slab 180 minutes after the beginning of the drying process. (From McCarthy, M. J., Perez, E., and Özilgen, M., *Biotechnology Progress*, 7, 540–43, 1991.)

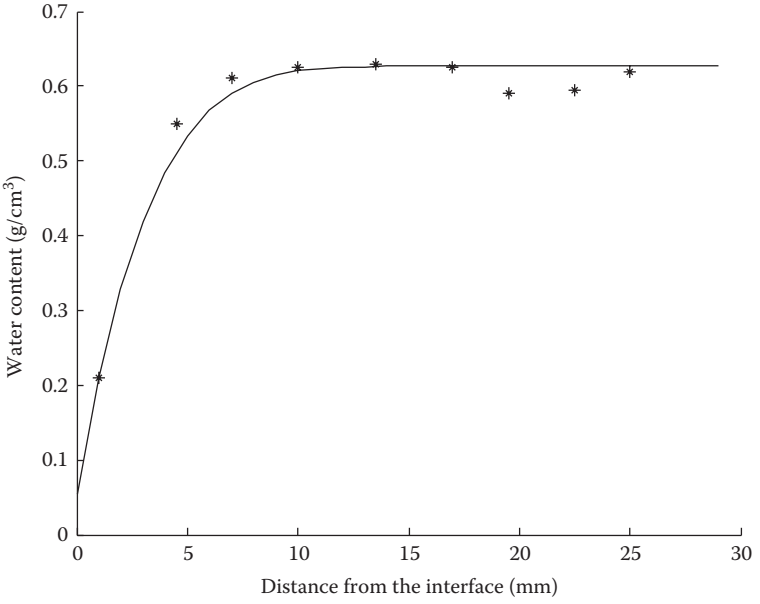


FIGURE E.2.29.2
Moisture profile along the apple slab 570 minutes after the beginning of the drying process. (From McCarthy, M. J., Perez, E., and Özilgen, M., *Biotechnology Progress*, 7, 540–43, 1991.)

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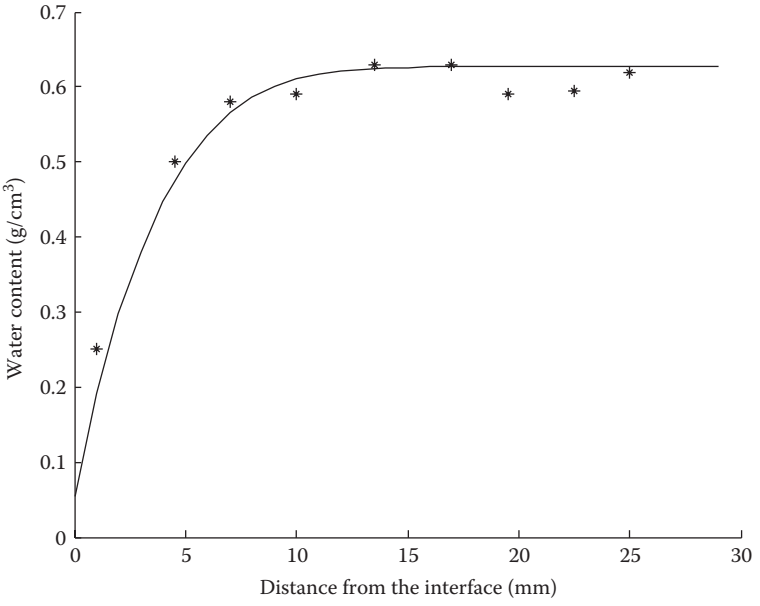


FIGURE E.2.29.3
Moisture profile along the apple slab 810 minutes after the beginning of the drying process. (From McCarthy, M. J., Perez, E., and Özilgen, M., *Biotechnology Progress*, 7, 540–43, 1991.)

When $v_r = v_\theta = v_\phi = \psi_G = \partial T/d\theta = dT/d\phi = 0$, Equation 2.18 becomes

$$\frac{\partial T}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(r^2\alpha\frac{\partial T}{\partial r}\right). \tag{E.2.30.1}$$

When α = constant, Equation E.2.30.1 may be rearranged as

$$\frac{\partial^2 T}{\partial r^2} + \frac{2}{r}\frac{\partial T}{\partial r} = \frac{1}{\alpha}\frac{\partial T}{\partial t} \tag{E.2.30.2}$$

with

$$\text{IC: } T(r,0) = T_0, \tag{E.2.30.3}$$

$$\text{BC1: } \frac{dT}{dr} = 0 \text{ at } r = 0, \tag{E.2.30.4}$$

$$\text{BC2: } -k\frac{dT}{dr} = h\left(T_R - T_w\right. \text{ at } r = R, \tag{E.2.30.5}$$

where R = radius of the sphere, k = thermal conductivity of the food, h = convective heat transfer coefficient, and T_w = blanching water temperature. Each term in Equation E.2.30.1 is converted into a finite difference notation:

Partial Derivative	Finite Difference Equivalent	
$\partial^2 T/\partial r^2$	$1/\Delta r^2(T_{i+1,j} - 2T_{i,j} + T_{i-1,j})$	central difference
$\partial T/\partial r$	$1/2\Delta r(T_{i+1,j} - T_{i-1,j})$	central difference
$\partial T/\partial t$	$1/\Delta t(T_{i,j+1} - T_{i,j})$	forward difference

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After substituting the finite difference equivalents, Equation E.2.30.1 becomes

$$\frac{1}{\Delta r^2}\left(T_{i+1,j}-2T_{i.j}+T_{i-1,j}\right)+\frac{1}{(i-1)\Delta r^2}\left(T_{i+1,j}-T_{i-1,j}\right)=\frac{1}{\alpha}\frac{1}{\Delta t}\left(T_{i,j+1}-T_{i,j}\right). \tag{E.2.30.6}$$

Since $i = 1$ is the center and at $i = 2$ we have $r = \Delta r$, substitution of the form $r = (i - 1)\Delta r$ was made in the second term. We may rearrange Equation E.2.30.6 as

$$T_{i,j+1}=\frac{\alpha\Delta t}{\Delta r^2}\left[\left(\frac{i-2}{i-1}\right)T_{i-1,j}+\left(\frac{\Delta r^2}{\alpha\Delta t}-2\right)T_{i.j}+\left(\frac{i}{i-1}\right)T_{i+1,j}\right], \tag{E.2.30.7}$$

where $2 \le i \le n - 1$ (n = number of the nodes along the radial direction, $i = 1$ is the center, and $i = n$ is the surface). Equation E.2.30.7 represents all the inner points of the sphere with the exception of the center where $(2/r)(\partial T/\partial r)$ is not defined. We may use the L'Hopital's rule on the second term:

$$\lim_{r\to\infty}\left(\frac{2}{r}\frac{\partial T}{\partial r}\right)=\lim_{r\to\infty}\left\{2\frac{\partial}{\partial r}\left(\frac{\partial T}{\partial r}\right)/\frac{\partial}{\partial r}(r)\right\}=\left[\frac{\partial^2 T}{\partial r^2}\right]_{r=0}. \tag{E.2.30.8}$$

Therefore at $r = 0$, Equation E.2.30.2 should be expressed as

$$3\frac{\partial^2 T}{\partial r^2}=\frac{1}{\alpha}\frac{\partial T}{\partial t}. \tag{E.2.30.9}$$

The finite difference equivalent of Equation E.2.30.9 is

$$\frac{3}{\Delta r^2}\left(T_{2,j}-2T_{1.j}+T_{0,j}\right)=\frac{1}{\alpha\Delta t}\left(T_{1,j+1}-T_{1,j}\right), \tag{E.2.30.10}$$

which may be rearranged as

$$T_{1,j+1}=T_{1,j}+\frac{3\alpha\Delta t}{\Delta r^2}\left(T_{2,j}-2T_{1.j}+T_{0,j}\right). \tag{E.2.30.11}$$

The $T_{1,j}$ is the center temperature, but $i = 0$ is not defined, therefore, the $T_{0,j}$ of Equation E.2.30.11 is a fictitious temperature. We may express Equation E.2.30.4 in the finite difference form as

$$\frac{1}{2\Delta r}\left(T_{2,j}-T_{0,j}\right)=0, \tag{E.2.30.12}$$

which indicates $T_{0,j} = T_{2,j}$, then Equation E.2.30.11 becomes

$$T_{n,j+1}=\left\{1-\frac{6\alpha\Delta t}{\Delta r^2}\right\}T_{1,j}+\frac{6\alpha\Delta t}{\Delta r^2}T_{2,j}. \tag{E.2.30.13}$$

The surface boundary condition may be approximated with a backward difference:

$$-\frac{k}{\Delta r}\left(T_{n,j+1}-T_{n-1,j+1}\right)=h\left(T_{n,j+1}-T_W\right), \tag{E.2.30.14}$$

which may be rearranged as

$$T_{n,j+1}=-\frac{1}{1+(h/k)\Delta r}\left\{T_{n-1,j}+\frac{h\Delta r}{k}T_W\right\}. \tag{E.2.30.15}$$

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Equations E.2.30.7, E.2.30.13, and E.2.30.15 represent the temperature variation with time at the selected nodes in radial direction. We will choose eight nodes ($n = 8$) along the radial direction to calculate the temperature, therefore

$$2 \le i \le 7$$

and

$$\Delta r = \frac{R}{8} = \frac{0.041}{7} = 0.005857 \text{ m}.$$

The most restrictive stability criterion is associated with the surface equation (Incropera et al. 2007):

$$Fo(1 + Bi) \le \frac{1}{2}. \tag{E.2.30.16}$$

After substituting $\text{Bi} = h\Delta r/k = 0.74$ in Equation E.2.30.16 we will obtain $\text{Fo} \le 0.287$, since $\text{Fo} = (\alpha \Delta t/\Delta r^2)$ we should have $\Delta t \le 51.88\ s$ and choose $\Delta t = 50\ s$.

After substituting numbers in Equations E.2.30.7, E.2.30.13, and E.2.30.15:

$$T_1^{j+1} = -0.6616T_1^j + 1.6616T_2^j, \tag{E.2.30.17a}$$

$$T_2^{j+1} = 0.4461T_2^j + 0.5539T_3^j, \tag{E.2.30.17b}$$

$$T_3^{j+1} = 0.1385T_2^j + 0.4461T_3^j + 0.4154T_4^j, \tag{E.2.30.17c}$$

$$T_4^{j+1} = 0.1846T_3^j + 0.4461T_4^j + 0.3692T_5^j, \tag{E.2.30.17d}$$

$$T_5^{j+1} = 0.2077T_4^j + 0.4461T_5^j + 0.3462T_6^j, \tag{E.2.30.17e}$$

$$T_6^{j+1} = 0.2215T_5^j + 0.4461T_6^j + 0.3223T_7^j, \tag{E.2.30.17f}$$

$$T_7^{j+1} = 0.2308T_6^j + 0.461T_7^j + 0.3221T_8^j, \tag{E.2.30.17g}$$

$$T_8^{j+1} = 0.5744T_7^j + 158.64. \tag{E.2.30.17h}$$

At $t = 0$ $T_1^1 = T_2^1 = T_3^1 = T_4^1 = T_5^1 = T_6^1 = T_7^1 = T_8^1 = 291\text{K}$. After substituting them in Equation E.2.30.17 we can easily calculate, $T_1^2,\ T_2^2,\ T_3^2,\ T_4^2,\ T_5^2,\ T_6^2,\ T_7^2$ and T_8^2, the same procedure may be repeated to calculate the temperature at the same nodes at different times. A spreadsheet program may be used to do the calculations. The first column of the program may contain the initial temperatures $T_1^1,\ T_2^1,\ T_3^1,\ T_4^1,\ T_5^1,\ T_6^1,\ T_7^1$, and T_8^1, the second column may be calculated using Equation E.2.30.17 and the first column. Calculations may be propagated columnwise until covering the required heating period:

	A	B	C	D	E	F	G	H
1	291	291	291					
2	291	291	291					
3	291	291	291					
4	291	291	291					
5	291	291	291					
6	291	291	291					
7	291	291	302.3					
8	291	325.9	325.9					

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Cells from A_1 to A_8 should contain the initial temperatures at each node (i.e., $A_1 = A_2 = \ldots = A_8 = 291$ K), thus

$$B_1 = -0.6616A_1 + 1.6616A_2 = 291 \text{ K}$$
$$B_2 = 0.4461A_2 + 0.5539A_3 = 291 \text{ K}$$
$$B_3 = 0.1385A_2 + 0.4461A_4 + 0.4154A_4 = 291 \text{ K}$$
$$B_4 = 0.1846A_3 + 0.4461A_4 + 0.3692A_5 = 291 \text{ K}$$
$$B_5 = 0.2077A_4 + 0.4461A_5 + 0.3462A_6 = 291 \text{ K}$$
$$B_6 = 0.2215A_5 + 0.4461A_6 + 0.3323A_7 = 291 \text{ K}$$
$$B_7 = 0.2308A_6 + 0.4461A_7 + 0.3221A_8 = 291 \text{ K}$$
$$B_8 = 0.5347A_7 + 158.64 = 325.9 \text{ K}$$

$$C_1 = -0.6616B_1 + 1.6616\ B_2 = 291 \text{ K}$$
$$C_2 = 0.4461B_2 + 0.5539\ B_3 = 291 \text{ K}$$
$$C_3 = 0.1385B_2 + 0.4461\ B_3 + 0.4154\ B_4 = 291 \text{ K}$$
$$C_4 = 0.1846B_3 + 0.4461\ B_4 + 0.3692\ B_5 = 291 \text{ K}$$
$$C_5 = 0.2077B_4 + 0.4461\ B_5 + 0.3462\ B_6 = 291 \text{ K}$$
$$C_6 = 0.2215B_5 + 0.4461\ B_6 + 0.3323\ B_7 = 291 \text{ K}$$
$$C_7 = 0.2308B_6 + 0.4461\ B_7 + 0.3221\ B_8 = 302.3 \text{ K}$$
$$C_8 = 0.5347B_7 + 158.64 = 325.9 \text{ K}$$

The remaining cells will be filled with the same procedure:

	$t = 0$	$t = 50$	$t = 100$	$t = 150$	$t = 200$	$t = 250$	$t = 300$	$t = 350$	$t = 400$	$t = 450$
T_1	291	291	291	291	291	291	291	291	291.1	291.5
T_2	291	291	291	291	291	291	291	291.1	291.3	291.9
T_3	291	291	291	291	291	291	291.1	291.6	292.3	293.2
T_4	291	291	291	291	291	291.4	292.2	293.4	294.8	296.5
T_5	291	291	291	291	292.3	294.0	296.1	298.3	300.6	302.9
T_6	291	291	291	294.7	298.0	301.5	304.8	307.9	310.8	313.5
T_7	291	291	302.3	307.3	312.5	316.5	320.1	323.1	325.9	328.4
T_8	291	325.9	325.9	332.4	335.2	338.2	340.5	342.6	344.4	345.9

	$t = 500$	$t = 550$	$t = 600$	$t = 650$	$t = 700$	$t = 750$	$t = 800$	$t = 850$	$t = 900$
T_1	292.1	292.9	294.0	295.3	296.7	298.3	300.0	301.7	303.6
T_2	292.6	293.6	294.8	296.1	296.7	299.3	301.0	302.8	304.7
T_3	294.4	295.7	297.2	298.9	300.6	302.4	304.3	306.2	308.1
T_4	298.2	300.1	302.0	304.0	305.9	307.9	309.9	311.9	313.8
T_5	305.3	307.5	309.8	312.0	314.1	316.1	318.1	320.0	321.9
T_6	316.1	318.5	320.7	322.9	324.9	326.8	328.6	330.3	332.0
T_7	330.6	332.7	334.6	336.3	337.9	339.4	340.9	342.2	343.4
T_8	347.4	348.7	349.8	350.9	351.9	352.8	353.7	354.5	355.3

The same problem may also be easily solved with MATLAB® code E.2.30 and Figure E.2.30.

Example 2.31: Temperature Profiles Along a Spherical Potato Tuber During Thermal Processing in a Can

A cylindrical can ($D = 10$ cm, $L = 15$ cm) is filled with 150 reconstituted spherical potatoes ($r = 1$ cm, $k = 0.554$ W/mK, $\alpha = 0.19\ 10^{-6}$ m²/s) and enough water to fill up the rest ($c_{pw} = 4.2$ kJ/kg K). The can was at an initial temperature of 18°C and placed in a retort operating at constant

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MATLAB® CODE E.2.30

Command Window:

```
clear all
close all

% time (sec) - X50
t = 900;

% Define constants
Tw = 100; n=8;
a = 0.19e-6; k = 0.554; R = 0.041;
h = 70; dt = 50; dr = R / (n-1);

A = a * dt / (dr^2);
B = h * dr / k;

% Initial condition
for i=1:n
    T(i,1) = 291;
    length(i) = i*(R / (n-1)) - R / (n-1);
end

% Solve with finite difference method
for j=1:(t/dt)
    T(1,j+1) = (1 - 6 * A) * T(1,j) + 6 * A * T(2,j);
    for i=2:n-1
        T(i,j+1) = A * (((i-2)/(i-1)) * T(i-1,j) + ((1/A) - 2) *
T(i,j) + (i/(i-1)) * T(i+1,j));
    end
    T(n,j+1) = (1 / (1 +( (h/k)*dr))) * (T(n-1,j) + B * (Tw+273));
end

% Plot the results
figure; hold on;
ylabel('TEMPERATURE (K)');
xlabel('Distance from The Center (mm)');
plot(length, T(:,j));
```

When we run the code Figure E.2.30 will appear on the screen.

temperature at 121°C. The convective heat transfer coefficient between potatoes and water is 50 W/m²K and the overall heat transfer coefficient from retort to can is 1800 W/m²K. Contents of the can are mixed with the effect of natural convection, therefore water may be assumed to have uniform temperature. The governing equation for water temperature is

$$m_w c_{pw} \frac{dT_w}{dt} = U_0 A_c \left(T_s - T_w\right) + h_p A_p \left[T_w - T_p\left(t,R\right)\right], \tag{E.2.31.1}$$

where m_w = mass of water, U_0 = overall heat transfer coefficient from retort to can, A_c = heat transfer area between retort and can, h_p = convective heat transfer coefficient between potatoes and water, A_p = heat transfer area between potatoes and water, and $T_p(t,R)$ = surface temperature of

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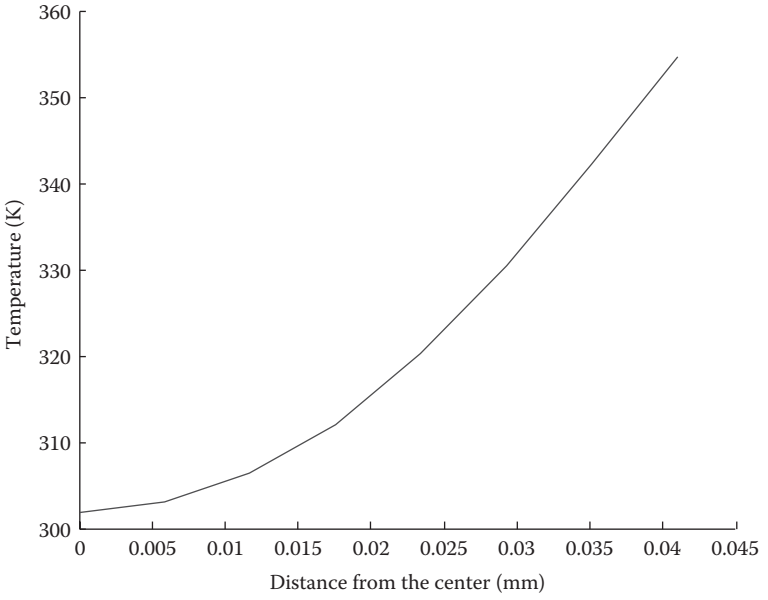


FIGURE E.2.30
Variation of the temperature along the radial direction 900 minutes after the beginning of the heating process.

the potatoes at time *t*. Equation E.2.31.1 may be converted into a finite difference equation after substituting a forward difference formula for the derivative as

$$m_w c_{pw} \frac{T_{w,j+1} - T_{w,j}}{\Delta t} = U_0 A_c \left(T_s - T_w\right) + h_p A_p \left[T_w - T_p\left(t,R\right)\right], \tag{E.2.31.2}$$

which may be solved for the water temperature at the new time:

$$T_{w,j+1} = T_{w,j} + \frac{\Delta t}{m_w c_{pw}} \left\{U_0 A_c \left(T_s - T_w\right) + h_p A_p \left[T_w - T_p\left(t,R\right)\right]\right\}. \tag{E.2.31.3}$$

Equations E.2.30.7, E.2.30.13, and E.2.30.15 are employed to describe the governing equation of heat transfer within the particles with variable T_w. After solving the necessary difference equations, plot variation of the water and the can center temperatures with time. We may calculate the following with the given data:

$$\text{total volume of the potatoes} = V_{\text{potatoes}} = N\frac{4}{3}\pi r^3 = 0.000628\, m^3,$$

$$\text{volume of the can} = \mathrm{V}_{\text{can}} = \pi r^2 L = 0.001178\, \mathrm{m}^3,$$

$$\text{volume water in the can} = \mathrm{V}_{\text{water}} = \mathrm{V}_{\text{can}} - \mathrm{V}_{\text{potatoes}} = 0.00055\, m^3,$$

$$\text{mass of water in the can} = \mathrm{m}_{\text{water}} = \rho_{\text{water}} \mathrm{V}_{\text{water}} = 0.55\, \mathrm{kg},$$

$$\text{heat transfer area between retort and the can} = A_c = 2\pi R^2 + 2\pi RL = 0.063\ \mathrm{m}^3,$$

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and

$$\text{heat transfer area between potatoes and water} = A_p = \text{N}4\pi R^2 = 0.1885 \text{ m}^2.$$

We will choose $n = 11$ (number of nodes along the potato); therefore, the internal nodes of the potato will be denoted by subscript i when $2 \le i \le 10$. With $\Delta r = 0.001$ cm the Biot number is

$$\text{Bi} = \frac{h\Delta r}{k} = 0.090. \tag{E.2.31.4}$$

The stability criterion is (Incropera et al. 2007)

$$\text{Fo}(1+\text{Bi}) \le \frac{1}{2}. \tag{E.2.31.5}$$

After substituting Bi = 0.090 in Equation E.2.31.5 we will obtain Fo ≤ 0.459, since Fo = $(\alpha\Delta t/\Delta r)^2$ we should have $\Delta t \le 2.4$ *s* and choose $\Delta t = 2$ *s*.

After substituting numbers in Equations E.2.30.7, E.2.30.13, and E.2.30.15:

$$T_1^{j+1} = -0.28T_1^j + 1.28T_2^j, \tag{E.2.31.6a}$$

$$T_2^{j+1} = 0.24T_2^j + 0.76T_3^j, \tag{E.2.31.6b}$$

$$T_3^{j+1} = 0.19T_2^j + 0.24T_3^j + 0.57T_4^j, \tag{E.2.31.6c}$$

$$T_4^{j+1} = 0.2533T_3^j + 0.24T_4^j + 0.5067T_5^j, \tag{E.2.31.6d}$$

$$T_5^{j+1} = 0.285T_4^j + 0.24T_5^j + 0.475T_6^j, \tag{E.2.31.6e}$$

$$T_6^{j+1} = 0.304T_5^j + 0.24T_6^j + 0.456T_7^j, \tag{E.2.31.6f}$$

$$T_7^{j+1} = 0.3167T_6^j + 0.24T_7^j + 0.4433T_8^j, \tag{E.2.31.6g}$$

$$T_8^{j+1} = 0.3257T_7^j + 0.24T_8^j + 0.4343T_9^j, \tag{E.2.31.6h}$$

$$T_9^{j+1} = 0.3325T_8^j + 0.24T_9^j + 0.4275T_{10}^j, \tag{E.2.31.6i}$$

$$T_{10}^{j+1} = 0.3378T_9^j + 0.24T_{10}^j + 0.4222T_{11}^j, \tag{E.2.31.6j}$$

$$T_{11}^{j+1} = 0.9172T_{10}^j + 0.0828T_w^j. \tag{E.2.31.6k}$$

After substituting numbers in Equation E.2.32.3:

$$T_w^{j+1} = 0.91T_w - 0.0082T_{11}^j + 38.58, \tag{E.2.31.6l}$$

where $T_{11} = T(t,R)$ = surface temperature of the reconstituted potatoes. Equations 2.31.6a through l are solved with MATLAB® code E.2.31 (see Figure E.2.31).

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MATLAB® CODE E.2.31

Command Window:

```
clear all
close all
clc

% enter the initial temperature
T1_0 = 291;  T2_0 = 291;
T3_0 = 291;  T4_0 = 291;
T5_0 = 291;  T6_0 = 291;
T7_0 = 291;  T8_0 = 291;
T9_0 = 291;  T10_0 = 291;
T11_0 = 291; Tw_0 = 291;
Ts=273+121;
Tw_control = 273+18;

% enter equations [E.2.31.6.a] - [E.2.31.6.m]
Tw(1) = 0.91*Tw_0 - 0.0082*T11_0 + 38.58;
T11(1)=0.9172*T10_0 + 0.0828*Tw_0;
T10(1)=0.3378*T9_0 + 0.24*T10_0 + 0.4222*T11_0;
T9(1)=0.3325*T8_0 + 0.24*T9_0 + 0.4275*T10_0;
T8(1)=0.3257*T7_0 + 0.24*T8_0 +0.4343*T9_0;
T7(1)=0.3167*T6_0 + 0.24*T7_0 +0.4433*T8_0;
T6(1)=0.304*T5_0 + 0.24*T6_0 +0.456*T7_0;
T5(1)=0.285*T4_0 + 0.24*T5_0 +0.475*T6_0;
T4(1)=0.2533*T3_0 + 0.24*T4_0 +0.5067*T5_0;
T3(1)=0.19*T2_0 + 0.24*T3_0 +0.57*T4_0;
T2(1)=0.24*T2_0 +0.76*T3_0;
T1(1)=-0.28*T1_0 +1.28*T2_0;
i=2;

%while(Tw_control<=Ts)
for(i=2:100)
    Tw(i) = 0.91*Tw(i-1) - 0.0082*T11(i-1) + 38.58;
    T11(i) = 0.9172*T10(i-1) + 0.0828*Tw(i-1);
    T10(i) = 0.3378*T9(i-1) + 0.24*T10(i-1) + 0.4222*T11(i-1);
    T9(i) = 0.3325*T8(i-1) + 0.24*T9(i-1) + 0.4275*T10(i-1);
    T8(i) = 0.3257*T7(i-1) + 0.24*T8(i-1) + 0.4343*T9(i-1);
    T7(i) = 0.3167*T6(i-1) + 0.24*T7(i-1) + 0.4433*T8(i-1);
    T6(i) = 0.304*T5(i-1) + 0.24*T6(i-1) + 0.456*T7(i-1);
    T5(i) = 0.285*T4(i-1) + 0.24*T5(i-1) + 0.475*T6(i-1);
    T4(i) = 0.2533*T3(i-1) + 0.24*T4(i-1) + 0.5067*T5(i-1);
    T3(i) = 0.19*T2(i-1) + 0.24*T3(i-1) + 0.57*T4(i-1);
    T2(i) = 0.24*T2(i-1) + 0.76*T3(i-1);
    T1(i) = -0.28*T1(i-1) + 1.28*T2(i-1);
    Tw_control = Tw(i);
    i=i+1;
end
Tw=[Tw_0,Tw]' ;
T1=[T1_0,T1]' ;

 % plot the water temperature and the temperature at the center of
the potato
plot(0:2:200,Tw, ':')
```

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```
hold on
plot (0:2:200,T1,'-')
xlabel('time (s)')
ylabel[{fix spelling here? temperature}]('temprature (K)')
```

When we run the code Figure E.2.31 will appear on the screen.

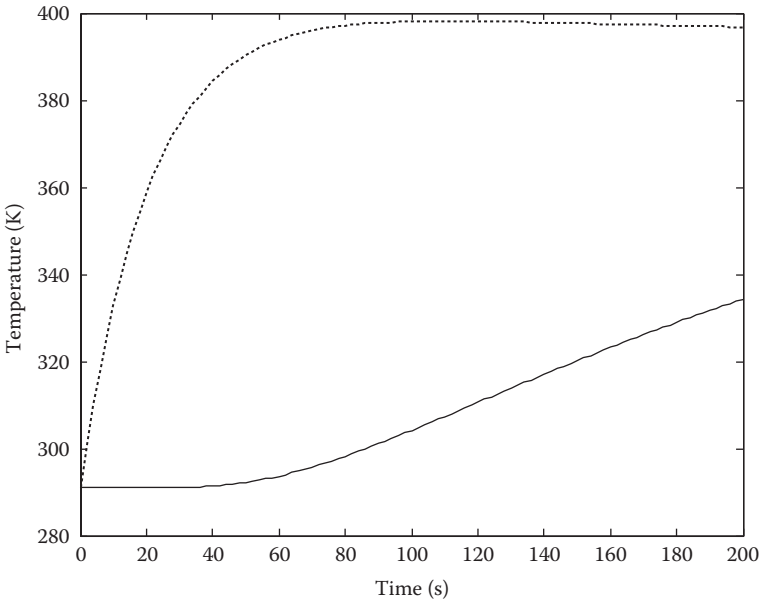


FIGURE E.2.31
Variation of the water and the center temperature of the potatoes with time.

Questions for Discussion and Problems

1. Explain the meaning and significance of each term in

$$N_A = x_A(N_A + N_B) - D_{AB}\frac{dc_A}{dz}$$

In the following experiment, under what conditions may you neglect any of its terms.
EXPERIMENT: An injection port and two sensors are placed on a pipe as shown in the following figure:

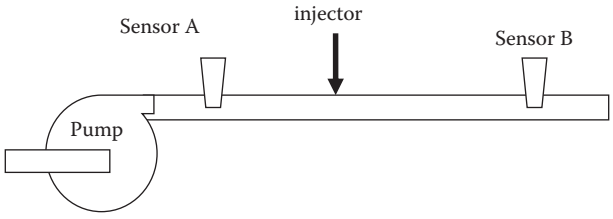


FIGURE Q.2.1
Experimental set-up.

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i. When the pipe is filled with water and *pump is not running*, NaCl is injected at time $t = 0$ into the pipe at room temperature. Explain:
   a. Can you detect salt in sensors A and B? If your answer is YES explain your reasoning of why and how the ions travel from the injector to the sensors.
   b. If you should increase the temperature to 70°C will you detect NaCl at point B faster than that of case **(a)** or not? Explain your reasoning.
   c. If you should decrease the temperature to 1°C, will you detect NaCl faster or slower than that of cases **(a)** and **(b)**? Explain your reasoning.
   d. If you should freeze the system at –20°C, how will it affect the time you detect the salt at the site of the sensors?

ii. When you repeat the experiment with the *pump running*:
   a. Can you detect salt at the location of the sensors A and B? Explain your reasoning of why and how the ions travel from the injector to the sensors.
   b. What is different in the mechanism of the movement of the ions in the cases (i) and (ii)?

2. Suggest differential equations with their ICs and BCs (do not solve, but explain your reasoning) for the following problems:
   i. A spherical potato tuber dipped in boiling water for 2 minutes; salt diffuses from water to potato (you may assume constant temperature through the tuber).
   ii. A spherical potato tuber dipped in boiling water; ascorbic acid diffuses from potato to water and undergoes first-order degradation reaction (you may assume constant temperature through the tuber).
   iii. A slice of carrot ($r = 1.5$ cm, $h = 1$ cm) dipped in boiling water for 5 minutes, a nutrient diffuses out and undergoes first-order degradation reaction (you may assume constant temperature through the slice).
   iv. A cucumber ($h = 15$ cm, $r = 1$ cm) is dipped in brine, salt diffuses in.
   v. The same cucumber is sliced, each slice has 1 cm of thickness ($r = 1$ cm).
   vi. A single spherical hazelnut is suspended in a tunnel drier for 3 minutes; water diffuses through the hazelnut to reach the surface. Air flow rate is high enough to neglect the external mass transfer resistance.
   vii. A single spherical hazelnut is suspended in the air. Air flow rate is zero and the external mass transfer resistance is very high (diffusional resistance is negligible inside the hazelnut when compared to the external resistance).
   viii. Hazelnut paste is being dried in a tray (dimensions: $30 \times 70 \times 3$ cm). Only the upper surface of the tray is available for mass transfer. Air flow rate is high and the external mass transfer resistance is negligible.

3. Under what conditions may it be appropriate to use the following models to calculate diffusion coefficients (describe what is diffusing in what and what are the basic assumptions of the model)?
   i. Stokes–Einstein equation
   ii. Eyring's theory
   iii. Film model
   iv. Penetration and surface renewal models
   v. When we discuss diffusion through a solid media we had $D_{eff} = D_{AB}\varepsilon/\tau$. Explain the meaning and significance of each term here.

4. The structure of a porous food is described in the following figure. Concentration of salt is maintained at a constant concentration c_A on the left-hand reservoir, and there is initially no salt in the cell on the right-hand side. Salt will diffuse through the porous structure.

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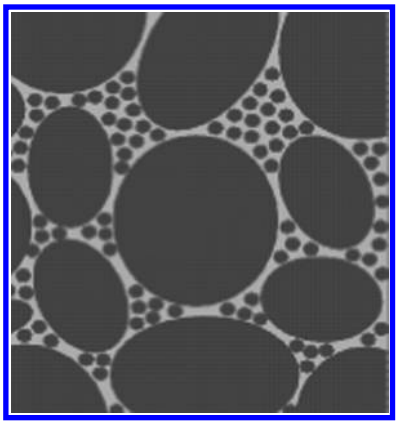


FIGURE Q.2.4.I
Structure of the porous food.

i. Obtain an expression for the concentration profile along the porous structure *at the beginning* of the experiment.
ii. Obtain an expression for the concentration profile along the porous structure a *long time after the beginning* of the experiment.
iii. The porous material is replaced with the one given here; what kind of a change would you expect in the numerical value of the diffusivity? Explain with appropriate equations.

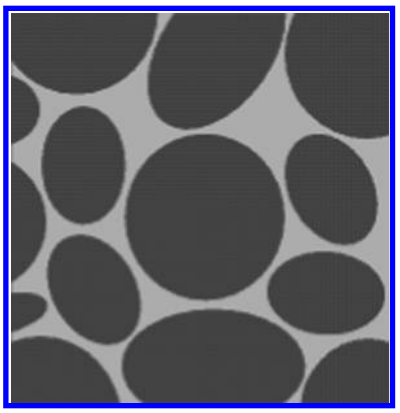


FIGURE Q.2.4.II
Structure of the porous food after replacement.

5. Solve Example 2.6c with

$$T_{\text{wall}} = T_{w0} + aZ + bZ^2.$$

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6. A $10 \times 10 \times 10$ cm cheese block is dipped into a salt solution, concentration profiles of salt along the cheese block has been found to be represented as:

$$\frac{c_1 - c}{c_1 - c_0} = erf\left(\frac{x}{2\sqrt{Dt}}\right).$$

   i. Calculate the salt concentration at 3 mm depth from the surface at the end of the second day after dipping the blocks into brine, when $c_0 = 0$ g salt/cm^3, $c_1 = 2$ g salt/cm^3, and $D = 0.33 \times 10^{-9}$ m^2/s.
   ii. This problem was solved after stating that the solution is valid for short time after putting the blocks into the solution with the BCs and IC:

   BC1: $c = c_1$ at $x = 0$ when $t > 0$
   BC2: $c = c_0 = 0$ as $x \to \infty$ when $t > 0$
   IC: $c = c_0$ at $x > 0$ when $t = 0$

   When you look at these BCs and the IC why do you think that the solution is valid for short times after putting the block into the salt solution? Explain.
7. Solve Example 2.13 to obtain a figure similar to Figure E.2.13 for the concentration profile along the cheese after 5 days of brining.
8. In a continuous plug flow disinfection process a chemical disinfectant is introduced into the plug flow disinfector through the porous walls of the cylindrical pipe and diffuses into the process stream. Disinfectant is provided in large quantities; therefore, its concentration c_w may be regarded as constant at the wall surface. Starting with the equation of change, obtain an appropriate differential equation describing the variation of the disinfectant concentration $c(z)$ along the flow direction.
   i. Solve the differential equation when c_w is constant. Show that the solution confirms the BCs $c = c_0$ at $z = z_0$ and $c \to c_w$ when $z \to \infty$.
   ii. Solve the differential equation when the disinfectant concentration at the wall increases with distance: $c_{\text{wall}} = c_{w0} + \alpha z$ where α is a constant.
9. A cylindrical porous tube is being used as a filter. Its length is 5 m, outer diameter is 30 mm in diameter, and the inside diameter is 10 mm. There is turbulent flow outside the tube and laminar flow inside and a stagnant layer of 0.25 mm thickness is determined to be established along the inside diameter.
   i. Start with the general form of the equation of change and obtain an expression to describe mass transfer inside the tube.
   ii. Suggest expressions to describe mass transfer on the inside and outside surfaces of the tube.

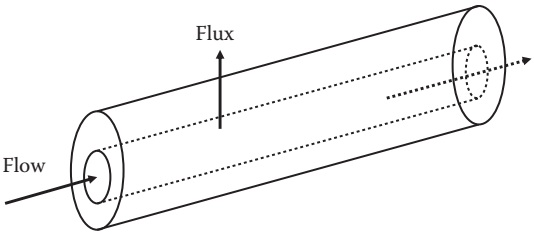


FIGURE Q.2.9
Cylindrical porous tube.

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10. A cylindrical piece of pasta with a 2 mm diameter and 15 cm length has been dipped into sauce at time $t = 0$. Sauce is diffusing into the piece of pasta with a constant diffusivity.
    i. Write down the appropriate form of the equation of change in the appropriate coordinate system.
    ii. Simplify the equation to describe the phenomena; when you neglect a term explain the reason in detail.
    iii. Convert the equation into a finite difference equation.
    iv. Rearrange the finite difference equation in a convenient format, so we can write a simple computer program to describe variation of the paint concentration at any location in the cylinder at any time.
    v. If the length of the cylinder would be 4 mm (diameter is still 2 mm) what would be the final form of the equation of continuity (you do NOT need to put it into finite difference form).
11. In a spaghetti factory the raw materials are brought together in the presence of water, mixed thoroughly, shaped, dried, and then put into the packages.
    i. Write down the simultaneous heat and mass transfer equations to describe the drying process in the constant rate period.
    ii. Write down the simultaneous heat and mass transfer equations to describe the drying process in the second falling rate period.
    iii. Write down the ICs and the BCs for the above equations.
    iv. What is meant by each of these equations? What does each term represent and what mass and heat transfer mechanisms they refer to. Explain in detail.
12. Simultaneous heat and mass transfer is modeled with the following equations during drying of the slab shown in the figure as

$$\rho_L \frac{\partial x}{\partial t} = \frac{\partial}{\partial z}\left(D_L \rho_L \frac{\partial x}{\partial z} \right) \quad \rho c \frac{\partial T}{\partial t} = \frac{\partial}{\partial z}\left(k \frac{\partial T}{\partial z} \right).$$

    i. What is meant by each of these equations? Explain in detail.
    ii. The slab geometry is given in the following figure. Write down the initial and the boundary conditions of these equations, and explain the meaning of each BC or IC in plain English.

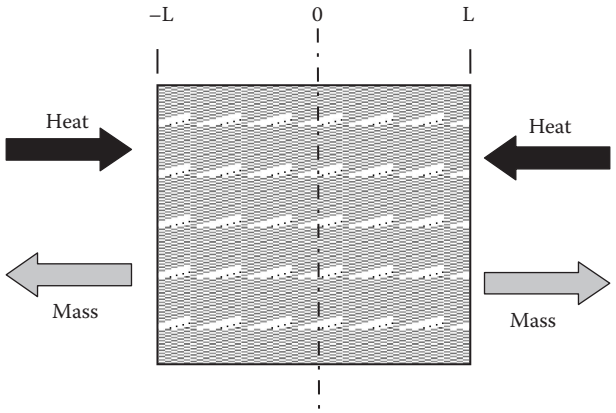


FIGURE Q.2.12
Schematic drawing of the slab.

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iii. Explain in detail how water is transported from the depths of the solid to the surface and how heat is transported to the depths of the solids by referring to the above equations, ICs, and BCs. While answering the question explain the dominant mechanism of heat transfer (i.e., conduction, convection, radiation, or a combination of two or three mechanisms). What stage of the drying process (i.e., constant drying rate, first falling rate, second falling rate, etc.) is modeled with these equations? Explain in detail.
iv. Why do we prefer a slab thickness of 2*L*?
v. If the effective diffusivity of water is described as $D_{eff} = D_{AB}\varepsilon/\tau$, how D_{AB}, ε and τ would change as the drying process continues. In some processes, while porous material is being dried, small amounts of water is sprayed to the interface. Can you explain the reason?

13. i. Under what conditions do we use empirical equations to model interfacial mass transfer?
ii. Give three examples to these equations.
iii. How will the theoretical approach be used to find expressions to their constants (explain in detail)?

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3

Kinetic Modeling

3.1 Kinetics and Food Processing

Chemical reactions and microbial growth or product formation are among the most common causes of food spoilage. Typical examples to food deterioration reactions may include lipid oxidation, thermal, or photocatalytic degradation processes. Toxins, enzymes, or chemicals of microbial origin are the *microbial products* causing food deterioration. Microbial growth and product formation are achieved via metabolic activity involving sets of chemical reactions occurring mostly in the microbial cell. Some form of metabolic activity also continues in the plant tissues after harvesting or inside the animal cells after slaughtering. Slowing down the deteriorative chemical reactions or microbial, postmortem, or postharvest metabolic activity is indeed the goal of most food processing and preservation methods. The initial objective of the experimental kinetics studies is the development of a mathematical model to describe the reaction rate as a function of the experimental variables.

A chemical reaction may actually involve many elementary steps as explained in the following example:

$$A_2 \rightleftharpoons 2A^* \qquad \text{elementary reaction 1}$$

$$A^* + B_2 \rightleftharpoons AB + B^* \qquad \text{elementary reaction 2}$$

$$A^* + B^* \rightarrow 2AB \qquad \text{elementary reaction 3}$$

$$A_2 + B_2 \rightarrow 2AB \qquad \text{overall reaction}$$

In this example, the sum of the *elementary reactions* gives the *overall reaction*, A* and B* are the intermediates, which have a very short life and convert into other components immediately after being formed. The intermediates usually may not be detected; therefore, their concentrations may not be monitored with the conventional direct measurement techniques. Their presence may be understood after getting them reacted with the externally added chemicals. The overall reaction may also be called the *observed reaction*.

The order of an elementary reaction is equal to the number of molecules entering the reaction. The forward reaction $A_2 \rightarrow 2A^*$ in the elementary step 1 is a first order with respect to A_2, because only one molecule is converted into 2*A**, but the reverse reaction $2A^* \rightarrow A_2$ is a second order with respect to *A**, since two molecules of *A** are involved. The overall order of an elementary step is the sum of the orders with respect to each species. With the same reasoning we can easily find out that the overall orders of both the forward and reverse reactions of the elementary step 2 and that of step 3 are 2.

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We have both forward and reverse reactions associated with the elementary steps 1 and 2, which are called *reversible reactions*. There is only a forward reaction associated with the elementary step 3, and the reaction may not be reversed under the pertinent experimental conditions. The elementary step 3 is called an *irreversible reaction*.

A chemical reaction may be prevented via eliminating one of the reactants. Dipping the potatoes in water, or waxing the apples after cutting into half may reduce the availability of the oxygen for the color change reactions. Fermenting eggs eliminate glucose, thus preventing it from entering into deteriorative reactions during the dried egg production (Hill and Sebring 1990). Eliminating intermediates from the stepwise propagating reactions may slow down spoilage. Antioxidants react with free radicals and slow down the lipid oxidation reactions.

Increasing product concentration may establish equilibrium between the reactants and products of a reaction, thus slowing down the metabolic activity. Carbon dioxide in a controlled atmosphere gas mixture may slow down the carbon dioxide producing reactions of the Krebs cycle and consequently the whole metabolic activity.

A chemical reaction may be slowed down via eliminating the enzyme catalyzing the reaction. In thermal processing, heat is applied to convert the enzymes into inactive proteins (Chapter 4). Off-odors in unblanched or under blanched frozen vegetables may be caused by enzymatic oxidation of lipids. Lipoxigenase is the catalyst involved in these oxidation reactions. It is inactivated upon blanching and development of off-odors during the subsequent storage is prevented (Fennema, Powrie, and Marth 1973). Ionizing radiation radiolizes water and may cause the formation of reactive intermediates including excited water $(H_2O)^*$, free radicals ($OH^{\cdot}$ and $H^{\cdot}$), ionized water molecules $(H_3O)^+$, and a hydrated electron $\left(e_{aq}^-\right)$, which may consequently react with food components including the proteins. Ionizing radiation may cause cross-linking or scission of the proteins (Karel 1975). When the enzymes undergo such changes, they lose their activity and may not be able to catalyze the deteriorative reactions.

Changing the pH of the food with an acid addition or fermentation may denature the enzymes. Drying the foods may eliminate water needed for the enzyme activity. Some chemical reactions occur with the effect of light. Opaque packaging prevents light reaching the light sensitive foods or beverages.

Refrigeration is among the most common food preservation methods and slows down spoilage via reducing the rate constants of the deterioration reactions.

Food deterioration usually occurs via a large number of chemical reactions. The slowest reaction involving into a process is referred to as the *rate determining step* and its rate may be equal to the spoilage rate. Preventing a single reaction in a set of deterioration reactions may create a new rate determining steps and slowing down the process and increasing the shelf life of food. Since the chemical reactions are among the major causes of food spoilage, their kinetics may deserve special attention.

3.2 Rate Expression

Consumption rate R_A of the species A with reaction $A \xrightarrow{k_1} 2B$ may be expressed as $R_A = -dc_A/dt = k_1 c_A$. The minus sign implies that A is a reactant, therefore its concentration c_A is decreasing with time. The parameter k_1 is called the reaction rate constant. The term $-k_1 c_A$ implies that the higher the concentration of reactant A, the higher the rate. The reaction rate also increases with k_1. If this reaction should describe loss of a nutrient in storage,

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the preservation methods would try to minimize the value of k_1 to slow down the nutrient loss. The production rate of B is $R_B = dc_B/dt = -2dc_A/dt = 2k_1c_A$ implying that two molecules of B are produced for each molecule of A consumed.

With the reaction $2A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} C$ the consumption rates of A and B and the production rate of C are $-dc_A/dt = -2dc_B/dt = 2dc_C/dt = k_1c_A^2c_B - k_2c_C$. There are actually two reactions represented here. The forward reaction implies that two molecules of A and one molecule of B react together with the rate constant k_1 to produce one molecule of C. The reverse reaction implies that one molecule of C disintegrates with the reaction rate constant k_2 to produce two molecules of A and one molecule of B. When the rate of the forward reaction, $k_1c_A^2c_B$, is larger than that of the reverse reaction, k_2c_C, components A and B are depleted and C is produced with the net rate predicted by the rate expression. When the rate of the forward reaction becomes the same as that of the reverse reaction, the production rate of each component becomes the same as its depletion rate, and their concentrations do not change with time. This is called a *chemical equilibrium*. Since two molecules of A are involved into a reaction, the power of c_A is 2 on the right-hand side of the rate expression. When a reaction represents the actual mechanism at the molecular level, the power of the concentration term on the right-hand side of the rate expression is the number of the molecules involved into the reaction. It is also possible that a chemical conversion may involve many reactions and the net change may be expressed with an apparent expression summing up the involving steps. In the rate expression of such reactions, the powers of the species concentration may not be equal to the net number of the molecules involving into the apparent expression. The forward rate expression is second order in A and first order in B. The order of the overall forward rate expression is three (i.e., sum of the orders with respect to each components). There is only one mole of chemical species involved into the reverse reaction and it is a first order.

Deterioration of the foods may be simulated in analogy with first- or zero-order irreversible monatomic reactions (Labuza 1980):

$$\frac{dc_A}{dt} = -kc_A, \tag{3.1}$$

or

$$\frac{dc_A}{dt} = -k. \tag{3.2}$$

This does not mean that the reactions taking place are very simple reactions, rather it shows that complex systems can be simulated with simple apparent mathematical models. Other simple chemical reactions that may involve into food processing and preservation with their differential and integrated rate expressions are given in Table 3.1.

Units of the rate constant are determined by the reaction. With any elementary reaction, units of k are expressed in (concentration)$^{1-n}$/time, where n = overall reaction rate order. With the zero-order reaction (i.e., Equation 3.2), k has the units of concentration/time, with a first-order reaction (i.e., Equation 3.1), k has the units of 1/time.

The rate expressions are arranged such that the rate constants are evaluated from the slopes of the differential or integrated rate expressions. The *differential methods* are based on the rate expressions evaluated via differentiation of the experimentally determined concentration versus time data. The *integral methods* (Examples 3.1 through 3.3) are based on an integration of the reaction rate expression. The numerical differentiation techniques are usually unstable, therefore, the integral methods are usually preferred over the differential methods.

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TABLE 3.1

Elementary Reactions and their Rate Expressions

Reaction	Differential Rate Expression	Integrated Rate Expression
$A \xrightarrow{k}$ products	$\frac{dc_A}{dt} = -k$	$c_A = c_{A0} - kt$
$A \xrightarrow{k}$ products	$\frac{dc_A}{dt} = -kc_A$	$\ln c_A = \ln c_{A0} - kt$
$A + B \xrightarrow{k}$ products	$\frac{dc_A}{dt} = \frac{dc_B}{dt} = -kc_A c_B$	$\int_0^{x_A} \frac{dx_A}{(1-x_A)(\gamma - x_A)} = kc_{A0}\int_0^t dt$ where $\gamma = \frac{c_{B0}}{c_{A0}}$, $x_A = \frac{c_{A0} - c_A}{c_{A0}}$
Without catalyst $A \xrightarrow{k_1} R$ With catalyst $A + \text{cat} \xrightarrow{k_c} R + \text{cat}$	$\frac{dc_A}{dt} = -kc_A$ $\frac{dc_A}{dt} = -k_c c_A$	$\ln c_A = \ln c_{A0} - k_c t$ where $k_c = k_1 + k_2 c_{\text{cat}}$
$A \xrightarrow{k_1} R$	$\frac{dc_A}{dt} = -(k_1 + k_2)c_A$	$\ln c_A = \ln c_{A0} - (k_1 + k_2)t$
$A \xrightarrow{k_2} S$	$\frac{dc_R}{dt} = k_1 c_A$ $\frac{dc_S}{dt} = k_2 c_A$	$c_R = c_{R0} + \frac{k_1}{k_2}(c_S - c_{S0})$
$A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} R$	$\frac{dc_A}{dt} = -\frac{dc_R}{dt} = -k_1 c_A + k_2 c_R$	$-\ln(1 - \frac{x_A}{x_{Ae}}) = \frac{k_1(\gamma + 1)}{(\gamma + x_{Ae})}t$ where x_{Ae} = value of x_A at equilibrium

Example 3.1: Ascorbic Acid Loss in Packaged and Nonpackaged Broccoli

Reduced ascorbic acid retention in packaged and nonpackaged broccoli were measured by Barth et al. (1993) as

t (h)	Packaged c_A (mg/g)	Nonpackaged c_A (mg/g)
0	5.6	5.6
24	5.38	4.82
48	4.76	3.86
72	4.59	3.75
96	4.42	3.25

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a. Find out if the data may be represented by Equation 3.1 or Equation 3.2.

Solution: Integrating Equation 3.1 gives: $\ln(c_A) = \ln(c_{A0}) - kt$, where c_{A0} is the initial concentration of the reduced ascorbic acid in broccoli. Substituting the data into the integrated equation gives: $\ln(c_A) = 1.69 - 5.54 \times 10^{-3} t$ with $r = -0.98$ and $s_e = 0.037$ with nonpackaged broccoli and $\ln(c_A) = 1.72 - 2.58 \times 10^{-3} t$ with $r = -0.97$ and $s_e = 0.006$ with packaged broccoli.

Integrating Equation 3.2 gives: $c_A = c_{A0} - kt$. Substituting the data into the integrated equation gives: $C_A = 5.41 - 0.024t$ with $r = -0.97$ and $s_e = 0.28$ with nonpackaged broccoli and $c_A = 5.58 - 0.013t$ with $r = -0.97$ and $s_e = 0.011$ with packaged broccoli. Since the correlation coefficient and the standard error of both models are very good, we may conclude that both models may represent the data very well. It should be noted that these models are simple empirical equations and do not describe the actual mechanism of the reaction.

MATLAB® code E.3.1 plots the variation of ascorbic acid concentration with time. Generally, it is not expected to have two models to simulate the same model equally well especially when we have large changes during the experiments. The small range of the reduced ascorbic acid loss may contribute to our observation.

MATLAB® CODE E.3.1

Command Line:

```
clear all
close all
global k

% enter the data
tData = [0 24 48 72 96];
cData1 = [5.6 5.38 4.76 4.59 4.42]; % packaged
cData2 = [5.6 4.82 3.86 3.75 3.25]; % non-packaged

% FIRST ORDER MODEL

% plot the data
plot(tData,log(cData1),'s',tData,log(cData2),'o'); hold on
xlabel('t (h)');
ylabel('ln cA');
legend('packaged','non-packaged','Location','NorthEast')
grid on

% modeling
tspan = [0 100]; % time spanof the solution
c0 = [5.42 5.58]; % initial concentrations
k = [5.54e-3 2.58e-3]; % reaction rate constants
[t,c] = ode45(@ascorbicacid1,tspan,c0); % solve the model equations
plot(t,log(c(:,1)),'-',t,log(c(:,2)),':'); hold on % plot the model
% ZERO ORDER MODEL

% plot the data
figure
plot(tData,cData1,'s',tData,cData2,'o'); hold on
xlabel('t (h)');
ylabel('cA');
```

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```
legend('packaged','non-packaged','Location','NorthEast')
grid on

% modeling
% same time span and initial concentrations as the first order model
are employed
k=[0.024 0.013]; % reaction rate constants
[t,c]=ode45(@ascorbicacid2,tspan,c0); % solve the model equations
plot(t,c(:,1),'-',t,c(:,2),':'); hold on % plot the model
```

M-File1:

```
function f=ascorbicacid1(t,c)
global k
f1=-k(1).*c(1);
f2=-k(2).*c(2);
f=[f1; f2];
```

M-File2:

```
function f=ascorbicacid2(t,c)
global k
f1=-k(1);
f2=-k(2);
f=[f1; f2];
```

Figures E.3.1.1 and E.3.1.2 will appear on the screen when we run the code.

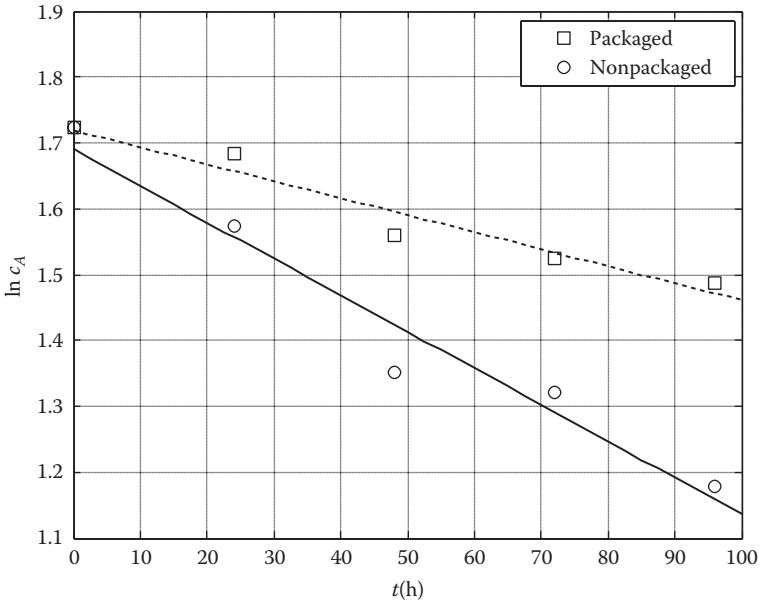


FIGURE E.3.1.1
Comparison of Equation 3.1 with the experimental data. (Adapted from Barth, M. M., Kerbel, E. L., Perry, A. K., and Schmidt, S. J., *Journal of Food Science,* 58, 140–43, 1993.)

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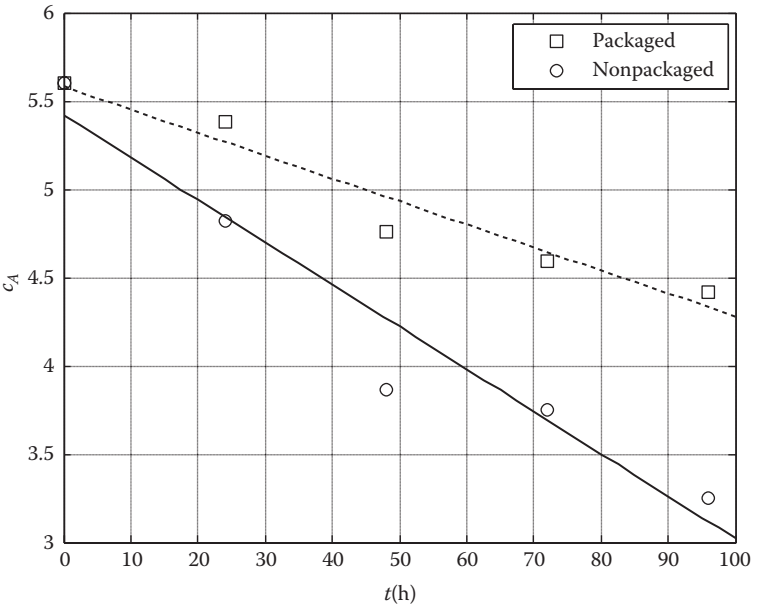


FIGURE E.3.1.2
Comparison of Equation 3.2 with the experimental data. (Adapted from Barth, M. M., Kerbel, E. L., Perry, A. K., and Schmidt, S. J., *Journal of Food Science,* 58, 140–43, 1993.)

b. Use Equations 3.1 and 3.2 to find out what percentage of the reduced ascorbic acid will remain after 100 hours of storage of the packaged broccoli.

Solution: Equations 3.1 and 3.2 are empirical equations and expected to simulate the data within the range of the experiments only. Although 100 hours of storage time is not in this range, it is close enough not to expect a drastic change in the trend with packaged broccoli. An integrated form of Equation 3.1 is $\ln(c_A) = \ln(c_{A0}) - kt$, after substituting $c_{A0} = 5.6$ mg/g and $k = 2.58\ 10^{-3}$ h^{-1} and $t = 100$ hours we obtain $c_A = 4.32$ mg/g. An integrated form of Equation 2.2 is $c_A = c_{A0} - kt$, after substituting $c_{A0} = 5.6$ mg/g and $k = 0.013$ mg/g h and $t = 100$ hours we obtain $c_A = 4.30$ mg/g.

Example 3.2: Simultaneous Nutrients and Toxin Degradation During Thermal Processing

The half-life of a bacterial toxin and a nutrient are 3 and 180 minutes, respectively, in a food at 121°C. Degradation processes may be described by Equation 3.1. Four log cycles of reduction is required in a toxin for safe food production. How much of the nutrient survives the heat treatment?

Solution: We have two reactions occurring in the same medium. Although these reactions do not interfere with each other, they inevitably take the same time. The half-life ($t_{1/2}$) of the chemical species is the time required to lose half of the initial value. An integrated form of Equation 2.1 is $\ln(c_A/c_{A0}) = -kt$ after substituting $c_A/c_{A0} = 0.5$ and $t_{1/2} = 3$ minutes we obtain $k = 0.231$ min^{-1} for the toxin. Similarly with $c_A/c_{A0} = 0.5$, and $t_{1/2} = 180$ we find $k = 0.004$ min^{-1} for the nutrient. After substituting $k = 0.231$ min^{-1} and $c_A/c_{A0} = 10^{-4}$ in the integrated model we will get $t = 40$ minutes = time required to reduce the toxin content by four log cycles. After substituting $k = 0.004$ min^{-1} and $t = 40$ minutes in the same integrated model, we will calculate $c_A/c_{A0} = 0.85$, implying that 85% of the nutrient will survive the heat treatment.

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Example 3.3 Shelf Life Calculation Based on Nutrient Loss

A micronutrient *A* undergoes a reaction $A + B \xrightarrow{k_1} C$ during storage of a food. The initial concentration of *A* is 2 g/kg and that of *B* is 75 g/kg. When the micronutrient concentration falls 75% of its initial level the food becomes inedible. Calculate shelf life of the food with $k_1 = 0.0001$ week^{-1} (g/kg)$^{-1}$.

Solution: The rate expression is $dc_A/dt = -kc_Ac_B$. Variation in *B* is negligible even after all of *A* is consumed with the reaction, since c_B is much larger than c_A. We may consider $k^\bullet = kc_B$ = constant, and the rate expression becomes $-dc_A/dt = -k^\bullet c_A$. This is called a pseudo first-order rate expression. An integrated pseudo first-order rate expression is $\ln(c_A/c_{A0}) = -k^\bullet t$. After substituting $k^\bullet = 0.0075$ week^{-1} and $c_A/c_{A0} = 0.75$, we may calculate the shelf life of the food $t = 38$ weeks.

Example 3.4: Kinetics of Nutrient Loss With Sequential Chemical Reactions

Nutrient *A* undergoes a degradation reaction $A \rightleftarrows B \rightarrow C$. The rate expressions for this reaction are

$$\frac{dc_A}{dt} = -k_1c_A + k_2c_B, \tag{E.3.4.1}$$

$$\frac{dc_B}{dt} = k_1c_A - (k_2 + k_3)c_B, \tag{E.3.4.2}$$

$$\frac{dc_C}{dt} = k_3c_B, \tag{E.3.4.3}$$

where the rate constants are $k_1 = 0.6$ weeks^{-1}, $k_2 = 0.2$ weeks^{-1}, and $k_3 = 0.1$ weeks^{-1}. Initial substrate concentrations were $c_{A0} = 35$ g/L, $c_{B0} = c_{C0} = 0$ g/L. Solve these differential equations simultaneously and plot variations of c_A, c_B, and c_C with time. When $c_C = 20$ g/L, the food is considered inedible. Determine the shelf life of the food from the plot.

Solution: We may rearrange the equations and solve as described in Table 2.6:

$$\begin{array}{rrrr} (D + k_1)c_A - & k_2c_B & & = 0 \\ -k_1c_A + & (D + k_2 + k_3)c_B & & = 0, \\ & -k_3c_B & Dc_C & = 0 \end{array}$$

where $D = d/dt$,

$$\Delta = \begin{vmatrix} D + k_1 & -k_2 & 0 \\ -k_1 & D + k_2 + k_3 & 0 \\ 0 & -k_3 & D \end{vmatrix} = (D + k_1)\begin{vmatrix} D + k_2 + k_3 & 0 \\ -k_3 & D \end{vmatrix} - (-k_1)\begin{vmatrix} -k_2 & 0 \\ -k_3 & D \end{vmatrix} + (0)\begin{vmatrix} -k_2 & 0 \\ D + k_2 + k_3 & 0 \end{vmatrix}$$

$$= (D + k_1)[(D + k_2 + k_3)(D) - (-k_3)(0)] + (k_1)[(-k_2)(D) - (-k_3)(0)] = D^3 + (k_1 + k_2 + k_3)D^2 + k_1k_2D,$$

$$\boldsymbol{D}c_A = \begin{vmatrix} 0 & -k_2 & 0 \\ 0 & D + k_2 + k_3 & 0 \\ 0 & -k_3 & D \end{vmatrix} = 0,\ \boldsymbol{D}c_B = \begin{vmatrix} D + k_1 & 0 & 0 \\ -k_1 & 0 & 0 \\ 0 & 0 & D \end{vmatrix} = 0,\ \boldsymbol{D}c_C = \begin{vmatrix} D + k_1 & -k_2 & 0 \\ -k_1 & D + k_2 + k_3 & 0 \\ 0 & -k_3 & 0 \end{vmatrix} = 0,$$

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$$\Delta c_A = \boldsymbol{D}\, c_A$$

$$\frac{d^3c_A}{dt^3} + \left(k_1 + k_2 + k_3\right)\frac{d^2c_A}{dt^2} + k_1k_3\frac{dc_A}{dt} = 0, \tag{E.3.4.4}$$

$$\Delta c_B = \boldsymbol{D}\, c_B$$

$$\frac{d^3c_B}{dt^3} + \left(k_1 + k_2 + k_3\right)\frac{d^2c_B}{dt^2} + k_1k_3\frac{dc_B}{dt} = 0, \tag{E.3.4.5}$$

and

$$\Delta c_C = \boldsymbol{D}\, c_C$$

$$\frac{d^3c_C}{dt^3} + (k_1 + k_2 + k_3)\frac{d^2c_C}{dt^2} + k_1k_3\frac{dc_C}{dt} = 0. \tag{E.3.4.6}$$

Assume a solution $y = Ce^{\lambda t}$, therefore, $dy/dt = \lambda e^{\lambda t}$, $d^2y/dt^2 = \lambda^3 d^{\lambda t}$, and $d^3y/dt^3 = \lambda^3 e^{\lambda t}$ substitutes all in the differential equation and obtains the characteristic equation:

$$\lambda^3 + \left(k_1 + k_2 + k_3\right)\lambda^2 + k_1k_3\lambda = 0. \tag{E.3.4.7}$$

Solutions of the characteristic equation (after substituting values of the rate constants) $\lambda_1 = 0$, $\lambda_2 = -0.072$, and $\lambda_3 = -0.827$, therefore

$$c_A = K_1 + K_2e^{-0.072t} + K_3e^{-0.827t}, \tag{E.3.4.8}$$

$$c_B = K_4 + K_5e^{-0.072t} + K_6e^{-0.827t}, \tag{E.3.4.9}$$

$$c_C = K_7 + K_8e^{-0.072t} + K_9e^{-0.827t}. \tag{E.3.4.10}$$

We have three equations with nine unknown constants. We may determine the constants if we can reduce their number to three. After substituting the solutions for c_A and c_B in

$$\frac{dc_A}{dt} = -k_1c_A + k_2c_B,$$

we will get

$$-0.072K_2e^{-0.072t} - 0.827K_3e^{-0.827t} = -0.6\left(K_1 + K_2e^{-0.0727t} + K_3e^{-0.827t}\right)$$
$$+ 0.2\left(K_4 + K_5e^{-0.072t} + K_6e^{-0.827t}\right).$$

The same exponential terms must have the same coefficients on both sides of the equation, therefore

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Term	Equal Coefficients	Relation Between Constants
e^0	$0 = 0.6\ K_1 + 0.2\ K_4$	$K_4 = -0.3\ K_1$
$e^{-0.072t}$	$-0.072\ K_2 = -0.6\ K_2 + 0.2\ K_5$	$K_5 = 2.64\ K_2$
$e^{-0.827t}$	$-0.827\ K_3 = -0.06\ K_3 + 0.2\ K_6$	$K_6 = -1.135\ K_3$

After substituting the solutions for c_B and c_C in $dc_c/dt = k_3 c_B$, we will get

$$-0.072K_8e^{-0.072t} - 0.827K_9e^{-0.827t} = 0.1\left(-0.3K_1 + 2.64K_2e^{-0.072t} - 1.135K_3e^{-0.827t}\right).$$

The same exponential terms must have the same coefficients on both sides of the equation, therefore

Term	Equal Coefficients	Relation Between Constants
e^0	$0 = -0.03\ K_1$	$K_1 = 0$
$e^{-0.072t}$	$-0.072\ K_8 = 0.264\ K_2$	$K_8 = -3.67\ K_2$
$e^{-0.827t}$	$-0.827\ K_9 = -0.114\ K_3$	$K_9 = 0.137\ K_3$

After substituting the constants we will have

$$c_A = K_2\ e^{-0.072t} + K_3\ e^{-0.827t}, \tag{E.3.4.11}$$

$$c_B = -3.67K_2\ e^{-0.072t} + 0.137K_3\ e^{-0.827t}, \tag{E.3.4.12}$$

$$c_C = K_7 + 5.25K_2\ e^{-0.072t} + 0.19K_3\ e^{-0.827t}. \tag{E.3.4.13}$$

Equations E.3.4.11 through E.3.4.13 have three unknown constants (K_2, K_3, K_7); we may solve these constants by using the initial conditions:

$$35 = K_2 + K_3,$$

$$0 = 2.64K_2 - 1.135K_3,$$

$$0 = K_7 - 3.667K_2 + 0.137K_3.$$

Therefore, $K_2 = 10.5$, $K_3 = 24.48$, $K_7 = 35.23$, and

$$c_A = 10.5\ e^{-0.072t} - 24.47\ e^{-0.827t}, \tag{E.3.4.14}$$

$$c_B = 27.72\ e^{-0.072t} - 27.78\ e^{-0.827t}, \tag{E.3.4.15}$$

$$c_C = 35.23 - 38.5\ e^{-0.072t} - 3.35\ e^{-0.827t}. \tag{E.3.4.16}$$

An incomparably easy solution may also be obtained with MATLAB® code E.3.4. Variations of c_A, c_B, and c_C during the storage period are shown in Figure E.3.4. It may also be seen from the figure that the shelf life of the food ($c_C = 20$ g/L) is about 13 weeks.

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MATLAB® CODE E.3.4

Command Window:

```
clear all
close all
global k

% enter the constants of the model
k = [0.6 0.2 0.1]; % reaction rate constants
c0 = [35 0 0]; % initial concentrations

% solve the model equations
tspan = [0 13]; % time spanof the solution
[t,c] = ode45(@nutrient,tspan,c0);

% plot the model
plot(t,c(:,1),'-',t,c(:,2),'-.',t,c(:,3),'--'); hold on
xlabel('t (weeks)');
ylabel('c (g/L)');
legend('c_A','c_B','c_C')
grid on
```

M-File:

```
function dc = nutrient(t,c)
global k
dca = -k(1)*c(1) + k(2)*c(2);
dcb = k(1)*c(1) - ((k(2) + k(3))*c(2));
dcc = k(3)*c(2);
dc = [dca;dcb;dcc];
```

When we run the code Figure E.3.4 will appear on the screen.

3.3 Why Do Chemicals React?

In nature all the systems try to lower their energy and increase their disorder. The same rule is also valid for chemicals. A chemical reaction occurs spontaneously if the total Gibbs free energy of formation of the products is smaller than that of the reactants. When molecules collide, bonds of the molecules are broken first and new bonds are established to produce an activated complex. The lifetime of the activated complex is very short, it rearranges its molecular structure very rapidly to form the products. The rate of a chemical reaction may be computed by assuming either collision or dissociation of the activated complex as the rate-limiting steps.

When we consider the reaction (A and B are ideal gases):

$$A + B \rightarrow \text{products},$$

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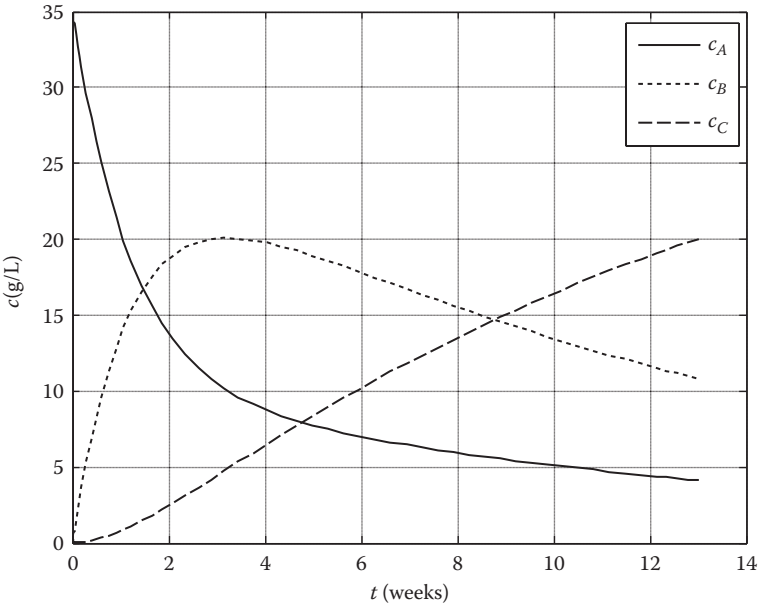


FIGURE E.3.4
Variation of c_A, c_B, and c_C in storage.

with the rate

$$R = kc_A c_B. \tag{3.3a}$$

The number of collisions (z_{AB}) of A with B in unit volume in unit time is

$$z_{AB} = \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \frac{N_{Av}^2}{10^6} \sqrt{8\pi\kappa T\left(\frac{1}{M_A} + \frac{1}{M_B}\right)}, \tag{3.3b}$$

where σ = diameter of a molecule; M_A, M_B = molecular weights, κ = Boltzmann constant. Only the collisions involving with more than a minimum activation energy E_a may lead to a reaction. The fraction of all bimolecular collisions involving more energy than E_a is $\exp(-E_a/RT)$; therefore, the rate of the reaction and the rate constant are

$$R = z_{AB} \exp\left(-\frac{E_a}{RT}\right) c_A c_B, \tag{3.3c}$$

$$k = \left(\frac{\sigma_A + \sigma_B}{2}\right)^2 \frac{N_{Av}^2}{10^6} \sqrt{8\pi\kappa T\left(\frac{1}{M_A} + \frac{1}{M_B}\right)} \exp\left(-\frac{E_a}{RT}\right). \tag{3.3d}$$

When the dissociation of the activated complex is the rate-limiting step, we need to compute the activated complex AB^* concentration from the chemical reaction:

$$A + B \underset{k_2}{\overset{k_1}{\rightleftarrows}} AB^*. \tag{3.4a}$$

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There is an equilibrium between the reactants and the activated complex at all times:

$$K_{eq} = \frac{k_1}{k_2} = \frac{c^*_{AB}}{c_A c_B}. \tag{3.4b}$$

The activated complex undergoes decomposition as

$$AB^* \xrightarrow{k_3} \text{products}. \tag{3.4c}$$

The rate constant of decomposition is the same for all reactions:

$$k_3 = \frac{\kappa T}{h}, \tag{3.4d}$$

where h = Planck constant.

The product formation rate and the rate constant are

$$R = k_3 c^*_{AB} = \frac{\kappa T}{h} K_{eq} c_A c_B, \tag{3.4e}$$

$$k = \frac{\kappa T}{h} K_{eq}. \tag{3.4f}$$

Variation of the Gibbs free energy along the reaction path is described in Figure 3.1. The higher the Gibbs free energy of the activated complex, the smaller is the fraction of the molecules that can gain sufficient energy to exceed the energy barrier. A catalyst makes it possible to form an activated complex with a lower activation energy barrier, therefore, a higher fraction of the molecules may pass through it and the reaction rate increases (Figure 3.2).

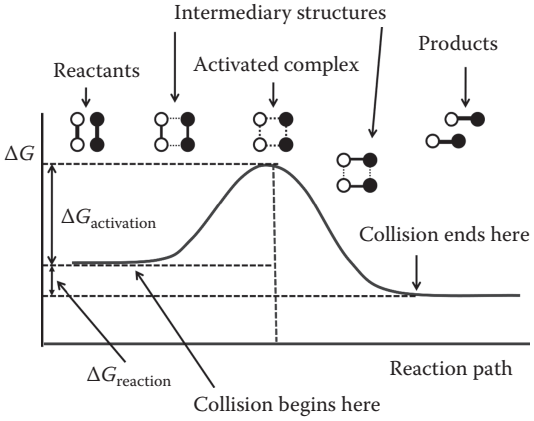


FIGURE 3.1
Schematic description of the Gibbs free energy levels at different reaction coordinates. $\Delta G_{activation}$ is the activation energy barrier.

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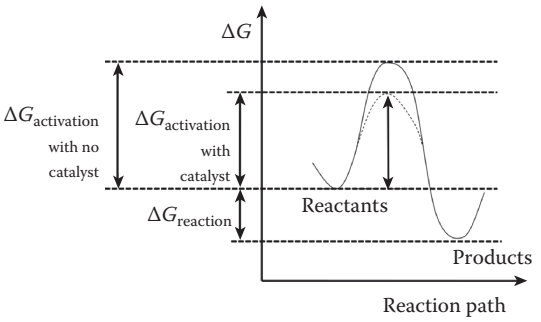


FIGURE 3.2
A different activated complex with smaller activation free energy forms when a catalyst is used. More molecules will be eligible to pass through the activation energy barrier when the $\Delta G_{activation}$ is lower.

Collision theory and transition state theory permit computation of the rates of the reactions involving idealistic cases, which are beyond the scope of this book, but they form the basis for the analogy models, which will be discussed extensively under numerous titles.

3.4 Temperature Effects on Reaction Rates

Temperature effects on the rate constants may be described with the *Arrhenius expression*:

$$k = k_0 \exp\left\{-\frac{E_a}{RT}\right\}, \tag{3.5}$$

where k = rate constant, k_0 = preexponential constant, E_a = activation energy, R = gas constant, and T = absolute temperature.

Example 3.5: Vitamin Loss in a Snack Food

Loss of a vitamin in a snack food agrees with Equation 3.1. Estimate the time required to lose 15% of the initial vitamin content at 22°C if half-lives of the vitamin at different storage temperatures were

T (°C)	10	15	20	25
$t_{1/2}$ (days)	2900	1600	925	530

Solution: Half-life ($t_{1/2}$) is the time required to lose half of the initial vitamin content. An integrated form of Equation 3.1 is $\ln(c_A/c_{A0}) = -kt$ after substituting $c_A/c_{A0} = 0.5$ and $t = t_{1/2}$ we obtain

T (°C)	10	15	20	25
k (day^{-1})	$2.4\ 10^{-4}$	$4.3\ 10^{-4}$	$7.5\ 10^{-4}$	$1.3\ 10^{-3}$

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Equation 3.5 may be rewritten as $\ln(k) = \ln(k_0) - E/RT$, then data are

1/T (K^{-1})	**3.53 10^{-3}**	**3.47 10^{-3}**	**3.41 10^{-3}**	**3.36 10^{-3}**
ln *k*	–8.33	–7.75	–7.20	–6.65

After plotting ln *k* versus 1/*T* (Figure E.3.5) we may obtain the best line $\ln(k) = 26.23 - 9.810^3/T$ ($r = -1.0$) with the intercept $\ln(k_0) = 26.23$ and the slope $E_a/R = 9.8\ 10^3 K^{-1}$. After substituting these parameters and $T = 295$ K in Equation 3.5, we obtain = 9.2 10^{-4} day^{-1} at 22°C. We may substitute the calculated value of *k* and $c_A/c_{A0} = 0.85$ in $\ln(c_A/c_{A0}) = -kt$ to estimate the time required to lose 15% of the initial vitamin content at 22°C at 177 days. The details of the computations are available in MATLAB® code E.3.5.

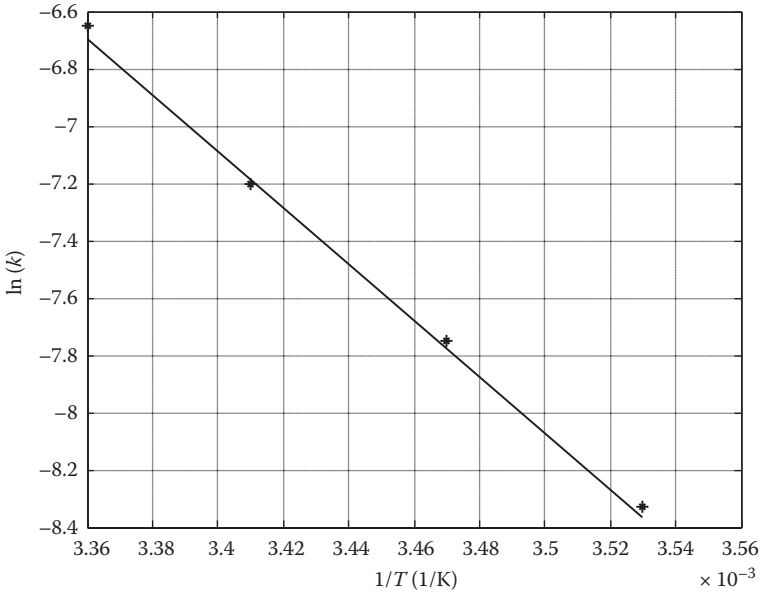


FIGURE E.3.5
Comparison of the best fitting line with the data as produced by the MATLAB® code E.3.5.

MATLAB® CODE E.3.5

Command Line:

```
clear all
close all
format compact

% enter the data
InvT = [3.53e-3 3.47e-3 3.41e-3 3.36e-3]; % 1/T (K)
k = [-8.33 -7.75 -7.20 -6.65];

% plot the data
plot(InvT,k,'*'); hold on
```

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```
% enter the constants of the model
ko = exp(26.23);
EaR = 9.8e3; % Ea/R

% compute the reaction rate constant
k = ko*exp(-EaR.*InvT);

% plot the model
plot(InvT,log(k)); hold on
ylabel('ln(k)');
xlabel('1/T (1/K)');
grid on

% estimate the time to lose 15 % of vitamin C at 22 oC
T = 22; % (K)
k = ko*exp(-EaR/(T + 273));
t = log(0.85)/(-k)
```

When we run the code the following will appear on the screen:

```
t =
  176.5101
```

Example 3.6: Total Amounts of Nutrient Loss After Sequences of a Canning Process

Initial nutrient content of a fresh vegetable is 5 g/kg. The degradation rate of the nutrient and the temperature effects on the rate constant may be described with Equations 3.1 and 3.5, respectively, with frequency factor $k_0 = 0.2$ min^{-1} and activation energy $E_a = 5030$ J/mole. The following operations occur during processing at the given average temperatures: (i) blanching 5 minutes at 100°C, (ii) canning 15 minutes at 60°C, (iii) thermal processing 20 minutes at 121°C. What will be the remaining concentration of the nutrient at the end of processing?

Solution: Amounts of the nutrient surviving may be calculated from $c_A = c_{A0} \exp\{-kt\}$, where $k = k_0 \exp\{-E_a/RT\}$ and $R = 8.314$ J/mole K. After substituting the numbers,

i. Blanching $T = 373$ K, $k = 0.040$ min^{-1}, $c_{A0} = 5$ g/kg, $c_A = 4.09$ g/kg.
ii. Canning $T = 333$ K, $k = 0.033$ min^{-1}, $c_{A0} = 4.09$ g/kg, $c_A = 2.60$ g/kg.
iii. Thermal processing $T = 394$ K, $k = 0.043$ min^{-1}, $c_{A0} = 2.60$ g/kg, $c_A = 1.10$ g/kg = remaining concentration of the nutrient at the end of processing.

MATLAB® code E.3.6 carries out the computations.

3.5 Precision of Reaction Rate Constant and Activation Energy Determinations

A general nth order rate expression ($n \neq 1$) is

$$\frac{dc_A}{dt} = kc_A^n, \tag{3.6a}$$

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MATLAB® CODE E.3.6

Command Line:

```
clear all
close all
format compact

% enter the data
T = [100 60 121]; % temperature of process stages (oC)
t = [5 15 20]; % time length of each process stage (min)
c(1) = 5; % initial concentration of the nutrient before processing
(g/kg)

% enter the constants of the model
k0 = 0.2; % pre-exponential constant (1/min)
Ea = 5030; % activation energy (kJ/kg mol)
R = 8.314; % gas constant (kJ/kg mole K)

% computation of the nutrient loss in each stage of processing
for i = 2:(length(T) + 1)
  k(i-1) = k0*exp(-Ea/(R*(T(i-1) + 273)));
  c(i) = c(i-1)*exp(-k(i-1)*t(i-1));
end

% computation of the nutrient at the end of processing
Remaining_Concentration = c(length(T) + 1)
```

When we run the code the following line will appear on the screen:

```
Remaining_Concentration =
   1.0650
```

after rearrangement and integration the rate constant will be

$$k = \frac{c_{A1}^{n-1} - c_{A2}^{n-1}}{(n-1)(t_2 - t_1)c_{A2}^{n-1}c_{A1}^{n-1}}, \tag{3.6b}$$

where subscripts 1 and 2 denote the beginning and the end of an interval, respectively. In the completely general case of dependent variable $y = f(x_1, x_2,...,x_n)$ the relative error in y due to the relative errors of $x_1, x_2,...,x_n$ is given by

$$\left(\frac{\Delta y}{y}\right)^2 = \sum_{i=1}^{n}\left(\frac{\partial f}{\partial x_i}\right)^2\left(\frac{\Delta x_i}{x_i}\right)^2. \tag{3.6c}$$

If we can assume that errors in c_{A1}, c_{A2}, t_1, and t_2 are independent we may calculate the relative error in k after using Equation 3.6c as (Hill and Grieger-Block 1980)

$$\left(\frac{\Delta k}{k}\right)^2 = \left(\frac{\Delta t_1}{t_2 - t_1}\right)^2 + \left(\frac{\Delta t_2}{t_2 - t_1}\right)^2 + \left(\frac{(n-1)c_{A2}^{n-1}}{c_{A1}^{n-1} - c_{A2}^{n-1}}\right)^2\left(\frac{\Delta c_{A1}}{c_{A1}}\right)^2 + \left(\frac{(n-1)c_{A1}^{n-1}}{c_{A1}^{n-1} - c_{A2}^{n-1}}\right)^2\left(\frac{\Delta c_{A2}}{c_{A2}}\right)^2. \tag{3.6d}$$

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In the case of $n = 1$, the corresponding equation is:

$$\left(\frac{\Delta k}{k}\right)^2 = \left(\frac{\Delta t_1}{t_2 - t_1}\right)^2 + \left(\frac{\Delta t_2}{t_2 - t_1}\right)^2 + \left(\frac{1}{\ln(c_{A1}/c_{A2})}\right)^2 \left(\frac{\Delta c_{A1}}{c_{A1}}\right)^2 + \left(\frac{1}{\ln(c_{A1}/c_{A2})}\right)^2 \left(\frac{\Delta c_{A2}}{c_{A2}}\right)^2. \quad (3.6e)$$

Activation energy E_a may be calculated from the Arrhenius expression 3.5 as

$$E_a = \frac{RT_1T_2}{T_2 - T_1}\ln(k_2/k_1), \quad (3.6f)$$

where subscripts 1 and 2 denote the beginning and the end of an interval, if the errors in each of the quantities k_1, k_2, T_1, and T_2 are random, the relative error in the Arrhenius activation energy is given after using Equation 3.6c as

$$\left(\frac{\Delta E}{E_a}\right)^2 = \left(\frac{T_2}{T_2 - T_1}\right)^2 \left(\frac{\Delta T_1}{T_1}\right)^2 + \left(\frac{T_2}{T_2 - T_1}\right)^2 \left(\frac{\Delta T_2}{T_2}\right)^2 + \left\{\frac{1}{\ln(k_1/k_2)}\right\}^2 \left\{\left(\frac{\Delta k_1}{k_1}\right)^2 + \left(\frac{\Delta k_2}{k_2}\right)^2\right\}. \quad (3.6g)$$

Equation 3.6g shows that the relative error in the activation energy is strongly dependent on the size of the temperature interval chosen and the error involved in the temperature measurements.

Example 3.7: Precision of the Rate Constant

Determine the uncertainty involved in the determination of the reaction rate constant and the activation energy (of the Arrhenius equation) of the following reaction:

$$\frac{dc_A}{dt} = -kc_A^2. \quad (E.3.7)$$

Data were recorded at $t_1 = 0$ and at $t_2 = 100$ minutes, uncertainty in each time measurement was $\Delta t_1 = 1$ s and $\Delta t_2 = 1$ s. At time $t_2 = 100$ minutes it was found that $c_{A1} = 0.5c_{A0}$ and relative uncertainty ($\Delta c/c$) in each concentration measurement was 1%. It was also observed that the reaction rate constant increases by 5% when temperature increases from 40 to 60°C. MATLAB® code E.3.7

MATLAB® CODE E.3.7

Command Line:

```
clear all
close all
format compact

% enter the temperature and model constants
T1 = 40; % (oC)
T2 = 60; % (oC)
k1 = 1.0e-2; % mol/min
k2 = 1.05*k1; % mol/min
deltaTime1 = 1; % error in determination of time1 (oC)
deltaTime2 = 1; % error in determination of time2 (oC)
```

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```
deltaTemp1 = 0.01; % error in determination of T1 (oC)
deltaTemp2 = 0.01; % error in determination of T2 (oC)
errorC1 = 0.01; % error in c1
errorC2 = 0.01; % error in c2
t1_t2 = 100*60; % t1-t2 = 100s
R = 8.32; % gas constant (J/mol K)

% COMPUTE the ACTIVATION ENERGY
Ea = (8.324*(273 + T1)*(273 + 60)/((273 + 60) - (273 + 40)))/log(k2/k1)

% COMPUTE the ERROR in k
errorK2 = (deltaTime1/t1_t2)^2 + (deltaTime2/t1_t2)^2 + ((errorC1/
(1-0.5))^2) + ((errorC2/(0-0.5))^2); % error ratio squarred
error_in_k = sqrt(errorK2)

% COMPUTE the ERROR in Ea
error_in_E_squared = (deltaTemp1/(T2-T1))^2 + (deltaTemp2/
(T2-T1))^2 + ((1/log(k2/k1))^2)*(((error_in_k/k1)^2) + (error_in_k/
k2)^2); %
error_in_E = sqrt(error_in_E_squared)
```

When we run the code the following line will appear on the screen:

```
Ea =
  8.8912e+005
error_in_k =
   0.0283
error_in_E =
   80.0583
```

uses Equations 3.6d and 3.6g to compute the uncertainty in the reaction rate constant and the activation energy determinations.

Therefore the values of the reaction rate constant and the activation energy are $k_1 = 0.60 \pm 0.03$ s^{-1}; $k_2 = 0.63 \pm 0.03$ s^{-1}; $E_a = 889120 \pm 80$ J/mol K.

3.6 Enzyme-Catalyzed Reaction Kinetics

Enzymes are the natural protein catalysts of the cellular reactions. They are usually very specific and catalyze only one reaction involving only one substrate. They lose their activity if the natural folding pattern of the protein changes. A single enzyme catalyzed one substrate reaction may be expressed as

$$S \xrightarrow{E} P, \tag{3.7a}$$

where the reaction rate is

$$v = -\frac{dc_S}{dt} = \frac{dc_P}{dt}. \tag{3.7b}$$

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The terms $-dc_S/dt$ is the substrate consumption rate and dc_p/dt is the product formation rate. The rates of the enzyme catalyzed reactions were referred to as *velocity* in the pioneering biology literature, therefore they are conventionally denoted with the letter v. The mechanism for a single enzyme catalyzed one substrate reaction was first suggested by Michaelis and Menten (1913) as

$$S + E \underset{k_2}{\overset{k_1}{\rightleftarrows}} SE, \tag{3.7c}$$

$$SE \xrightarrow{k_3} P + E. \tag{3.7d}$$

The first elementary reaction of this mechanism is considered as an equilibrium step with the dissociation constant

$$K_M = \frac{c_E c_S}{c_{ES}}, \tag{3.7e}$$

where K_M = Michaelis constant, c_E = enzyme concentration, c_S = substrate concentration, and c_{ES} = concentration of the *ES* complex. The total enzyme concentration was initially c_{E0}, after making the *ES* complex, the concentration of the free enzyme c_E may be calculated as

$$c_E = c_{E0} - c_{ES}. \tag{3.7f}$$

The second reaction is slow, therefore its rate is the same as the rate of the overall apparent reaction. The slowest reaction in such a mechanism is called the rate determining step. The rate of the second elementary reaction is

$$v = \frac{dc_P}{dt} k_3 c_{ES}. \tag{3.7g}$$

It is not usually possible to measure c_{ES}, therefore we may use Equations 3.7a through f to rearrange Equation 3.7g as

$$v = \frac{v_{\max} c_S}{K_M + c_S}. \tag{3.8}$$

This is called the Michaelis–Menten equation, where

$$v_{\max} = k_3 c_{E0}. \tag{3.9}$$

It was later claimed by Briggs and Haldane (1925) that 3.7[c] may not be an equilibrium step, and the material balances for the substrate and the intermediary complex *ES* were expressed as

$$v = -\frac{dc_S}{dt} = k_1 c_S c_E - k_2 c_{ES}, \tag{3.10a}$$

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TABLE 3.2

Linear Arrangements of the Michaelis–Menten Equation

Lineweaver–Burk arrangement (Lineweaver and Burk, 1934)	$\frac{1}{v} = \frac{1}{v_{\max}} + \frac{K_M}{v_{\max}} \frac{1}{c_S}$
Eadie–Hofstee arrangement (Eadie, 1942; Hofstee, 1959)	$v = v_{\max} - K_M \frac{v}{c_S}$
Hanes–Woolf arrangement (Hanes, 1932; Haldane and Stern, 1932)	$\frac{c_S}{v} = \frac{K_M}{v_{\max}} + \frac{1}{v_{\max}} c_S$

$$\frac{dc_{ES}}{dt} = k_1 c_S c_E - k_2 c_{ES} - k_3 c_{ES}. \tag{3.10b}$$

The complex does not accumulate, i.e.,

$$\frac{dc_{ES}}{dt} = 0. \tag{3.10c}$$

After using Equations 3.10a through c, Equation 3.8 is obtained with the Michaelis constant

$$K_M = \frac{k_2 + k_3}{k_1}. \tag{3.10d}$$

Enzymes belonging to the classification of hydrolases are the typical examples to the single enzyme catalyzed one substrate reactions.

The Michaelis–Menten equation has a variable apparent order. When $K_M >> c_S$ the apparent rate is $v = k_{app} c_S$ (first order in c_s), where $k_{app} = v_{\max}/K_M$; when $K_M << c_S$ the apparent rate is $v = v_{\max}$ (zero order in c_s). The Michaelis–Menten equation is generally arranged in three different linear forms to evaluate the apparent constants $v_{\max}$ and K_M from the slopes and the intercepts of the plots of the experimental data (Table 3.2). A number of advantages and disadvantages are associated with each type of plot. Even spacing of the data points along the line and best fit of the data points to a straight line are among the factors to be considered while making such a decision. More workers use a Lineweaver–Burk method than the other two combined.

Example 3.8 Kinetics of Linolenic Acid Peroxidation by Sunflower Lipoxygenase

Strong lipoxygenase activity is observed during the first days of sunflower seed germination, which may cause lipid peroxidation under unfavorable storage conditions. Linolenic acid is a substrate for sunflower lipoxygenase. The following data were evaluated from a publication by Leoni, Iori, and Palmeri (1985).

c (mM)	0.0025	0.0033	0.0052	0.0080	0.012	0.05	0.015	0.25
v (U/mg protein)	21	27	33	43	50	60	53	54

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If the apparent reaction agrees with the Michaelis–Menten scheme, determine the constants of the rate expression.

i. Double reciprocal (Lineweaver–Burk) plot.
Equation 3.8 and the data may be rearranged as

$$\frac{1}{v} = \frac{1}{v_{\max}} + \frac{K_M}{v_{\max}} \frac{1}{c}.$$

$1/c$ (mM)$^{-1}$	400	303	192	125	83	20	6.6	4
$1/v$ (U/mg protein)$^{-1}$	0.0476	0.0370	0.0303	0.0232	0.0200	0.0167	0.0189	0.0185

The best fitting line to the data is

$$\frac{1}{v} = 0.0161 + 7.35 \times 10^{-5} \frac{1}{c} \qquad (r = 0.98).$$

The intercept is $1/v_{\max}$, therefore $v_{\max} = 62$ U/mg protein and the slope is $K_M/v_{\max}$, therefore $K_M = 5 \times 10^{-6}$ M. The Lineweaver–Burk plot is shown in Figure E.3.8.1.

ii. Eadie–Hofstee plot.
Equation 3.8 and the data may be rearranged as

$$v = v_{\max} - K_M \frac{v}{c}.$$

v/c (U/mg protein mM)	8400	8181.8	6346.1	5375	4166.7	1200	3533.3	216
v (U/mg protein)	21	27	33	43	50	60	53	54

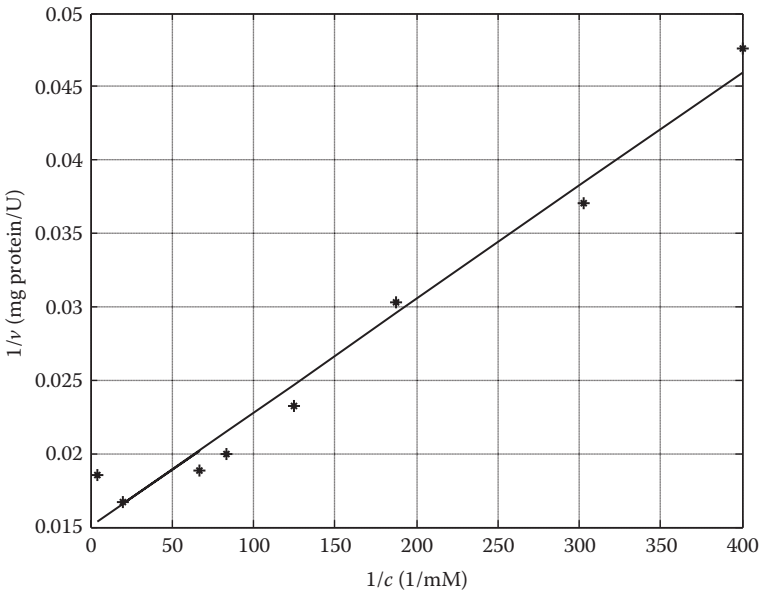


FIGURE E.3.8.1
The Lineweaver–Burk plot to determine kinetic constants K_M and $v_{\max}$.

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The best fitting line to the data is

$$v = 63 - 0.0044\frac{v}{c} \qquad (r = -0.94).$$

The intercept is v_{max}, therefore $v_{max} = 63$ U/mg protein and the slope is K_M, therefore $K_M = 4.4 \times 10^{-6}$ M. The Eadie–Hofstee plot (Eadie, 1942; Hofstee, 1959) is shown in Figure E.3.8.2. Details of the computations are given in MATLAB® code E.3.8.

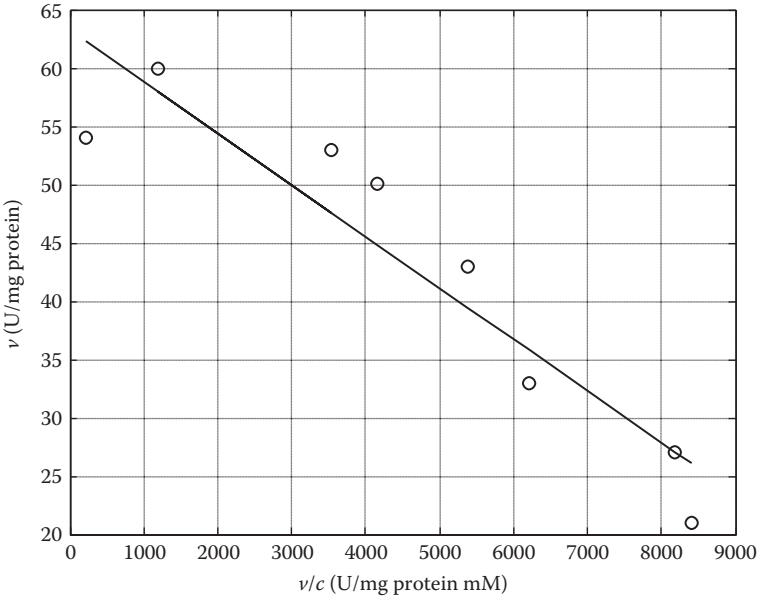


FIGURE E.3.8.2
The Eadie–Hofstee plot to determine kinetic constants K_M and v_{max}.

MATLAB® CODE E.3.8

Command Line:

```
clear all
close all
format compact

% enter the data
cData = [0.0025 0.0033 0.00532 0.0080 0.012 0.05 0.015 0.25];
vData = [21 27 33 43 50 60 53 54];

% LINEWEAVER BURK PLOT
% convert the data into appropriate format for the plot
for i = 1:length(cData)
   cInv(i) = 1/cData(i);
   vInv(i) = 1/vData(i);
   vc(i) = vData(i)/cData(i);
end
```

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```
plot(cInv,vInv,'*'); hold on % plot the data
ylabel('1/v (mg Protein/U)')
xlabel('1/c (1/mM)')

% compute the constants of the model
N = 1; % fit a first order polynomial
f = polyfit(cInv,vInv,N);
fp = polyval(f, cInv);
Vmax_Lineweaver = 1/f(2)
Km_Lineweaver = Vmax_Lineweaver*f(1)

plot(cInv, fp); hold on % plot the model
grid on

% evaluate the correlation coefficient
rmatrix = corrcoef(cInv,vInv);
r1 = rmatrix(1,2);
Corr_Coef_Lineweaver = r1

% evaluate the standard error
for i = 1:length(cData);
     d1(i) = (vInv(i)-(f(2) + f(1)*cInv(i)))^2;
end;

Se1 = sqrt(mean(d1));
Standard_Error_Lineweaver = Se1

% EADIE HOFTSEE PLOT
figure
plot(vc,vData,'o'); hold on % plot the data
ylabel('v (U/mg Protein)')
xlabel('v/c (U/mg Protein mM)')

% compute the constants of the model
k = polyfit(vc,vData,1);
kp = polyval(k, vc);
Vmax_Eadie = k(2)
Km_Eadie = -k(1)

plot(vc, kp); hold on % plot the model
grid on

% evaluate the correlation coefficient
rmatrix = corrcoef(vc,vData);
r2 = rmatrix(1,2);
Corr_Coef_Eadie = r2

% evaluate the standard error
for i = 1:length(cData);
     d2(i) = (vData(i)-(k(2) + k(1)*vc(i)))^2;
end;

Se2 = sqrt(mean(d2));
```

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```
Standard_Error_Eadie = Se2
```

Figures E.3.8.1 and E.3.8.2 will appear on the screen with the following after running the code:

```
Vmax_Lineweaver =
   66.4933
Km_Lineweaver =
    0.0051
Corr_Coef_Lineweaver =
    0.9872
Standard_Error_Lineweaver =
    0.0016
Vmax_Eadie =
   63.2320
Km_Eadie =
    0.0044
Corr_Coef_Eadie =
   -0.9353
Standard_Error_Eadie =
    4.6783
```

Enzymatic reactions involved in food processing and preservation may also involve two substrates:

$$A + B \rightarrow E \rightleftarrows P + Q. \tag{3.11}$$

Three different mechanisms are suggested for these reactions (Whitaker 1994). The ordered and the random mechanisms suggest that the products may be released only after both of the substrates bound to the enzyme. In the *ordered mechanism*, it is always the same substrate bound to the enzyme first, and the same product is released first. In the *random mechanism* there is no priority in binding of the substrates or removal of the products. The ordered and random mechanisms result in the same rate expression:

$$v = \frac{v_{\max} c_A c_B}{(c_A + K_A)(c_B + K_B)}. \tag{3.12}$$

In a *ping pong mechanism* the first product is released after binding the first substrate; then the second substrate is bound and subsequently the second product is formed, leading the rate expression:

$$v = \frac{v_{\max} c_A c_B}{c_A c_B + K_A c_B + K_B c_A}. \tag{3.13}$$

The $K_A K_B$ term is missing in the denominator of Equation 3.13 since there is no ternary complex in the mechanism. It should be noticed that Equations 3.12 and 3.13 are valid when c_A and c_B are maintained at constant levels and there is no product accumulation in the reaction medium. Kinetic constants of Equations 3.12 and 3.13 may be evaluated by performing two sets of experiments. In the first set of experiments where c_A is constant

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and c_B is variable, the first set of apparent kinetic constants may be obtained treating the data as explained for the single substrate reactions. The remaining kinetic constants may be obtained after making experiments with variable c_A and constant c_B (Whitaker 1994).

In aqueous solutions H^+ and OH^- ions interact with the enzyme as

$$E + H^+ \underset{\longleftarrow}{\overset{K_{EH}}{\longrightarrow}} EH^+, \tag{3.14a}$$

$$E + OH^- \underset{\longleftarrow}{\overset{K_{EOH}}{\longrightarrow}} EOH^+. \tag{3.14b}$$

When we combine the temperature and the pH effects we end up with the following equation:

$$c_{\text{active}} = \frac{\text{Act}_0}{\left(1 + \frac{c_{H^+}}{K_{EH}} + \frac{K_W}{K_{EOH}}\frac{1}{c_{H^+}}\right)}. \tag{3.15}$$

Where Act_0 is the maximum attainable activity of the enzyme. MATLAB® code 3.1 simulates the pH effects on hazelnut lipase.

MATLAB® CODE 3.1

Command Line:

```
clear all
close all

% enter the data
ActData = [0.08 0.10 0.12 0.4 0.41 0.45 0.77 0.81 0.82 0.85 0.85 0.90
0.99 1.00 1.02 0.95 0.88 0.87 0.80 0.85 0.80 0.81 0.82 0.80 0.79 0.75
0.6 0.3 0.2 0.35 0.35 0.28 0.38 0.34 0.50 0.46 0.44 0.42 0.40 0.38
0.35 0.4 0.38 0.40]; % experimentally determined enzyme activities
pHData = [3.6 3.6 3.6 4.0 4.0 4.0 4.25 4.25 4.25 4.25 4.5 4.5 4.5 4.5
4.75 4.75 4.75 4.75 4.75 5.0 5.0 5.0 5.0 5.25 5.25 5.25 5.75 6.5 6.5
7.0 7.25 7.25 7.25 7.50 7.50 7.50 7.50 7.75 7.75 7.75 7.75 8.0 8.0
8.75]; % pH values were the ActData were obtained

% plot the experimental data
plot(pHData,ActData,'*'); hold on
xlabel('pH')
ylabel('Activity')
xlim([3 9])

% enter the model parameters and experimental constraints
EsR = 4141.7;%EsR = Es/R
Tref = 45;% reference temperature (^oC)
T = 25;% temperature of the experiments (^oC)
KEH1 = 6.371e-5;
KEH2 = 1.106e-7;
KEOH1 = 2.872e-9;
```

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```
KEOH2 = 3.405e-6;
Kw = 1e-14;
Act0_1 = 1.35;
Act0_2 = 0.6;

% modeling
pH1 = 3.0:0.1:6.5;
pH2 = 6.5:0.1:9.0;

for i = 1:length(pH1)
    H1(i) = exp(-2.303*pH1(i));
    ActpH1(i) = Act0_1/(1 + (H1(i)/KEH1) + Kw/(KEOH1*H1(i)));
end

for j = 1:length(pH2)
H2(j) = exp(-2.303*pH2(j));
ActpH2(j) = Act0_2/(1 + (H2(j)/KEH2) + Kw/(KEOH2*H2(j)));
end

% plot the model
plot(pH1,ActpH1,'-',pH2,ActpH2,':'); hold on
grid on
```

When we run the code Figure E.3.3. will appear on the screen.

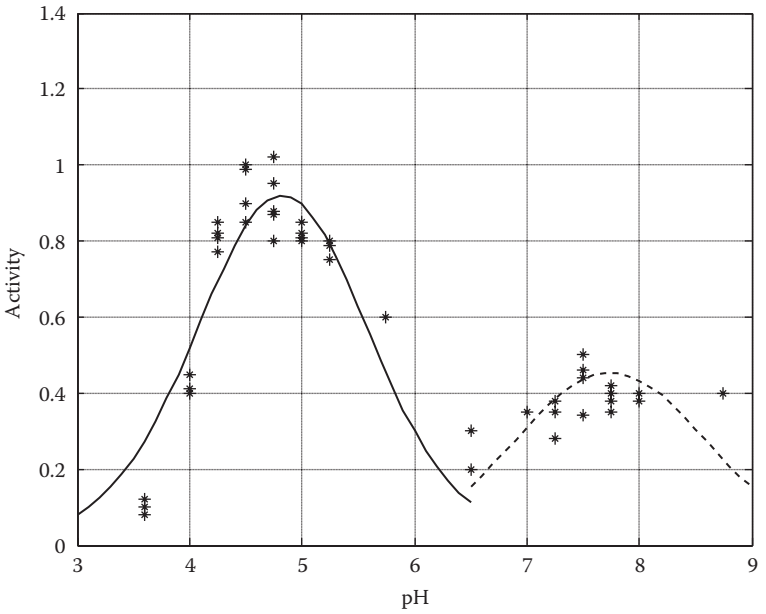


FIGURE 3.3
Effect of the pH variations on the hazelnut lipase. The first iso-enzyme has the maximum activity at about pH = 4.75, the second iso-enzyme has the maximum activity at about pH = 7.75. (Experimental data and constants of the model adapted from Seyhan, F., Tijskens, L. M. M., and Evranuz, O., *Journal of Food Engineering,* 52, 387–95, 2002.)

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Any substance that reduces the rate of an enzyme catalyzed reaction is called an *inhibitor*. A *competitive inhibitor* competes with the substrate for the active site of the enzyme, whereas a *noncompetitive inhibitor* does not.

Under competitive inhibition the Michaelis–Menten mechanism prevails

$$\begin{array}{ccccccccc} E & + & S & \overset{K_S}{\rightleftharpoons} & SE & \xrightarrow{k_p} & P & + & E \\ + & & & & & & & & \\ I & & & & & & & & , \\ \downarrow\uparrow K_i & & & & & & & & \\ EI & & & & & & & & \end{array} \tag{3.16a}$$

where

$$K_s = \frac{c_E c_S}{c_{ES}}, \tag{3.16b}$$

and

$$K_i = \frac{c_E c_I}{c_{EI}}. \tag{3.16c}$$

The product formation rate is

$$v = \frac{dc_p}{dt} = k_p c_{ES}. \tag{3.16d}$$

Equation 3.16b may be rearranged as

$$v = k_p \frac{c_{E0}}{c_E + c_{ES} + c_{EI}} c_{ES}, \tag{3.16e}$$

where $c_{E0} = c_E + c_{ES} + c_{EI}$. After substituting $v_{\max} = k_p c_{E0}$ and using Equations 3.16b and 3.16c to eliminate c_{ES} and c_{EI}, Equation 3.16e becomes

$$v = \frac{v_{\max} c_S}{c_S + K_s\left(1 + \frac{c_I}{K_i}\right)}. \tag{3.16f}$$

After comparing Equation 3.16f with Equation 3.8 we see that the competitive inhibitor increased the Michaelis constant K_M by a factor of $(1 + c_I/K_i)$. Equation 3.16f implies that v decreases with c_I and increases with K_i. When $c_s \gg K_s(1 + c_I/K_i)$, an inhibitor may not have a considerable effect on the reaction rate. After substituting $K_I = K_s(1 + c_I/K_i)$, Equation 3.16f may be rearranged as

$$\frac{1}{v} = \frac{1}{v_{\max}} + \frac{K_I}{v_{\max}} \frac{1}{c_S}. \tag{3.17}$$

The type of an inhibition where $v_{\max}$ remains approximately the same with all inhibitor concentrations is referred to as the noncompetitive. A noncompetitive inhibitor binds to a

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site different than that of the substrate. If the Michaelis–Menten mechanism prevails, after including the inhibitor we will have

$$\begin{array}{ccccccccc} E & + & S & \overset{K_S}{\rightleftharpoons} & SE & \xrightarrow{k_p} & P & + & E \\ + & & & & + & & & & \\ I & & & & I & & & & , \\ \downarrow\uparrow K_i & & & & \downarrow\uparrow K_i & & & & \\ EI & + & S & \overset{K_S}{\rightleftharpoons} & ESI & & & & \end{array} \tag{3.18a}$$

where the dissociation constants are

$$K_s = \frac{c_E c_S}{c_{ES}} = \frac{c_{EI} c_S}{c_{ESI}}, \tag{3.18b}$$

$$K_i = \frac{c_E c_I}{c_{EI}} = \frac{c_{ES} c_I}{c_{ESI}}, \tag{3.18c}$$

The product formation rate is

$$v = \frac{dc_p}{dt} = k_p c_{ES}. \tag{3.18d}$$

Equation 3.18d may be rearranged as

$$v = k_p \frac{c_{E0}}{c_E + c_{ES} + c_{EI} + c_{ESI}} c_{ES}, \tag{3.18e}$$

where $c_{E0} = c_E + c_{ES} + c_{EI} + c_{ESI}$. After substituting $v_{\max} = k_p c_{E0}$ and using Equations 3.18b and 3.18c to eliminate c_{ES} and c_{EI}, Equation 3.18e becomes

$$v = \frac{v_{app} c_S}{c_S + K_s}, \tag{3.18f}$$

where $v_{app} = v_{\max}/(1 + c_I/K_i)$. After comparing Equation 3.18f with Equation 3.8 we see that the noncompetitive inhibitor decreased the apparent maximum rate $v_{\max}$ by a factor of $(1 + c_I/K_i)$. Equation 3.18f implies that v decreases with c_I. Increasing c_S does not affect v_{app}. Equation 3.18f may be rearranged as

$$\frac{1}{v} = \frac{1}{v_{app}} + \frac{K_S}{v_{app}} \frac{1}{c_S}. \tag{3.19}$$

Parameters v_{app} and K_S may be evaluated from intercept and slope.

MATLAB® code 3.2 describes determination of the type of inhibition and numerical values of parameters $v_{\max}$ and K_I during inhibition of mushroom tyrosinase by o-toluic acid.

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MATLAB® CODE 3.2

Command Line:

```
clear all
close all
format compact

% enter the data
cInv = [1.0 1.5 2.0 2.5 3.0]; % 1/(substrate concentration)
(1/micro mole)
vInv = [0.015 0.0175 0.021 0.025 0.028;0.011 0.014 0.016 0.018
0.021;0.010 0.011 0.0145 0.0165 0.0175]; % 1/(reaction rate) (min/
micro mole)
cI = [0.75 0.25 0]; % inhibitor concentration
cInvModel = -1:0.1:4;

% Lineweaver Burk Plot
plot(cInv,vInv(1,:),'s', cInv,vInv(2,:),'o', cInv,vInv(3,:),'d');
hold on % plot the data
xlim([-1 4])
ylim([0 0.035])
ylabel('1/v (micro mole/min)^-^1')
xlabel('1/c (1/mM)^-^1')
legend('0 mM' , '0.25 mM', '0.75 mM','Location','SouthEast')
grid on

N = 1; % fit a first order polynomial
for i = 1:3
f = polyfit(cInv,vInv(i,:),N);
fp = polyval(f, cInvModel);
Vmax(i) = 1/f(2);
KI(i) = Vmax(i)*f(1);
plot(cInvModel, fp); hold on % plot the model
end

% plot the model parameters as a function of the inhibitor
concentration
figure
[AX,H1,H2] = plotyy(cI,Vmax,cI, KI,'plot'); hold on
set(H1,'LineStyle','o')
set(H2,'LineStyle','+')
axes(AX(1)); hold on; line( cI, polyval(polyfit(cI, Vmax,1),cI));
axes(AX(2)); hold on; line( cI, polyval(polyfit(cI, KI,1),cI));
xlabel('inhibitor concentration (mM)')
set(get(AX(1),'ylabel'), 'string', 'v_m_a_x (mM/min)')

set(get(AX(2),'ylabel'), 'string', 'K_I (mM)')
legend('v_m_a_x', 'K_I',2,'Location','SouthEast')
grid on
```

Figure 3.4a and b will appear on the screen after running the code.

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Parameters v_{max} and K_I may be evaluated from the intercept and slope as explained with a typical example in Figure 3.4a. Increasing the concentration of the inhibitor results in a family of lines with different slopes and intercepts. They also intercept each other when 1/c ≅ –0.75. Since both K_I and v_{max} varies with an o-toluic acid concentration (Figure 3.4b) inhibition is referred to as mixed type.

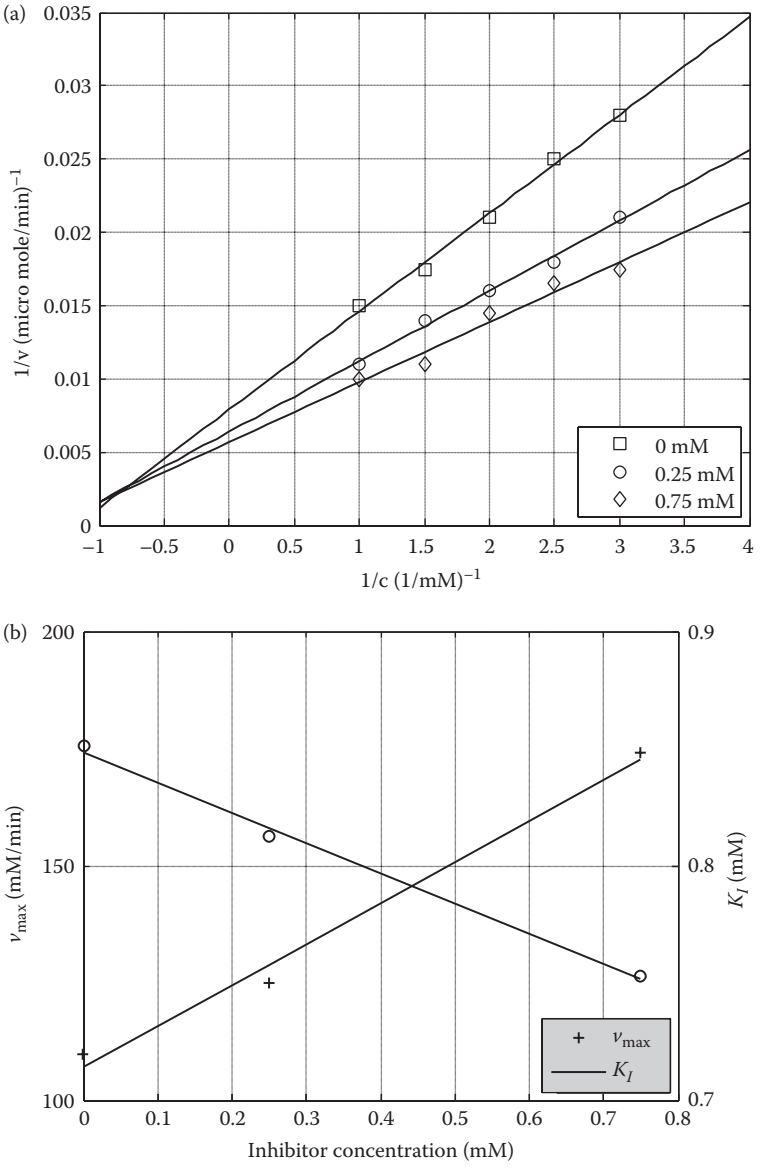


FIGURE 3.4
(a) Double reciprocal plot to evaluate kinetic constants under noncompetitive inhibition of mushroom tyrosinase by o-toulic acid. (b) Variations of the model parameters v_{max} and K_M with inhibitor (o-toluic acid) concentration. (Adapted from Huang, X.-H., Chen, Q.-X., Wang, Q., Song, K.-K., Wang, J., Sha, L., and Guan, X., *Food Chemistry*, 94, 1–6, 2006.)

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The maximum attainable rate v_{max} in Equation 3.8 was defined when the initial enzyme activity c_{E0} was constant as

$$v_{max} = k_3 c_{E0}. \tag{3.9}$$

Temperature effects on the rate constant k_3 may be simulated with the Arrhenius expression:

$$k_3 = k_0 \exp\left\{-\frac{E_a}{RT}\right\}. \tag{3.5}$$

Denaturation of the enzyme may be expressed with a first-order rate expression:

$$\frac{dc_E}{dt} = -k_d c_E. \tag{3.20}$$

At a constant temperature T when the enzyme undergoes denaturation, after integrating Equation 3.20 and combining with Equations 3.5 and 3.9 we may express the temperature dependence of the enzyme activity as

$$v = \frac{c_S c_{E0} k_0 e^{-k_d t} e^{-E_a/RT}}{K_M + c_S}. \tag{3.21}$$

Example 3.9: Kinetic Compensation Relations for Pectinesterase Inactivation During Pasteurization of Orange Juice

Enzyme inactivation during thermal processing of the foods may be described in analogy with unimolecular, irreversible, first-order chemical reaction (Ulgen and Özilgen 1991):

$$\underset{\text{active enzyme}}{E} \rightarrow \underset{\text{inactive enzyme}}{E_i}$$

$$\frac{dc_E}{dt} = -k_d c_E. \tag{3.20}$$

After integrating Equation 3.20 we will have

$$\ln c_E = \ln c_{E0} - k_d t. \tag{E.3.9.1}$$

When we plot $\ln(c_E)$ versus time during inactivation at a constant temperature, the slope of the line gives k_d as exemplified in Figure E.3.9.1. MATLAB® code E.3.9 evaluates the inactivation model constants from the data obtained at 60 and 70°C.

Kinetic constants k_0 and E_a of the Arrhenius expression are not usually independent of each other in a family of related systems where parameters k_0 and E_a change due to slight variations in the experimental conditions (like pH, sugar concentration, etc.). The variation in E_a may be compensated by the changes in k_0 with the relation (Figure E.3.9.2):

$$\ln(k_0) = \alpha E_a + \beta, \tag{E.3.9.2}$$

where α and β are constants. MATLAB® code E.3.9.b evaluates the compensation relation with the given $\ln k_0$ and E_a data.

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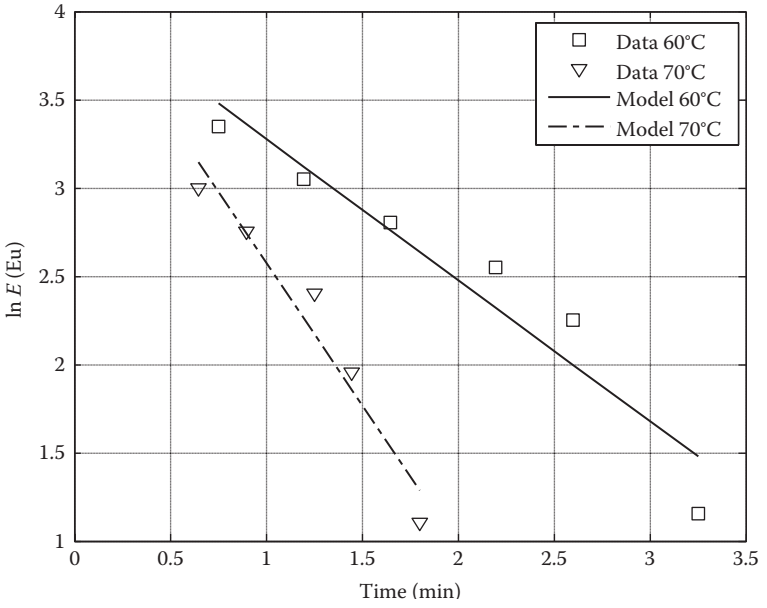


FIGURE E.3.9.1
Typical plots for pectinesterase inactivation (observed as a decrease in enzyme activity) during pasteurization of orange juice. (From Ulgen, N., and Özilgen, M. *Journal of the Science of Food and Agriculture,* 57, 93–100, 1991.)

MATLAB® CODE E.3.9.a

Command Window:

```
clear all
close all
format compact

% enter the inactivation data
lnE60 = [3.35 3.05 2.80 2.55 2.25 1.15]; % remaining enzme activities
at 60 oC
t60 = [0.75 1.20 1.65 2.20 2.60 3.25]; % times when enzyme activities
were determined at 60 oC
lnE70 = [3.0 2.75 2.40 1.95 1.10]; % remaining enzme activities at 70 oC
t70 = [0.65 0.90 1.25 1.45 1.80]; % times when enzyme activities were
determined at 70 oC

% plot the activity loss data
plot(t60, lnE60, 's'); hold on
plot(t70, lnE70, 'v'); hold on,
axis([0 3.5 1 4])
ylabel('ln E (Eu)')
xlabel('Time (min)')
grid on,

% enzyme inactivation model at T = 60 oC
N = 1; % fit a first order polynomial (line) to the data
f1 = polyfit(t60,lnE60,N);
```

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```
fp1 = polyval(f1, t60);
Slope60 = f1(1)

% determine the correlation coefficient
rmatrix = corrcoef(t60,lnE60);
r1 = rmatrix(1,2);
Corr_Coef_1 = r1

% determine the Standard error
for i = 1:length(t60);
    d1(i) = (lnE60(i)-(f1(2) + f1(1)*t60(i)))^2;
end;

Se1 = sqrt(mean(d1));
Standard_Error_1 = Se1

 % enzyme inactivation model at T = 70 oC
f2 = polyfit(t70,lnE70,N);
fp2 = polyval(f2, t70);
Slope70 = f2(1)

% determine the correlation coefficient
rmatrix = corrcoef(t70,lnE70);
r2 = rmatrix(1,2);
Corr_Coef_2 = r2

% determine the Standard error
for i = 1:length(t70);
    d2(i) = (lnE70(i)-(f2(2) + f2(1)*t70(i)))^2;
end;

Se2 = sqrt(mean(d2));
Standard_Error_2 = Se2

% plot the activity loss model
plot(t60, fp1); hold on
plot(t70, fp2, 'k-.'); hold on
legend('data o60 C','data 70 oC','model 60 oC', 'model 70 oC')
```

When we run the code the following lines and Figure E.3.9.1 will appear on the screen:

```
Slope60 =
   -0.8029
Corr_Coef_1 =
   -0.9578
Standard_Error_1 =
    0.2032
Slope70 =
   -1.6151
Corr_Coef_2 =
   -0.9739
Standard_Error_2 =
    0.1523
```

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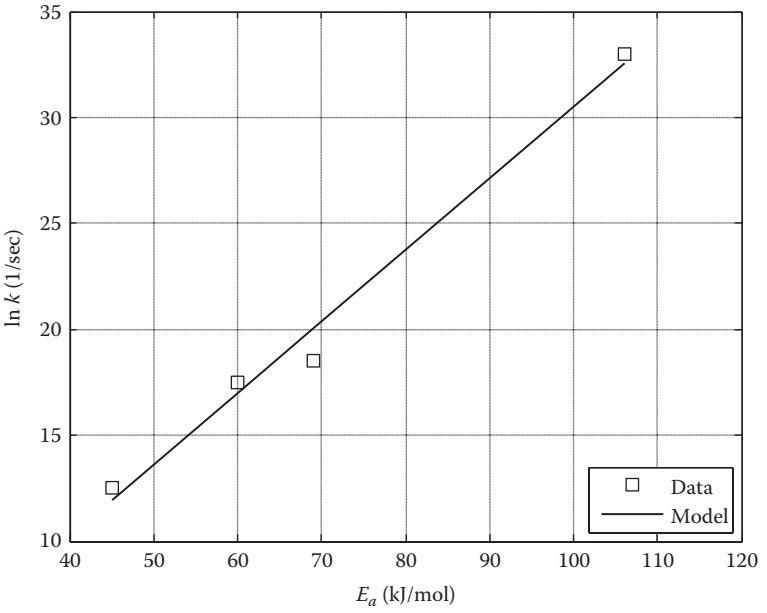


FIGURE E.3.9.2
Kinetic compensation relation for pectinesterase inactivation during pasteurization of orange juice. Equation of the line: $\ln(k_0) = 0.3373E_a - 3.24$. (From Ulgen, N., and Özilgen, M. *Journal of the Science of Food and Agriculture,* 57, 93–100, 1991.)

MATLAB® CODE E.3.9.b

Command Window:

```
clear all
close all
format compact

% enter the Arrhenius expression data
lnk0Data = [12.5 17.5 18.5 33]; % pre-exponential constants data
EaData = [45 60 69 106]; % activation energies
% plot the data
plot(EaData,lnk0Data,'s'); hold on
axis([40 120 10 35])
ylabel('ln k (1/sec)')
xlabel('Ea (kJ/mol)')
grid on

% compensation relation
N = 1; % fit a first order polynomial (line) to the data
f3 = polyfit(EaData,lnk0Data,N);
fp3 = polyval(f3, EaData);
slope3 = f3(1)
Intercept3 = f3(2)

% plot the model
plot(EaData, fp3); hold on
legend('data','model', 'Location', 'SouthEast')
```

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```
% evaluate the correlation coefficient
rmatrix = corrcoef(EaData,lnk0Data);
r3 = rmatrix(1,2);
Corr_Coef_3 = r3

% evaluate the standard error
for i = 1:length(EaData);
     d3(i) = (lnk0Data(i)-(f3(2) + f3(1)*EaData(i)))^2;
end;

Se3 = sqrt(mean(d3));
Standard_Error_3 = Se3
```

When we run the code the following lines and Figure E.3.9.2 will appear on the screen:

```
slope3 =
    0.3373
Intercept3 =
   -3.2353
Corr_Coef_3 =
    0.9932
Standard_Error_3 =
    0.8882
```

Example 3.10: Kinetics of Inactivation of the Peroxidase Iso Enzymes During Blanching of Potato Tuber

Peroxidase is usually present in the fruits and vegetables as a combination of various iso enzymes with different heat stabilities. During blanching of a spherical potato tuber the controlling equation of the temperature profile is (Example 2.9)

$$\frac{T - T_1}{T_0 - T_1} = \frac{R}{r}\left(\frac{2}{\pi}\right)\sum_{n=0}^{\infty}\left\{\frac{(-1)^{n+1}}{n}e^{-(\pi n)2}\sin\left(\frac{\pi nr}{R}\right)\right\}. \tag{E.3.10.1}$$

Inactivation kinetics of the enzyme may be described with separate first-order reactions for heat stable and heat labile fractions (Sarikaya and Özilgen 1991):

$$\frac{dc_{E1}}{dt} = -k_1 c_{E1}, \tag{E.3.10.2}$$

and

$$\frac{dc_{E2}}{dt} = -k_2 c_{E2}. \tag{E.3.10.3}$$

Total enzyme activity is

$$c_E = c_{E1} + c_{E2}. \tag{E.3.10.4}$$

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Temperature effects on the inactivation rate constants k_1 and k_2 were described with the Arrhenius expression:

$$k_1 = k_{10} \exp\left\{-\frac{E_{a1}}{R_g T}\right\}, \tag{E.3.10.5}$$

and

$$k_2 = k_{20} \exp\left\{-\frac{E_{a2}}{R_g T}\right\}. \tag{E.3.10.6}$$

MATLAB® code E.3.10 plots the model to describe the variation of temperature and enzyme activity as a function of time.

MATLAB® CODE E.3.10

Command Window:

```
clear all
close all

% enter the constants of the model
  T1 = [65 72 80]; % blanching water temperature
  k = ['k -', 'k :', 'k.- ']; % color and line characteristics
  T0 = 17.5; % initial temperature of the potato
  T(1) = T0;
  Rg = 8.3e-3; % gas constant(kj/mol K)
  alpha = (1.93e-7)*60; % thermal diffusivity (m2/min)
  k0 = 3e14; % pre-exponential constant
  Ea1 = 101.2; % activation energy (kJ/mol)
  Ea2 = 83.6; % activation energy (kJ/mol)
  E1(1) = 0.027; E2(1) = 0.028-E1(1); E(1) = E1(1) + E2(1);

  time(1) = 0;
  r = 0.6e-2; % distance from the center (m)
  R = 4.1e-2; % radius of the potato (m)

% temperature profile model
       for n = 0:100
          s(n + 9) = sin(pi*n*r/R);
        end
     Csin = sum(s)*(r/R);

for i = 1:length(T1)
     for t = 10:10:70
       for n = 0:100
        s(n + 9) = (Csin)*exp(-((pi*n)^2)*alpha*t/(R^2))*sin(n*pi*r/R);
       end
          T(t/10 + 1) = (R/(r))*(sum(s))*(T0-T1(i)) + T1(i);
          time(t/10 + 1) = t;
          ss(t/10 + 1) = sum(s);
          k1(t/10 + 1) = k0*exp(-Ea1/(Rg*(T(t/10 + 1) + 273)));
          k2(t/10 + 1) = k0*exp(-Ea2/(Rg*(T(t/10 + 1) + 273)));
```

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```
            E1(t/10+1)=E1(1)*exp(-k1(t/10+1)*t);
            E2(t/10+1)=E2(1)*exp(-k2(t/10+1)*t);
            E(t/10+1)=E1(t/10+1)+E2(t/10+1);
      end

% plot the temperature profile model
      figure(1)
      plot(time,T,k((3*i-2):(3*i))); hold on
      ylabel('Temperature (C)');
      xlabel('Time (min)');
      legend('65 oC','72 oC','80 oC',3,'Location','Best')
      grid on

% plot the enzyme inactivation model
      figure(2)
      plot(time,E,k((3*i-2):(3*i))); hold on % enzyme inactivation
      ylabel('E (Eu)');
      xlabel('Time (min)');
      legend('65 oC','72 oC','80 oC',3,'Location','Best')
      grid on
end
```

Figures E.3.10.1 and E.3.10.2 will appear on the screen when we run the code.

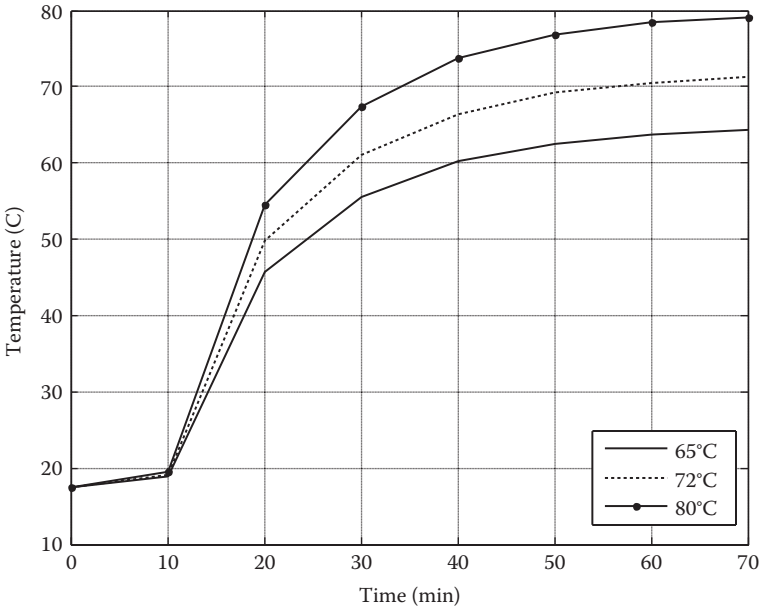


FIGURE E.3.10.1
Temperature profiles at $r = 0.6$ cm distance from the center during thermal processing of whole potatoes. (Constants of the model adapted from Sarikaya, A., and Özilgen, M., *Lebensmittel-Wissenschaft und Technologie*, 24, 159–63, 1991.)

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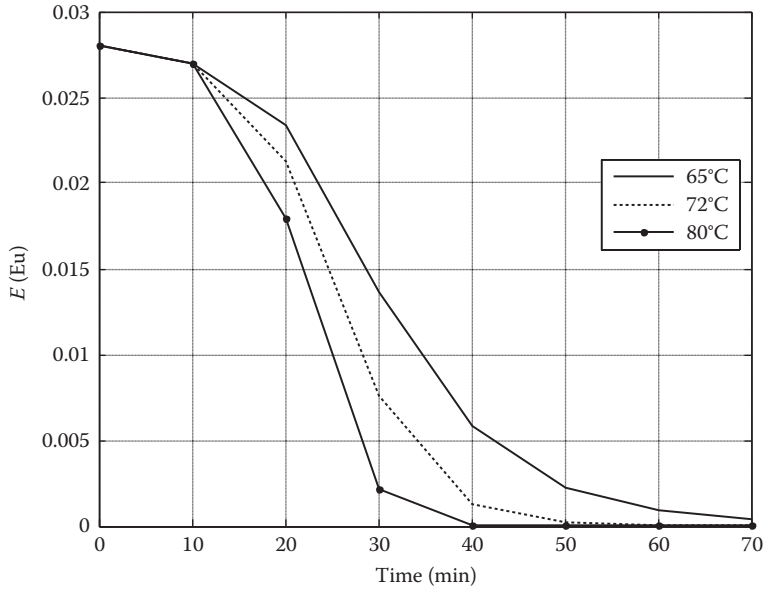


FIGURE E.3.10.2
Enzyme activity profiles at $r = 0.6$ cm distance from the center during thermal processing of whole potatoes. (Constants of the model adapted from Sarikaya, A., and Özilgen, M., *Lebensmittel-Wissenschaft und Technologie*, 24, 159–63, 1991.)

Enzyme activity may reappear some time after thermal processing, if heat treatment is not sufficient. The total Gibbs free energy of an enzyme suspension is (Shulz and Schirmer 1979)

$$\Delta G_{\text{total}} = \Delta H_{\text{chain}} - T\Delta S_{\text{chain}} + \Delta G_{\text{solvent}}, \tag{3.22}$$

where ΔG_{total} is the total Gibbs free energy of an enzyme plus the solvent, ΔH_{chain} is the binding enthalpy of the chain in a vacuum provided mostly by hydrogen bonding and van der Waals interactions in the chain, ΔS_{chain} is the chain entropy, T is the absolute temperature, and $\Delta G_{\text{solvent}}$ is the Gibbs free energy of solvent. The chain plus a solvent system attains the minimum ΔG_{total} (and maximum ΔS_{chain}) corresponding to the active folding pattern of the enzyme in its native environment (i.e., the vegetable or animal tissue). The secondary, tertiary, and the quaternary structure of the proteins are dictated by their primary structure. Destroying the protein structure at any level eliminates the enzyme activity, but the enzyme may fold back to the original structure and regain its activity due to the thermodynamic reasons, if the primary structure should not be destroyed. The primary structure of the proteins or their postproduction modifications, including the –S–S- bonds, are required to be destroyed irreversibly to prevent regaining of the enzyme activity.

In biological reactors or sensors, enzymes are frequently immobilized by using a carrier. Immobilization may be achieved via entrapment in the network or binding on the surface of a carrier. Either pure or crude enzyme preparations or the whole cell may be immobilized. When the enzymes are immobilized into the spherical particles Equation 2.14 (the

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equation of continuity in a spherical coordinate system) may be simplified under steady state conditions as

$$D_e \frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dc}{dr}\right) = \frac{v_{app} c}{c + K_M}, \tag{3.23a}$$

where $c = c(r)$ = substrate concentration in the particle and D_e = effective diffusivity of the substrate within the particle, v_{app} is the maximum attainable apparent rate of the immobilized enzyme, and K_M is the Michaelis constant of the free enzyme. The boundary conditions are

$$c = c_s \quad \text{at } r = R, \tag{3.23b}$$

$$\frac{dc}{dr} = 0 \quad \text{at } r = 0, \tag{3.23c}$$

where c_s is the substrate concentration on the surface of the particle. When $c << K_M$, Equation 3.23a becomes

$$\frac{1}{r^2}\frac{d}{dr}\left(r^2 \frac{dc}{dr}\right) = \frac{v_{app} c}{D_e K_M}. \tag{3.24a}$$

The solution to Equation 3.24a is (Bird, Stewart and Lightfoot 2007)

$$\frac{c(r)}{c_b} = r^* \frac{\sinh[\phi r^*]}{\sinh[\phi]}, \tag{3.24b}$$

where $r^* = r/R$ and parameter $\phi = R\sqrt{v_{\max}/D_e K_M}$. Parameter ϕ is called the *Thiele modulus*.

The reaction rate on the surface of the particle is

$$r_{\text{surface}} A_{\text{surface}} = 4\pi R^2 N_s = -4\pi R^2 D_e \left[\frac{dc}{dr}\right]_{r=R}. \tag{3.24c}$$

Where r_{surface} is the reaction rate per unit area of the surface and A_{surface} is the surface area of the particle. We will obtain the following equation after substituting Equation 3.24b in Equation 3.24c (Bird, Stewart and Lightfoot 2007):

$$r_{\text{surface}} A_{\text{surface}} = 4\pi R^2 D_e c_s \left[1 - \phi \coth(\phi)\right]. \tag{3.24d}$$

If the enzymes would not have been immobilized, the total reaction rate would be

$$r_{\text{volume}} V_{\text{particle}} = \frac{4}{3}\pi R^3 \left[\frac{v_m c_s}{K_M}\right]. \tag{3.24e}$$

The effectiveness factor η is defined as (Bird, Stewart and Lightfoot 2007; Wang et al. 1979)

$$\eta = \frac{r_{\text{surface}} A_{\text{particle}}}{r_{\text{volume}} V_{\text{particle}}} = \frac{3}{\phi}\left[\frac{1}{\tanh(\phi)} - \frac{1}{\phi}\right]. \tag{3.24f}$$

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Variation of the effectiveness factor with Thiele modulus is computed with MATLAB® code 3.3 and depicted in Figure 3.5.

The apparent value of Michaelis constant K_M and v_{max} may change upon immobilization. The support may reduce the activity of an immobilized enzyme toward large molecules via steric hindrance of the active site. An immobilized enzyme is also in a different

MATLAB® CODE 3.3

Command Window:

```
clear all
close all

fi = 0.4:0.01:100;

for i = 1:length(fi)
    eta(i) = (3/fi(i))*((1/tanh(fi(i)))-(1/fi(i))); % tanh = hyperbolic
tangent
end

semilogx(fi,eta); % temperature profiles
grid on
ylabel('Effectiveness Factor');
xlabel('Thiele Modulus');
xlim([0.4 100]);
```

Figure 3.5 will appear on the screen when we run the code.

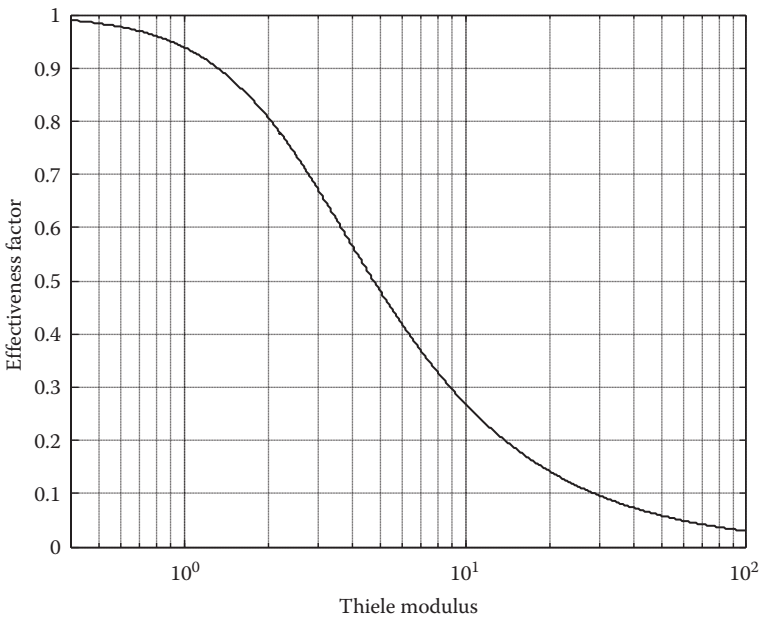


FIGURE 3.5
Theoretical relationship between the Thiele modulus and the effectiveness factor.

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medium than its native environment. When the support has a net charge, the pH of the microenvironment of the enzyme may be different than the pH of the bulk medium due to the electrostatic interactions (Goldstein, Levin, and Katchalski 1964):

$$\Delta pH = pH^i - pH^b = 0.43\frac{zF\psi}{RT}, \tag{3.25}$$

where $pH^i = pH$ of the microenvironment of the enzyme, $pH^b = pH$ of the bulk medium, z = net charge on the diffusing substrate, F = Faraday constant, y = electrostatic potential, R = gas constant. The intrinsic activity of the enzyme is altered by the local changes in pH and ionic constituents. Further alterations in the apparent kinetics are due to the repulsion or attraction of substrates or inhibitors. A similar expression may also be suggested for the variation of K_m upon immobilization (Wang et al. 1979):

$$\Delta pK_M = pK_M^i - pK_M^b = \log\left[\frac{K_M^b}{K_M^i}\right] = 0.43\frac{zF\psi}{RT}, \tag{3.26}$$

where K_M^b = Michaelis constant in the bulk medium and K_M^i = Michaelis constant in the microenvironment.

When the enzymes are bound and evenly distributed on the surface of a nonporous support material, substrate diffuses through a thin liquid film surrounding the support to reach the active sites of the enzymes. Under steady state conditions the reaction rate equals the mass transfer rate:

$$k(c_{Ab} - c_{As}) = \frac{v_{app}c_{As}}{c_{As} + K_{app}}, \tag{3.27}$$

where k = mass transfer coefficient, c_{Ab} = substrate concentration in the bulk liquid, c_{As} = substrate concentration on the surface, v_{app} and K_{app} = apparent kinetic constants. When the system is strongly mass transfer limited $c_{As} \cong 0$, since the reaction is rapid compared to mass transfer, and the system behaves as pseudo first order:

$$v = k\, c_{Ab} \quad \text{(when Da} \gg 1), \tag{3.28}$$

where a Damköhler number is defined as Da = v_{app}/kc_{Ab} = maximum attainable reaction rate/maximum attainable mass transfer rate. When the system is reaction limited the reaction rate is often expressed as

$$v = \frac{v_{app}c_{As}}{c_{As} + K_{app}} \quad \text{(when Da} \ll 1). \tag{3.29}$$

Under these circumstances the apparent constants may be obtained from the double-reciprocal plot.

3.7 Analogy Kinetic Models

Variation of the sensory properties of the foods may be studied in analogy with chemical kinetics. There are numerous examples to this approach in the literature.

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Example 3.11: Kinetics of Browning of Milk

The difference of color DC between samples and the raw milk reference were determined with the following equation:

$$\Delta C = \sqrt{\Delta a^2 + \Delta b^2 + \Delta L^2}, \tag{E.3.11.1}$$

where *a*, *b*, and *L* are the hunter color scale parameters. Kinetics of browning was expressed in analogy with zero-order kinetics:

$$\frac{d(\Delta C)}{dt} = k. \tag{E.3.11.2}$$

After integration we will have

$$\Delta C = \Delta C_0 + kt. \tag{E.3.11.3}$$

Where ΔC_0 is the intercept with $t = 0$ axis. Comparison of the integrated equation with the experimental data is shown in Figure E.3.11.

Further analysis of the data indicated that

$$\Delta C_0 = -13.8909 + 0.0385785T, \tag{E.3.11.4}$$

where *T* is the heating temperature in *K*. The rate constant was expressed with the Arrhenius equation:

$$k = 1.2 \times 10^{13} \exp\left\{-\frac{101.8}{8.314 \times 10^{-3} T}\right\} \tag{E.3.11.5}$$

Details of computations are depicted in MATLAB® code E.3.11.

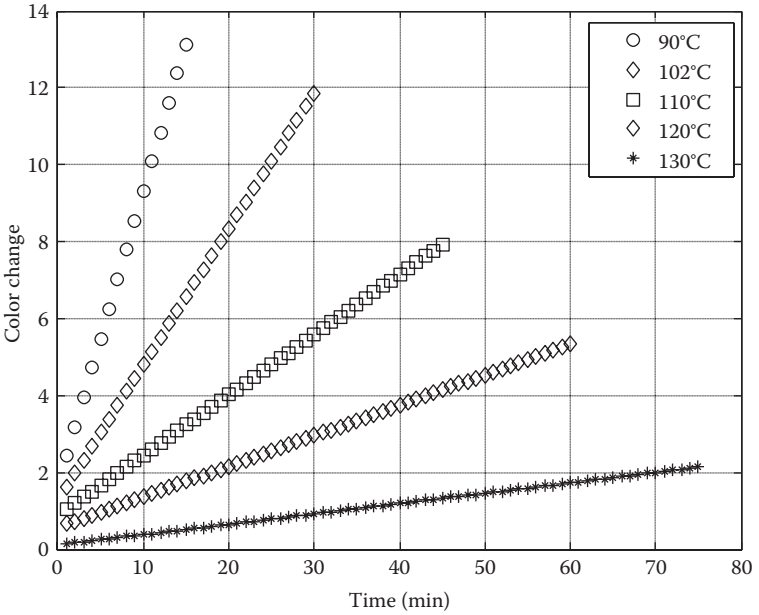


FIGURE E.3.11
Variation of ΔC with time at different temperatures. (From Pagliarini, E., Vernille, M., and Peri, C., *Journal of Food Science*, 55, 1766–67, 1990.)

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MATLAB® CODE E.3.11

Command Window:

```
clear all
close all

T = [90 102 110 120 130]; % temperature data
f = ['ro', 'bd', 'gv', 'ks', 'm*']; % define the color and the
legends (ro is red o, bd is blue diamond, gv is green triange, ks is
black square, m* is magenta *)

% modeling
for i = length(T):-1:1 % this loop works from i = 4 towards i = 1
    for t = 0:((6-i)*15)
      Co = -13.8909 + 0.0385785*(T(i) + 273);
      k = (1.2e13)*exp(-(101.8)/((8.314e-3)*(T(i) + 273))); % compute
the reaction rate constant
      C(t + 1) = Co + k*t;
      time(t + 1) = t; % model times
    end
    plot(time, C, f((2*(6-i)-1):(2*(6-i)))); hold on
end

xlabel('time (min)');
ylabel('color change');
legend('90 C','102 C','110 C', '120 C', '130 C')
grid on
```

Example 3.12: Kinetics of the Color Change and Polyphenol Oxidase Inactivation During Blanching of the Sultana Grapes

Sultana grapes were blanched in water then dried in a tray dryer. The effect of the blanching time on Hunterlab L values of raisins was expressed as an analogy with zero-order rate expression

$$\frac{dL}{dt} = k_L, \tag{E.3.12.1}$$

where k_L is the apparent rate constant. After integration

$$L = L_0 + k_L t, \tag{E.3.12.2}$$

where L_0 is the initial Hunterlab L value. The inactivation of polyphenol oxidase (PPO) was modeled with zero-order rate expression (Aguilera, Oppermann, and Sanchez 1987):

$$\frac{d(\text{PPO})}{dt} = -k_{\text{PPO}}, \tag{E.3.12.3}$$

where k_{PPO} is the apparent rate constant. After integration

$$\text{PPO} = \text{PPO}_0 - k_{\text{PPO}} t \tag{E.3.12.4}$$

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where PPO_0 is the initial polyphenol oxidase activity. The percentage of inactivation of the PPO may be expressed as (Aguilera, Oppermann, and Sanchez 1987)

$$\frac{PPO_0 - PPO}{PPO_0} \times 100 = k_{PPO} \frac{100}{PPO_0} t. \tag{E.3.12.5}$$

Equations E.3.12.2 and E.3.12.5 were compared with the experimental data in Figures E.3.12.1, and E.3.12.2, respectively. The apparent reaction rate constants were also found to agree with the Arrhenius expression (Figure E.3.12.3). Details of the computations are shown in MATLAB® code E.3.12.

Example 3.13: Kinetics of the Change in Texture of the Potatoes During Cooking

Changes in texture of the potatoes during cooking were simulated with zero-order model (Harada, Tirtohusodo, and Paulus 1985):

$$\frac{d(TJ)}{dt} = -k_{texture}. \tag{E.3.13.1}$$

Where TJ stands for the texture judgment and $k_{texture}$ is the apparent rate constant. After integration we will have

$$[TJ] = [TJ]_0 - k_{texture} t, \tag{E.3.13.2}$$

where $[TJ]_0$ is the numerical value of the texture judgment at $t = 0$. MATLAB® code E.3.13 evaluates the apparent rate constant and compares the model with the experimental data.

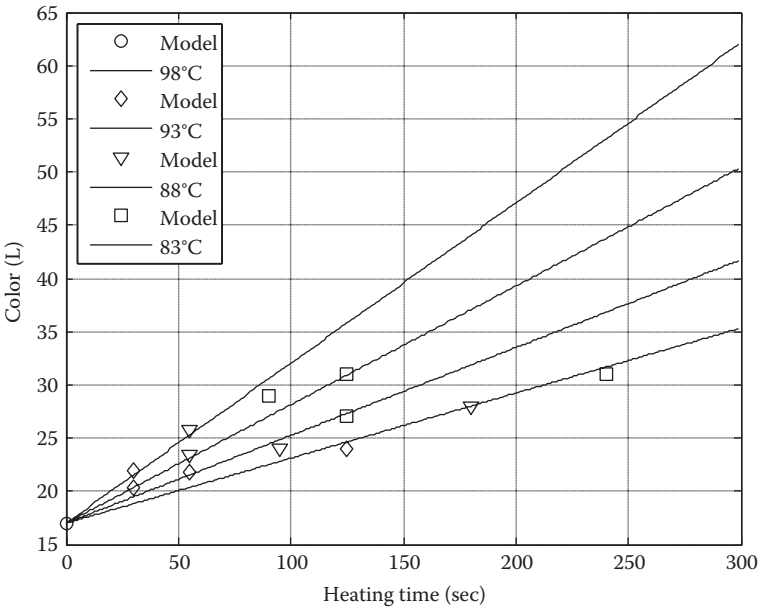


FIGURE E.3.12.1
Comparison of Equation E.3.12.2 with the experimental data (shown in symbols). (From Aguilera, J. M., Oppermann, K., and Sanchez, F., *Journal of Food Science*, 52, 990–93, 1987.)

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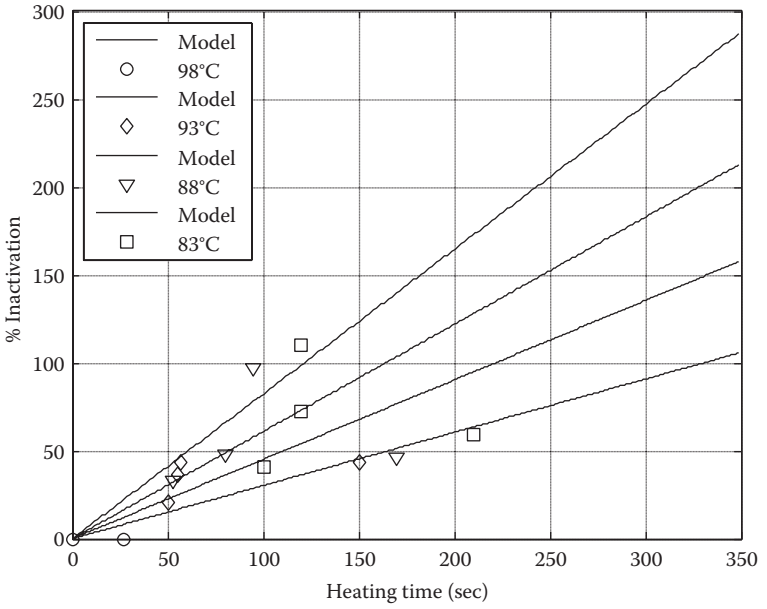


FIGURE E.3.12.2
Comparison of Equation E.3.12.5 with experimental data (shown in symbols). (From Aguilera, J. M., Oppermann, K., and Sanchez, F., *Journal of Food Science*, 52, 990–93, 1987.)

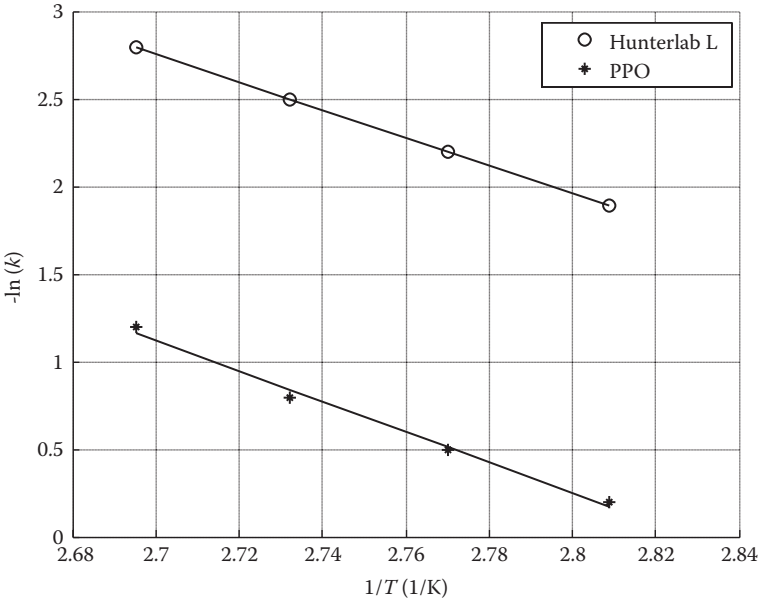


FIGURE E.3.12.3
Arrhenius plots for the inactivation rate constant of PPO (upper line) and Hunterlab L value (o). (From Aguilera, J. M., Oppermann, K., and Sanchez, F., *Journal of Food Science*, 52, 990–93, 1987.)

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MATLAB® CODE E.3.12

Command Window:

```
clear all
close all

% enter the data for figure(1)
L=[17 21.9 25.7 29 ;17 20.34 23.35 31 ;17 21.75 24 27 ;17 24 28 31];
t=[0 30 55 90 ;0 30 55 125 ;0 55 95 125 ; 0 125 180 240]; % time (s)
k(:,1)=[(9.025/60) (6.686/60) (4.953/60) (3.669/60)]; % reaction
rate constants (1/min)

% specify the color and legends for the plots
f=['ro', 'bd', 'gv', 'ks'];

% compute the model L's for figure(1)
for i=1:4
    for tm=0:299
      Lmodel(tm+1)=17+k(i,1)*tm; % model
      timeModel(tm+1)=tm;
      end
         % plot figure(1)
        figure(1)
        plot(t(:,i),L(:,i),f((2*i-1):(2*i)), timeModel,Lmodel,'k-');
hold on % plot the data and the model
end
xlabel('Heating Time (sec)');
ylabel('Color (L)');
legend('model','98 oC', 'model','93 oC', 'model', '88 oC',
'model','83 oC', 'Location', 'NorthWest')
grid on

% enter the data for figure(2)
I=[0 43 97 110 120;0 36 48 72 81;0 21 33 41 82;0 43 46 59 80];
ti=[27 57 95 120 150;27 55 80 120 150;0 50 53 100 195;0 150 170 210
300];
k(:,2)=[(49.4/60) (36.6/60) (27.11/60) (18.17/60)]; % reaction rate
constants (1/min)

 % compute the model inacivation valuess for figure(2)
for i=1:4
    for tm=0:349
       Im(tm+1)=k(i,2)*tm;
       time(tm+1)=tm;
  end

% plot figure(2)
    figure(2)
    plot(time,Im,'k-', ti(:,i),I(:,i),f((2*i-1):(2*i))); hold on %
plot the data and the model
end
```

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```
xlabel('Heating Time (sec)');
ylabel('% Inactivation');
legend('model','98 oC', 'model','93 oC', 'model', '88 oC',
'model','83 oC', 'Location', 'NorthWest' )
grid on

% enter the data for figure(3)
T = [83 88 93 98];
Tinv = (1./(T + 273))*1e3; % inverse temperatures in Kelvin scale
Tinv2 = Tinv';

% compute the best fitting line values for the Arrhenius plot of
figure(3)
k1Arrhenius(:,1) = log(k(:,1));
k2Arrhenius(:,1) = log(k(:,2));
p1 = POLYFIT(Tinv2,k1Arrhenius,1);
p2 = POLYFIT(Tinv2,k2Arrhenius,1);
k1model = p1(1)*Tinv2 + p1(2);
k2model = p2(1)*Tinv2 + p2(2);

% plot figure(3)
figure(3)
plot(Tinv,-log(k(:,1)),'o', Tinv,-log(k(:,2)),'*',Tinv,-k1model,'k-
',Tinv,-k2model,'k-'); hold on;
legend('Hunterlab L','PPO')
xlabel('1/T (1/K)')
ylabel('-ln(k)')
grid on
```

When we run the code Figures E.3.12.1, E.3.12.2, and E.3.12.3 will appear on the screen.

MATLAB® CODE E.3.13

Command Window:

```
clear all
close all
format compact

% enter the data
TJdata110 = [1 2.3 2.9 3.5 5.7 6.8]; % texture judgment data obtained
at 110 oC
tData110 = [0 1 2 3 4 5]; % times that the data were recorded at
110 oC (min)
TJdata100 = [1 2.2 3.3 4.2 5.1 6.8]; % texture judgement data
obtained at 100 oC
tData100 = [0 5 6 7 10 11]; % times that the data were recorded at
100 oC (min)
TJdata90 = [1 1.9 3.2 3.5 3.8 4.4 6.3 6.5]; % texture judgement data
obtained at 90 oC
tData90 = [0 12 18 23 27 35 41 47]; % times that the data were
recorded at 90 oC (min)
```

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```
% plot the data
plot(tData110, TJdata110,'ko', tData100, TJdata100,'kd', tData90,
TJdata90,'ks') ; hold on
ylabel('Texture Judgement')
xlabel('TIME (min)')
legend('110 oC','100 oC','90 oC','Location','SouthEast')

% MODELING at 110 oC
f = polyfit(tData110,TJdata110,1); % find the best fitting line at
110 oC
k110 = f(1) % apparent rate constant at 110 oC
TJo110 = f(2) % initial texture judgement at 110 oC

% find the best fitting line at 110 oC
Tmodel110 = polyval(f, tData110); % find the best fitting line at 110 oC

% find the correlation coefficient
rmatrix = corrcoef(tData110,TJdata110);
r110 = rmatrix(1,2) % correlation coefficient at 110 oC

% MODELING at 100 oC
f = polyfit(tData100,TJdata100,1);
k100 = f(2) % apparent rate constant at 100 oC
TJo100 = f(1) % initial texture judgement at 100 oC

% find the best fitting line at 100 oC
Tmodel100 = polyval(f, tData100);

% find the correlation coefficient
rmatrix = corrcoef(tData100,TJdata100);
r100 = rmatrix(1,2) % correlation coefficient at 100 oC

% MODELING at 90 oC
f = polyfit(tData90,TJdata90,1);
k90 = f(1) % apparent rate constant at 90 oC
TJo90 = f(2) % initial texture judgement at 90 oC

% find the best fitting line at 90 oC
Tmodel90 = polyval(f, tData90);

% find the correlation coefficient
rmatrix = corrcoef(tData90,TJdata90);
r90 = rmatrix(1,2) % correlation coefficient at 90 oC

% plot the model
plot(tData110, Tmodel110,'k-', tData100, Tmodel100,'k-.', tData90,
Tmodel90,'k--')
```

The following lines and Figure E.3.13 will appear on the screen when we run the code:

```
k110 =
    1.1371
TJo110 =
    0.8571
```

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```
r110 =
    0.9805
k100 =
    0.4873
TJo100 =
    0.5045
r100 =
    0.9580
k90 =
    0.1212
TJo90 =
    0.7494
r90 =
    0.9810
```

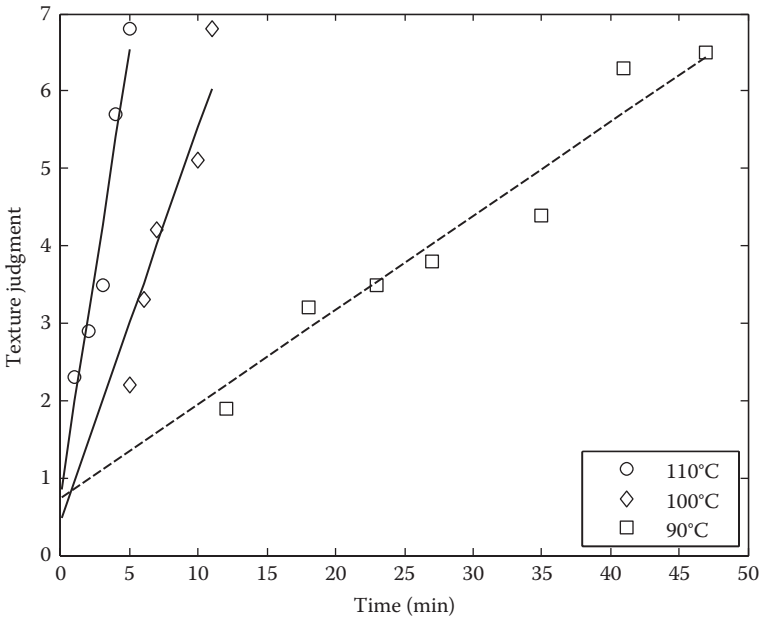


FIGURE E.3.13
Development of texture during cooking of potatoes. Texture judgment scores: 1 = very hard, 6 = optimal texture, 11 = pulpy. (From Harada, T., Tirtohusodo, H., and Paulus, K., *Journal of Food Science*, 50, 459–62, 472, 1985.) It should be noticed that the apparent similarity between the texture development and the first-order irreversible chemical reaction made it possible to develop an analogy model.

3.8 Metabolic Process Engineering

Metabolism is the set of a very large number of chemical reactions occurring in the cells to maintain life. Part of the metabolism, which consumes energy to maintain cellular activity and synthesizing chemicals, is named anabolism. Metabolic activity, which breaks down organic matter entering into the cells to supply raw material for energy metabolism and cellular synthesis is called catabolism.

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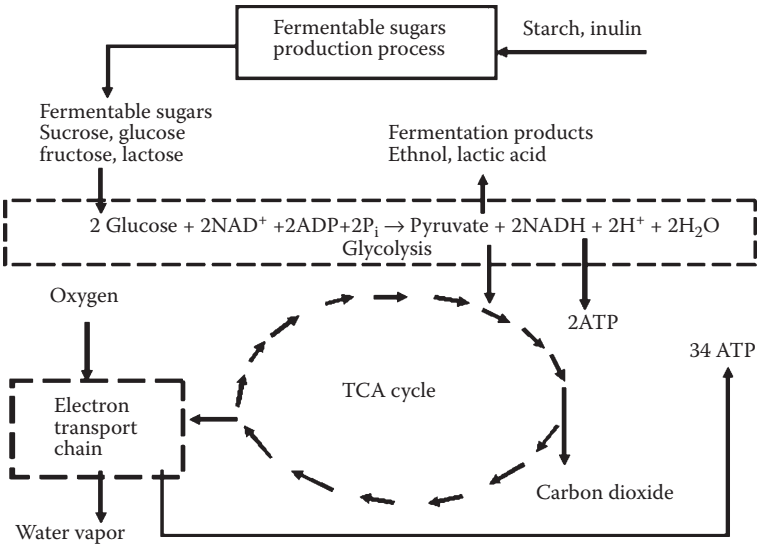


FIGURE 3.6
Schematic description of the metabolic pathways important in food processing and preservation. The glycolytic pathway is anaerobic, whereas the TCA cycle and electron transport chain are aerobic pathways. Pyruvate is produced in the glycolytic pathway, than either converted into ethanol, lactic acid, and so on, or sent to the aerobic metabolic pathways.

Organisms store carbohydrates and fats to establish their own energy reserve. Bonds of the energy reserve chemicals are broken or made as part of the energy exchange and transformation with the environment. Starch is the most common energy reserve of the plant cells. Carbohydrates have a strong affinity for water, which makes the storage of large amounts of carbohydrates inefficient due to the large molecular weight of the solvated water–carbohydrate complex. In the animal cells, carbohydrates are converted into fat; the hydrophobic character of lipids makes them more compact for energy storage when compared to the hydrophilic carbohydrates. Triglycerides coming from the foods are split into glycerol and fatty acids in the intestine, carried with the blood to the adipose tissue, rebuilt there, and stored as fat. When the body requires extra energy, the hormone glucagon signals the breakdown of the triglycerides and the free fatty acids released by lipolysis enter into the bloodstream and circulate throughout the body. The fatty acids are broken down in mitochondria to generate Acetyl-CoA, which enters into the TCA cycle. A schematic description of the metabolic pathways important in food processing and preservation are summarized in Figure 3.6.

Example 3.14: Enthalpy of Formation and Bond Energy of Glucose

Metabolic pathways produce intermediary chemicals for the synthesis of the cellular components and provide energy. The apparent reaction of aerobic respiration is

$$C_6H_{12}O_{6(aq)} + 6O_{2(g)} \rightarrow 6CO_{2(g)} + 6H_2O_{(l)} \quad \Delta H_R = -2880 \text{ kJ}.$$

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Where ΔH_R is the metabolic heat released as a result of respiration. Heat of formation of H_2O and CO_2 are given as

$$C_{graphite} + O_{2(g)} \rightarrow CO_{2(g)} \quad \Delta H_{f,CO_2} = -417 \text{ kJ/mol},$$

$$H_{2(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)} \quad \Delta H_{f,H_2O} = -286 \text{ kJ/mol}.$$

We may estimate the enthalpy of formation of glucose from the metabolic heat released during respiration as

$$\Delta H_R = 6\,\Delta H_{f,CO_2} + 6\,\Delta H_{f,H_2O} - \Delta H_{f,glucose} - 6\,\Delta H_{f,O_2}$$

where $\Delta H_{f,O_2} = 0$ by definition.

$$\Delta H_{f,glucose} = (2880) + (6)(-417) + (6)(-286) = -1338 \text{ kJ/mol}.$$

This is the enthalpy of formation of crystalline glucose. When glucose dissolves, OH groups make a hydrogen bond with the water and each hydrogen bond will have 20 kJ/mol of energy. Therefore the enthalpy of formation of dissolved glucose will be

$$\Delta H_{f,glucose(aq)} = \Delta H_{f,glucose(s)} + (5)\,\Delta H_{f,OH\ bond},$$

$$\Delta H_{f,glucose(aq)} = -1338 \text{kJ/mol} + (5)(20) = -1238 \text{ kJ/kg}.$$

$\Delta H_{f,glucose}$ calculated here is in very good agreement with $\Delta H_{f,glucose}$ given in the literature as –1262 KJ/mol.

Glucose is the starting molecule of the energy metabolism. Energy demand of the cell is met by metabolizing glucose; that is, extracting the energy hidden in its bonds, through glycolytic pathway, citric acid cycle, and electron transport chain. Structure of glucose is given in the literature as depicted in Figure E.3.14.

Solubility of glucose in water is very high due to the hydrogen bonds made between the OH groups and water. The total bond energy of the glucose molecule may be estimated by adding up the energies of all the bonds.

Bond	Bond Energy (kJ/mol)	Number of Bonds/ Molecule	Total Bond Energy/mol (kJ/mol)
C–H	410	7	2870
C–O	330	7	2310
C–C	334	5	1670
O–H	456	5	2280
Hydrogen bonds	20	5	100
		Total bond energy	9230

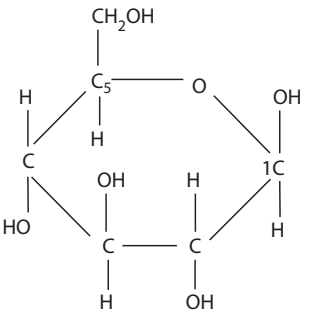


FIGURE E.3.14
Glucose molecule.

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Total bond energy of glucose implies that if the molecule should be divided into its atoms 9230 kJ/mol of energy may be released, implying an enthalpy change of –9230 kJ/mol and this is almost 7 times of $\Delta H_{f,glucose}$.

Metabolic activity in the fresh fruits and vegetable cells continue for some time after being detached from the plants. It alters the cellular composition in storage and reduces the quality. Enzymes that catalyze the metabolic reactions allow regulation of the rate of the metabolic activity by responding to the environmental conditions. Elevated carbon dioxide levels in storage environment forces the equilibrium at the CO_2 producing steps of the metabolism to reestablish in favor of the lower metabolic activity. Carbon dioxide also dissolves in the cells and lowers the pH of the medium and the rate of the reactions. Lowering the temperature reduces the rates of the metabolic reactions as described by the Arrhenius expression 3.5, therefore the shelf life of some fruits and vegetables may be extended by refrigeration or freezing. Metabolic activity of the microorganism responds to the composition and the temperature of the storage environment in a similar way as those of the fruits and vegetables, therefore controlled atmosphere storage might also slow down the microbial decay. The best storage conditions varies for every fruit and vegetable with cultivar and stage of maturity. Controlled atmosphere storage of apples and kiwi fruit are among the most popular commercial practices, where the shelf life may be extended to about 7 months when appropriate temperature and gas compositions are provided (Gormley 1985; Raffo et al. 2009).

Example 3.15: Kinetics of Oxygen Consumption and Carbon Dioxide Generation in Controlled Atmosphere Storage

The rate-limiting step of the aerobic pathways of the energy metabolism may be described as

$$\text{Enzyme}_1 + \text{S} + \text{O}_2 \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{AC}_1 \xrightarrow{k_3} \text{Enzyme}_1 + \text{CO}_2. \tag{E.3.15.1}$$

In the CO_2 rich controlled atmosphere, competitive and noncompetitive inhibition by CO_2 may be described as

$$\text{Enzyme}_1 + \text{CO}_2 \underset{k_5}{\overset{k_4}{\rightleftarrows}} \text{AC}_2, \tag{E.3.15.2}$$

and

$$\text{AC}_1 + \text{CO}_2 \underset{k_7}{\overset{k_6}{\rightleftarrows}} \text{AC}_3. \tag{E.3.15.3}$$

The respiration, for example, oxygen consumption and rate expression, based on the reaction mechanism described in Equations E.3.15.1 through E.3.15.3 is (Hertog et al. 1998)

$$r_{O_2} = \frac{\left[k_{0O_2} \exp\left\{-\frac{E_{aO_2}}{RT}\right\}\right] c_{O_2}}{\left(1 + \frac{c_{CO_2}}{K_{MCO_2}}\right) + c_{O_2}\left(1 + \frac{c_{CO_2}}{K_{MuCO_2}}\right)}. \tag{E.3.15.4}$$

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The rate-limiting step of the anaerobic pathway of the energy metabolism (glycolysis) may be described as

$$\text{Enzyme}_2 + \text{S} \underset{k_9}{\overset{k_8}{\rightleftarrows}} \text{AC}_4 \xrightarrow{k_{10}} \text{Enzyme}_2 + \text{CO}_2. \tag{E.3.15.5}$$

Competitive inhibitory effect of O_2 on glycolysis may be described as

$$\text{Enzyme}_2 + \text{O}_2 \underset{k_{12}}{\overset{k_{11}}{\rightleftarrows}} \text{AC}_5. \tag{E.3.15.6}$$

The competitive inhibitory effect of the excessive CO_2 of the controlled atmosphere on glycolysis may be described as

$$\text{Enzyme}_2 + \text{CO}_2 \underset{k_{14}}{\overset{k_{13}}{\rightleftarrows}} \text{AC}_6. \tag{E.3.15.7}$$

When we consider the mechanism described in Equations E.3.15.1 through E.3.9.5 and the Arrhenius type temperature dependence, carbon dioxide production rate during anaerobic glucose to ethanol conversion is stated as (Hertog et al. 1998)

$$r_{\text{CO}_2} = \frac{k_{0\text{CO}_2} \exp\left\{-\dfrac{E_{a\text{CO}_2}}{RT}\right\}}{K_{M\text{CO}_2}\left(1 + \dfrac{c_{\text{O}_2}}{K_{M\text{O}_2}} + \dfrac{c_{\text{CO}_2}}{K_{M\text{CO}_2}}\right) + 1}. \tag{E.3.15.8}$$

Total carbon dioxide production rate r_{CO_2} is described as

$$r_{\text{CO}_2,\text{total}} = (RQ)(r_{\text{O}_2}) + r_{\text{CO}_2}, \tag{E.3.15.9}$$

where RQ is the respiratory quotient (ratio between CO_2 production and O_2 consumption). MATLAB® code E.3.15 prepares a 3-D plot to describe the variation of $r_{CO_2,total}$, as a function of temperature, carbon dioxide, and oxygen concentrations.

Example 3.16: Logistic Model of Depletion of the Carbohydrate Reserve in Mushrooms During Storage

Mushrooms may accumulate mannitol reaching up to 60% of their dry weight. Carbohydrates or mannitol may be used in the energy metabolism as depicted in Figure 3.3. Their depletion rates due to metabolic activity may be described as

$$\frac{dc}{dt} = -k_c r_{\text{respiration}}\left(\frac{c(t) - c_{\min}}{c_{\min}}\right). \tag{E.3.16}$$

Where $c(t)$ describes the concentration of either mannitol, glucose, or glycogen in the plant tissue at time t. The term $(c(t) - c_{min})/c_{min}$ implies that depletion slows down as $c(t)$ approaches c_{min}.

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MATLAB® CODE E.3.15

Command Line:

```
clear all
close all

% constants
  Ea1 = 52875; % J/mol
  Ea2 = 52358; % J/mol
  R = 8.314; % J/mol K
  k10 = 610;
  k20 = 822;
  Km1 = 3.76;
  Km2 = 1;

% compute the model
% 1 stands for O2 and 2 stands for CO2

for i = 1:2 % temperature
    for j = 1:21 % O2 concentration
       for k = 1:21 % CO2 concentration
          T(i,j,k) = 273 + (i-1)*5;
          c1(i,j,k) = 0.190 + 0.01*j;
          c2(i,j,k) = 0.190 + 0.01*k ;
          % c2/KMu2 term of [E.3.15.4] is reported to be negligible
           r1(i,j,k) = ((k10.*exp(-Ea1./(R.*T(i,j,k)))).*c1(i,j,k))./
(1 + (c2(i,j,k)./Km2) + c1(i,j,k));
           r2(i,j,k) = (k20.*exp(-Ea2./(R.*T(i,j,k)))./
((Km2.*(1 + (c1(i,j,k)./Km1) + (c2(i,j,k)./Km2))) + 1);
           RQ(i,j,k) = r2(i,j,k)./r1(i,j,k);
           r2total = RQ.*r1 + r2;
        end
      end
end

% plot the respiration rates as a function of oxygen and carbon
dioxide concentrations at 273 K
    for j = 1:21
       for k = 1:21
          c11( j, k) = c1(1,j,k) ;
          c21(j,k) = c2(1,j,k) ;
          r21total(j,k) = r2total(1,j,k) ;
        end
end

surf(c11,c21,r21total); hold on
colormap gray
xlabel('% oxygen')
ylabel('% carbon dioxide')
zlabel('rCO2 total')
title('T = 273 K')
grid on
```

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```
% plot the respiration rates as a function of oxygen and carbon
dioxide concentrations at 278 K
figure
for j = 1:21
      for k = 1:21
         c11( j, k) = c1(2,j,k);
         c21(j,k) = c2(2,j,k);
         r21total(j,k) = r2total(2,j,k);
      end
end

surf(c11,c21,r21total); hold on
colormap gray
xlabel('% oxygen')
ylabel('% carbon dioxide')
zlabel('rCO2 total')
title('T = 278 K')
grid on
```

When we run the code Figures E.3.15.1 and E.3.15.2 will appear in the screen.

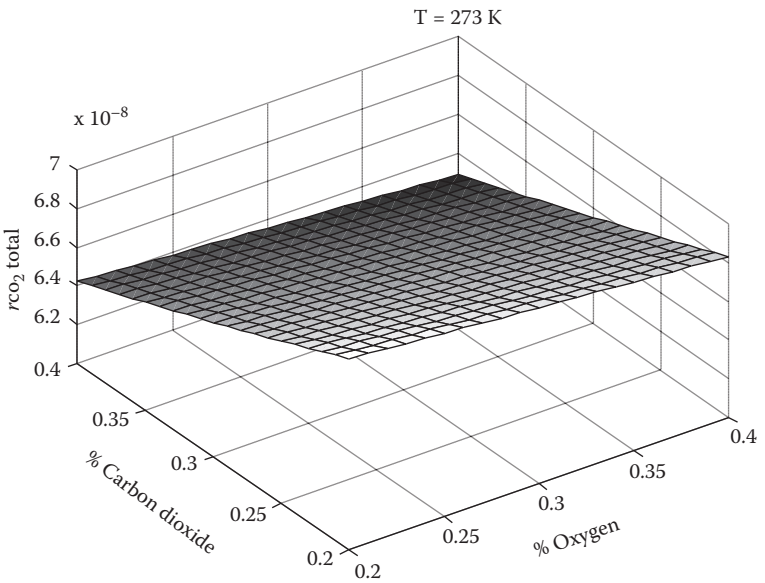


FIGURE E.3.15.1
Model describing the influence of oxygen and carbon dioxide concentrations on the carbon dioxide production rates of apples in the reduced atmosphere at $T = 273$ K. (Constants of the model adapted from Hertog et al. 1998.)

Parameter c_{min} may attain different values depending on the state of the overall metabolic activity. It should be noticed that Equation E.3.16 describes the apparent metabolic activity and is used with modeling purposes only. MATLAB® code E.3.16.a tests the validity of the model by comparing it with the experimental data.

The rate of the slowest reaction step involved in the metabolic activity determines the rate of the metabolism. As long as the rate-limiting step remains unchanged, the apparent rate of the metabolic

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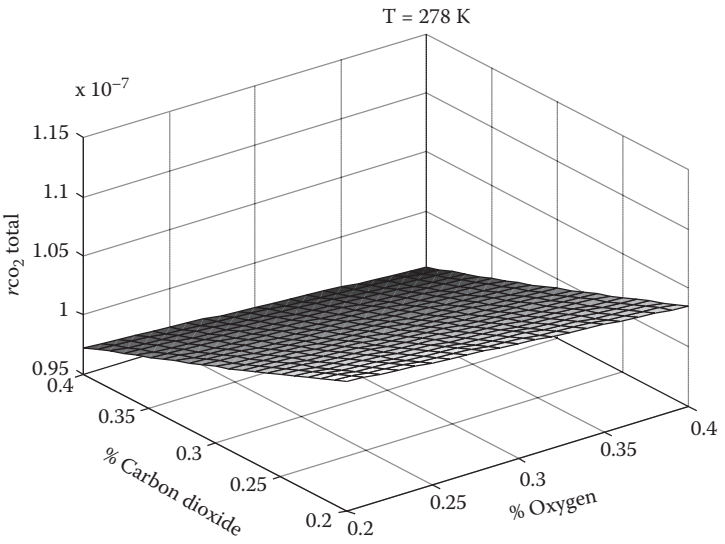


FIGURE E.3.15.2
Model describing the influence of oxygen and carbon dioxide concentrations on the carbon dioxide production rates of apples in the reduced atmosphere at $T = 278$ K. (Constants of the model were adapted from Hertog et al. 1998.)

MATLAB® CODE E.3.16.a

Command Line:

```
clear all
close all

% enter the experimental data
MntlD = [550 630 620 610 520 450]; % mannitol (g/kg dry matter)
tMntlD = [0 2 4 6 8 10];
GlygnD = [45 44 33 31 30 30 29 28 26 25]; % glycogen (g/kg dry matter)
tGlygnD = [0 1 2 3 4 6 7 8 9 10];
GlcsD = [8 11 5 10 5 5 2.5 3 2.5 2]; % glucose (g/kg dry matter)
tGlcsD = [0 1 2 3 4 6 7 8 9 10];
RrData = [2 2.1 2.7 3 3.2 3 2.9 3 3]; % respiration rate (mmol O2/kg
dry matter h)
tRrData = [0 1 2 3 4 6 5 7 8];

% constants
kRr1 = 1.05; % respiration rate constant
kRr2 = 4.5; % respiration rate constant
MaxRr1 = 3.3; % maximum attainable respiration rate
MaxRr2 = 3.0; % maximum attainable respiration rate
kGlygn1 = 17;
kGlygn2 = 3;
kGlcs1 = 3.3;
kGlcs2 = 0.3;
kMntl1 = 5.7;
```

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```
kMntl2 = 30;
GlygnMin1 = 30;
GlcsMin1 = 5;
MntlMin1 = 600;
GlygnMin2 = 25;
GlcsMin2 = 2.0;
MntlMin2 = 450;
tPhase1 = 1.0; % day
tPhase2 = 4.8; % days
deltaTime = 0.1; % time increment
kDgrdtn = 80; % degradation rate constant of the mannitol complexes
% initial values
tModel(1) = 0;
RrModel(1) = 2; % initial respiration rate
MntlM(1) = 550;
GlcsM(1) = 11;
GlygnM(1) = 45;

% first phase model
for i = 2:1:100
k = i-1;
tModel(i) = tModel(k) + deltaTime;
if tModel(i) <= tPhase1
RrModel(i) = RrModel(k);
MntlM(i) = MntlM(k) + kDgrdtn*deltaTime;
GlcsM(i) = GlcsM(k);
GlygnM(i) = GlygnM(k);
end

% second and third phase logistic models
if tModel(i) > tPhase1
if tModel(i) <= tPhase2
RrModel(i) = RrModel(k) + kRr1*RrModel(k)*(1-( RrModel(k)/
MaxRr1))*deltaTime;
GlygnM(i) = GlygnM(k)-kGlygn1*RrModel(k)*((GlygnM(k)-GlygnMin1)/
GlygnMin1)*deltaTime;
GlcsM(i) = GlcsM(k)-kGlcs1*RrModel(k)*((GlcsM(k)-GlcsMin1)/
GlcsMin1)*deltaTime;
MntlM(i) = MntlM(k)-kMntl1*RrModel(k)*((MntlM(k)-MntlMin1)/
MntlMin1)*deltaTime;
end
end

if tModel(i) > tPhase2
RrModel(i) = RrModel(k) + kRr2*RrModel(k)*(1-( RrModel(k)/
MaxRr2))*deltaTime;
GlygnM(i) = GlygnM(k)-kGlygn2*RrModel(k)*((GlygnM(k)-GlygnMin2)/
GlygnMin2)*deltaTime;
GlcsM(i) = GlcsM(k)-kGlcs2*RrModel(k)*((GlcsM(k)-GlcsMin2)/
GlcsMin2)*deltaTime;
MntlM(i) = MntlM(k)-kMntl2*RrModel(k)*((MntlM(k)-MntlMin2)/
MntlMin2)*deltaTime;
end
```

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```
end
% plot the experimental data
[AX,H1,H2] = plotyy(tGlygnD,GlygnD,tMntlD,MntlD,'plot'); hold on
set(H1,'LineStyle','o')
set(H2,'LineStyle','+')
ylim(AX(2), [400 700])
xlabel('t (days)')
ylabel('Glycogen (g/kg dry matter)')
set(get(AX(2),'ylabel'), 'string', 'Mannitol (g/kg dry matter)')
legend('Glycogen', 'Mannitol',2,'Location','SouthWest')
[AX,H7,H8] = plotyy(tModel,GlygnM, tModel, MntlM,'plot'); hold on
set(H7,'LineStyle','-')
set(H8,'LineStyle',':')
ylim(AX(2), [400 700])

figure
[AX,H5,H6] = plotyy(tGlcsD,GlcsD, tRrData,RrData,'plot'); hold on
set(H5,'LineStyle','d')
set(H6,'LineStyle','*')
legend(' Glucose', 'Respiration Rate', 2,'Location','NorthEast')
xlabel('t (days)')
ylabel('Glucose (g/kg dry matter)')
set(get(AX(2),'ylabel'), 'string', 'Respiration Rate (mmol O2/kg dry
matter h)')
[AX,H7,H8] = plotyy(tModel, GlcsM, tModel, RrModel,'plot'); hold on
set(H7,'LineStyle','-')
set(H8,'LineStyle',':'
```

When we run the code Figures E.3.16.1 and E.3.16.2 will appear in the screen.

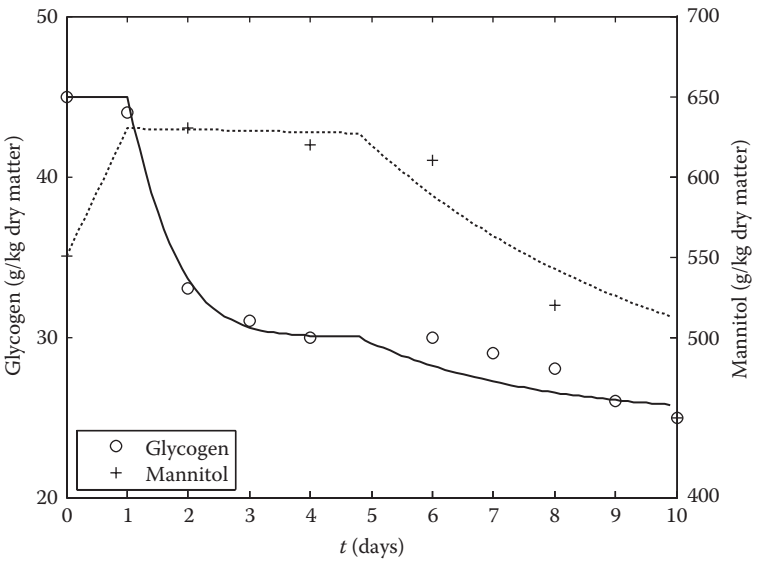


FIGURE E.3.16.1
Comparison of the logistic glycogen and mannitol consumption models with the data. The increase observed in the mannitol concentration in the first phase of the storage is assumed to be caused by the release of mannitol from degrading complex molecules. (Adapted from Varoquaux, P., Gouble, B., Barron, C., and Yildiz, F., *Postharvest Biology and Technology,* 16, 51–61, 1991.)

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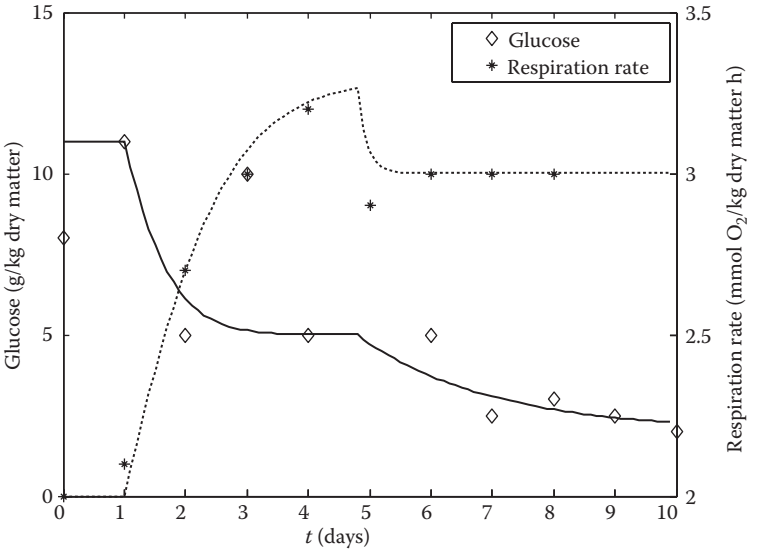


FIGURE E.3.16.2
Comparison of the logistic respiration rate and glucose consumption models with the data. (Adapted from Varoquaux, P., Gouble, B., Barron, C., and Yildiz, F., *Postharvest Biology and Technology*, 16, 51–61, 1991.)

activity may be studied the same way as the kinetics of the enzyme catalyzed reactions. Unfortunately, the rate-limiting step may change with temperature so the metabolic activity may not be studied like that of a simple reaction over a large range of experiments. The Arrhenius plot of the respiration rates is given in Figure E.3.16.3. Details of the computations are given in MATLAB® code E.3.16.b.

Alcoholic drink production processes are distinguished with respect to the source of the fermentable sugars and the additional flavor and quality improvement operations. The final product is ethanol in the case of beer, wine, sake, vodka, tequila, and whiskey; it is lactic acid in yogurt and cheese-making processes. The raw material of the metabolic final product industries depends on the availability determined by the climate. Europe may be divided into widely used (but loosely defined) wine, beer, and vodka belts. Wine, champagne, brandy (cognac), and the other wine-like products are produced in grape-growing countries of both the southern and northern hemisphere. Fresh grapes may not store economically for a long time, therefore wine is produced only for a few months of the year. Raisins (dried grapes) are stable over a year and used for raki (Turkish), ouzo (Greek), or arak (Arabic) like clear, colorless, unsweetened, aniseed-flavored distilled alcoholic drinks. The raki belt lies southeast of the wine belt and includes the Eastern Mediterranean and Northern African countries, where powerful solar energy makes it possible to dry the grapes easily. Rum is a distilled alcoholic drink produced from sugarcane juice or molasses in the tropical and subtropical countries. Molasses is the final by-product of the sugar industry. The carbon sources of wine-like, raki-like products (fructose and glucose), and rum (sucrose, glucose, and fructose) are readily fermentable and enter into the metabolic pathways of the microorganisms easily. Starch from grains is the carbon source of the fermentation processes leading to beer, whiskey, vodka, and saké production. Beer and saké (the Japanese alcoholic drink saké is also called rice-wine) are not distilled alcoholic drinks, whereas vodka and whiskey are. Starch is not readily fermentable, therefore some preparatory stages involve into beer, whiskey, vodka, and saké production, where large starch chains are cut into smaller sugars, to make their use possible in the metabolic pathways (Figure 3.3). Although starch, originating from

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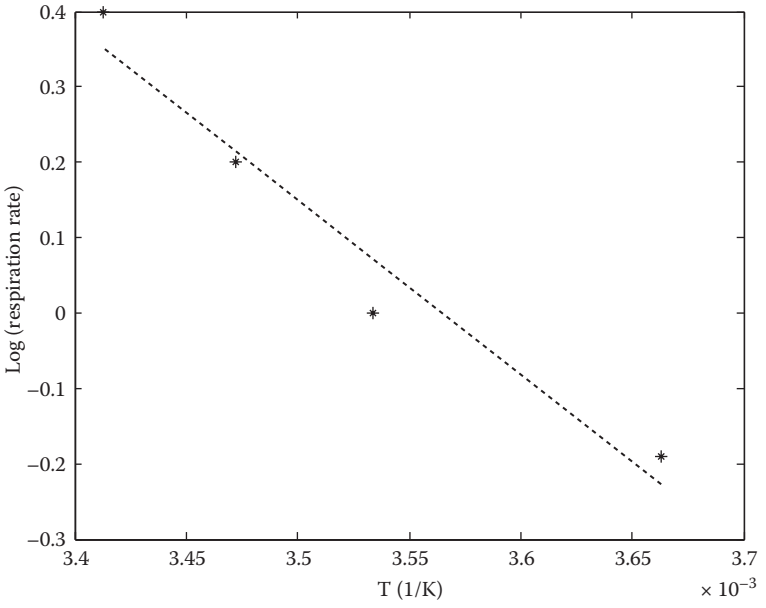


FIGURE E.3.16.3
Arrhenius plot of the respiration rates. (Adapted from Varoquaux, P., Gouble, B., Barron, C., and Yildiz, F., *Postharvest Biology and Technology,* 16, 51–61, 1991.)

MATLAB® CODE E.3.16.b

Command Window:

```
clear all
close all

% enter the data
T = [0 10 15 20]; % C
logRRdata = [-0.19 0 0.2 0.4]; % log(respiration rate)
% respiration rates are in mmol O2/kg dry matter h

R = 8.314;
% plot the data

for i = 1:4
    invT(i) = 1/(T(i) + 273);
end

plot(invT, logRRdata,'*' ); hold on;
ylabel('log(Respiration Rate)')
xlabel('T (1/K)')

% determine the model coefficients,
f1 = polyfit(invT,logRRdata,1);
fp1 = polyval(f1, invT);
EaR = - f1(1);
logRR0 = f1(2);
```

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```
% determine the correlation coefficient
rmatrix = corrcoef(logRRdata,invT);
r = rmatrix(1,2);

% determine the standard error
for j = 1:4;
  logRRmodel = logRR0-EaR*invT;
  d1 = (logRRdata-logRRmodel);
  d2 = d1*d1';
end;

Se = sqrt(mean(d2));

% print the model, correlation coefficient and the standard error
fprintf('\nArrhenius relation is log(Respiration Rate) = %.2g -%2g/T
and r = %2g se = %2g \n', logRR0, EaR, r, Se)

% plot the model
plot(invT, logRRmodel,':' );
```

When we run the code the following line and Figure E.3.16.3 will appear on the screen:

```
Arrhenius relation is log(Respiration Rate) = 8.3 -2319.33/T and
r = -0.976065 se = 0.0958086
```

the grains (mostly barley), is hydrolyzed prior to fermentation in the beer-making process, starch hydrolysis and fermentation occur simultaneously in the saké production.

Vodka is a distilled beverage made of grains (usually rye or wheat), potatoes or sugar beet molasses in the countries where cultivation of grapes is very difficult. Whiskey is also made of grains (barley, rye, and wheat), corn, or molasses.

Tequila is a distilled alcoholic drink made in Mexico by using the agave juice. When producing 100% agave tequila, the only carbohydrate source is inulin hydrolyzed from the plant tissue by cooking. Inulins are a group of plant polysaccharides formed by linking several simple sugars together. Most plants, which synthesize and store inulin, do not store other materials such as starch.

3.9 Microbial Kinetics

Predictive microbial models may be used to describe the behavior of microorganisms under different physical and chemical conditions, such as temperature, pH, and water activity. These models allow the prediction of microbial safety or shelf life of the products and facilitate development of the HACCP programs (Chapter 5; Whiting and Buchanan 1994). Microbial kinetics are mostly based on the analogy between the microbial processes and the chemical or enzyme catalyzed reactions. Proliferation of the microorganisms in a batch growth medium may include four ideal stages as explained in Table 3.3. Some of these growth phases may be prevented intentionally with an appropriate experimental design.

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TABLE 3.3

Ideal Growth Phases of Microorganisms in Batch Medium

Growth Phase	Growth Rate Expression		Comments
Lag phase	$\frac{dx}{dt} = 0$	(3.30)	Time required for adaptation of the microorganisms to a new medium or recovery from injury
Exponential phase	$\frac{dx}{dt} = \mu x$	(3.31)	Variation of the population size is proportional with the number of microorganisms in the culture
Stationary phase	$\frac{dx}{dt} = 0$	(3.32)	Microbial growth may stop because of the lack of a limited nutrient or product inhibition
Death phase	$\frac{dx}{dt} = -k_a x$	(3.33)	Microbial death may start after depletion of the cellular reserves in the stationary phase or with the effect of the unfavorable factors

Specific growth rate μ is a constant in the exponential growth phase, which implies that the growth rate is proportional with the viable microbial population, where all the members have equal potential for growth. The specific growth rate may be regarded as the frequency of producing new microorganisms by the ones already present. When microbial proliferation occurs in a substrate limited medium, specific growth rate may be related with the substrate concentration:

$$\mu = \frac{\mu_{\max} c_S}{c_S + K}, \tag{3.34a}$$

where μ_{max} is the maximum attainable specific growth rate. Equation 3.34a is called the Monod equation. There are numerous variations of the Monod equation available in the literature (Mulchandani and Luong 1989). The most common empirical modifications of Equation 3.34a to include substrate and product inhibition are

$$\mu = \frac{\mu_{\max} c_S}{c_S + K + \frac{c_s^2}{K_s}}, \tag{3.34b}$$

and

$$\mu = \frac{\mu_{\max} c_S}{c_S + K} \frac{K_p}{K_p + c_p}, \tag{3.34c}$$

where K_s and K_p are constants, c_p is the product concentration.

The logistic model is frequently used to simulate microbial growth when a microbial population inhibits its own growth via depletion of a limited nutrient, product accumulation, or unidentified reasons (Example 1.2):

$$\frac{dx}{dt} = \mu x \left(1 - \frac{x}{x_{\max}}\right), \tag{3.35}$$

where μ is the initial specific growth rate and x_{max} is the maximum attainable value of x. The logistic equation is an empirical model, it simulates the data when microbial growth curve follows a sigmoidal path to attain the stationary phase. It is mostly based on

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experimental observations only. When $x \ll x_{max}$, the term in parenthesis is almost one and neglected, then the equation simulates the exponential growth (i.e., Equation 3.31). When x is comparable with x_{max}, the term in the parenthesis becomes important and simulates the inhibitory effect of overcrowding on microbial growth. When $x = x_{max}$, the term in the parenthesis becomes zero, then the equation will predict no growth (i.e., stationary phase as described with Equation 3.35). The logistic equation may be integrated as

$$x = \frac{x_0 e^{\mu t}}{1 - \frac{x_0}{x_{max}}(1 - e^{\mu t})}. \tag{3.36}$$

The exponential growth model simulated with Equation 3.31 may be modified after substituting:

$$\mu = \mu_0 + \mu_1 x - \mu_2 x^2, \tag{3.37}$$

to simulate the *Allee effect*, which represents a population with maximum specific growth rate at intermediate microbial concentrations when μ_0, μ_1, and μ_2 are positive constants (Edelstein-Keshet 1988).

When μ of Equation 3.31 is a function of time such that

$$\frac{d\mu}{dt} = -\alpha\mu, \tag{3.38}$$

we obtain the Gompertz model, which may also be used to simulate the sigmoidal behavior of the microbial growth curve (α = constant). The Gompertz model is usually expressed in three equivalent versions (Edelstein-Keshet 1988):

$$\frac{dx}{dt} = \mu x, \frac{d\mu}{dt} = -\alpha\mu, \tag{3.39a}$$

$$\frac{dx}{dt} = (\lambda e^{-\alpha t})x, \tag{3.39b}$$

and

$$\frac{dx}{dt} = (\kappa \ln x)x, \tag{3.39c}$$

where λ and κ are constants.

Microbial products may be roughly categorized in four groups as depicted in Table 3.4.

Primary metabolites are produced by the microorganism for its own metabolic activity. Secondary metabolites are usually produced against the external factors; that is, production of antibiotics starts in the stationary phase to prevent consumption of the limited nutrients by the other microbial species. The yeast *Saccharomyces cerevisiae* may be regarded as a product itself when produced as an additive to achieve leavening in the bakery industry. Sugars are consumed in the energy metabolism, some microorganisms may not convert them into carbon dioxide, but follow a shorter path and excrete the metabolic end products such as ethanol or lactic acid. Product formation models relates the product formation rate

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TABLE 3.4

Microbial Products

Product	Examples
Biomass	Baker's yeast
Metabolic end products	Ethanol, lactic acid, carbon dioxide
Primary metabolites	Amino acids, enzymes, vitamins
Secondary metabolites	Antibiotics

to fermentation variables (i.e., growth rate, biomass, or substrate concentration, etc.). The Luedeking and Piret (1959) model is among the most popular product formation models of food processing interest:

$$\frac{dc_{Pr}}{dt} = \alpha x + \beta \frac{dx}{dt}, \tag{3.40}$$

where c_{pr} is the product concentration, α and β are the constants. The term αx represents the product formation rate by the microorganisms regardless of their growth; $\beta dx/dt$ represents the additional product formation rate during growth in proportion with the growth rate. This is an empirical equation, because it simply relates the experimental observations mostly without considerable theoretical basis. When growth-associated product formation rates are much greater than the nongrowth-associated product formation rates, Equation 3.40 may be written as

$$\frac{dc_{Pr}}{dt} = \beta \frac{dx}{dt}. \tag{3.41}$$

When nongrowth-associated product formation rates are much greater than the growth-associated product formation rates, Equation 3.40 becomes

$$\frac{dc_{Pr}}{dt} = \alpha x. \tag{3.42}$$

Structured and age distribution models relate cellular structure or age distribution to growth and product formation rates, but need more information for application, generally difficult to use and not widely employed in food research, therefore not considered here; an interested reader may refer to Bailey and Ollis (1986) for detailed discussion.

In a fermentation process a substrate (i.e., nutrient), is allocated to three basic uses:

$$\begin{pmatrix}\text{total rate}\\ \text{of substrate}\\ \text{utilization}\end{pmatrix} = \begin{pmatrix}\text{rate}\\ \text{of substrate}\\ \text{utilization}\\ \text{for biomass}\\ \text{synthesis}\end{pmatrix} + \begin{pmatrix}\text{rate}\\ \text{of substrate}\\ \text{utilization}\\ \text{for}\\ \text{maintenance}\end{pmatrix} + \begin{pmatrix}\text{rate}\\ \text{of substrate}\\ \text{utilization}\\ \text{for product}\\ \text{formation}\end{pmatrix}. \tag{3.43}$$

Substrate consumption to keep the cells alive without growth or product formation is referred to as *maintenance*. Equation 3.43 may be expressed in mathematical terms as

$$-\frac{dc_S}{dt} = \frac{1}{Y_{x/s}}\frac{dx}{dt} + k_M x + \frac{1}{Y_{p/s}}\frac{dc_{Pr}}{dt}, \tag{3.44}$$

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where $Y_{x/s}$ is the cell yield coefficient defined as grams of biomass produced per grams of substrate used, and $Y_{p/s}$ is the product yield coefficient (i.e., grams of product produced per grams of substrate used). The yield coefficients usually remain constant as long as the fermentation behavior remains unchanged, but there are also examples to the variable yield coefficients in the literature, which may indicate a shift in substrate preference, availability of oxygen, and so on during the course of the process (Özilgen, Ollis, and Ogrydziak 1988).

Microorganisms produce heat as a by-product of the energy metabolism that may be summarized with typical examples as

$$\text{Glucose} + 36P_i + 36\text{ADP} \xrightarrow{\text{respiration}} 6CO_2 + 42H_2O + 36\text{ATP} + Q, \tag{3.45}$$

$$\text{Glucose} + 2P_i + 2\text{ADP} \xrightarrow{\text{anaerobic fermentation}} 2\text{Lactate} + 2H_2O + 2\text{ATP} + Q, \tag{3.46}$$

where P_i and Q represent inorganic phosphate atoms and metabolic heat generation, respectively. The ADP and ATP are abbreviations for adenosine diphosphate and adenosine triphosphate, respectively. The ATP is the energy currency of the cell. The ATP to ADP conversion is coupled with the energy consuming metabolic reactions (i.e., biosynthesis, cellular transport, etc.) and make them thermodynamically feasible. The ADP is converted back to ATP through Equation 3.45 or Equation 3.46. Metabolic heat generation rate may be related with the growth rate as

$$\begin{pmatrix} \text{metabolic heat} \\ \text{generation rate} \\ \text{per unit volume} \\ \text{of fermentor} \end{pmatrix} = \frac{1}{Y_\Delta}\frac{dx}{dt}, \tag{3.47}$$

where Y_Δ is the heat generation coefficient defined as grams of biomass production coupled with one unit (i.e., kJ) of heat evaluation.

Most food and beverage fermentations involve mixed culture of microorganisms. Typical examples may include yogurt cultures (*Streptococcus thermophilus* and *Lactobacillus bulgaricus*), wine (*Saccharomyces cerevisiae* and wild microbial species), and cheese production (mixed culture of various microorganisms). The general interaction of two microorganisms are summarized in Table 3.5.

Table 3.5 indicates that when microbial species 1 and 2 benefit from an interaction it is called mutualism; when microbial species 1 benefits but microbial species 2 is not

TABLE 3.5

General Interaction Ways of Microbial Populations

		Microorganism 2		
		+	–	0
Microorganism 1	+	mutualism	predation	commensalism
	–		competition	amensalism
	0			neutralism

Note: Symbols + , –, and 0 indicate positive, negative, and no effect on the related microbial population.

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affected from an interaction it is called commensalism. Interactions shown in Table 3.5 depend on the culture conditions. An initially neutral relation may turn in competition during the course of fermentation with depletion of the limiting substrate, or two microbial populations may have mutualistic relation in one medium, but competitive relation in another medium.

Example 3.17: Mixed Culture Interactions Between *P. Vulgaris* and *S. Cerevisiae*

Proteus vulgaris prefers to utilize sodium citrate when both sodium citrate and glucose are available, also nicotinic acid is needed for its growth. *Saccharomyces cerevisiae* can utilize only glucose and produces nicotinic acid. By varying the concentrations of the medium components, various mixed culture interactions may be created as depicted in Table E.3.17.

The chemical reactor and fermentor design are based on similar principles. A CSTR is called a chemostat when there is only one limited substrate. Equation 3.57 may be applied to a chemostat for a population balance of the microorganisms to yield

$$Fx_0 - Fx + VR_x = \frac{d(Vx)}{dt}, \tag{3.48}$$

where x_0 is the concentration of the microorganisms in the input stream. Under steady state conditions $d(Vx)/dt = 0$, when the microorganisms are in exponential growth phase $R_x = \mu_x$, we may rearrange Equation 3.48 to obtain

$$x = \frac{Dx_0}{D - \mu}, \tag{3.49}$$

where x = microbial concentration in or at the exit of the fermentor,

$$D = \frac{F}{V} = \text{dilution rate} = \frac{1}{\tau} = \frac{1}{\text{residence time in the fermentor}}. \tag{3.50}$$

While working with sterile nutrients (i.e., $x_0 = 0$), Equation 3.49 will become

$$(D - \mu)x = 0. \tag{3.51}$$

Equation 3.51 implies that a nonzero population may be maintained under steady state conditions only when

$$D = \mu. \tag{3.52}$$

TABLE E.3.17

Mixed Culture Interactions Between *P. vulgaris* and *S.cerevisiae*

Sodium Citrate	Glucose	Nicotinic Acid	Interaction
Limiting concentration	limiting concentration	not added	commensalism
Not added	limiting concentration	not added	commensalism plus competition
Not added	limiting concentration	sufficient amount (not limiting)	competition
Excess amount	limiting concentration	not added	mutualism
Limiting concentration	limiting concentration	sufficient amount (not limiting)	neutralism

Source: Tseng, M. M.-C., and Phillips, C. R., *Biotechnology and Bioengineering*, 23, 1639–51, 1981.

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It should be noticed that even under these conditions, an output stream will have the same biomass concentration as in the chemostat (Bailey and Ollis 1986).

When nutrients are sterile and the biomass growth agrees with the Monod Equation 3.48, it will become

$$D = \mu_{\max} \frac{c_S}{K_s + c_S}, \tag{3.53}$$

where c_s is the substrate concentration in the fermentor. Equation 3.53 may be rearranged as

$$c_S = \frac{DK_s}{\mu_{\max} - D}. \tag{3.54}$$

Biomass yield coefficient $Y_{x/s}$ may be calculated as

$$Y_{x/s} = \frac{x - x_0}{c_{S0} - c_S}, \tag{3.55}$$

where c_{S0} is the substrate concentration in the input stream. When we use sterile nutrients ($x_0 = 0$), Equations 3.54 and 3.55 may be combined to calculate the biomass concentration in (also at the exit of) the fermentor:

$$x = Y_{x/s}\left(c_{S0} - \frac{DK_s}{\mu_{\max} - D}\right). \tag{3.56}$$

Equation 3.51 implies that stable fermentation operation may be maintained only when $c_{S0} > DK_s/\mu_{\max} - D$.

Example 3.18: Kinetics of Microbial Growth, Gas Production, and Dough Volume Increase During Leavening

Commercial baker's yeast contains strains of *Saccharomyces cerevisiae*, lactic acid bacteria, and low numbers of contaminating microorganisms. The yeast utilizes the simple sugars derived from flour and produces carbon dioxide. Growth of the microorganisms in the dough was simulated with a logistic equation (Akdogan and Özilgen 1992):

$$\frac{dx}{dt} = \mu x\left(1 - \frac{x}{x_{\max}}\right). \tag{3.35}$$

The Luedeking–Piret equation was used to model gas production (Akdogan and Özilgen 1992):

$$\frac{dG}{dt} = \alpha x + \beta \frac{dx}{dt}. \tag{3.40}$$

A fraction of the gas produced by the baker's yeast is retained in the dough and the remaining gas diffuses out. The retained gas increases the volume of the dough. The volume increase rates are expected to decrease as the volume of the dough gets larger and the walls of the gas cell get

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thinner due to stretching. The rate of the dough volume increase may be related to the gas production rate (Akdogan and Özilgen 1992):

$$\frac{dV}{dt} = \phi\left(1 - \frac{V}{V_{max}}\right)\frac{dG}{dt}, \tag{E.3.18.1}$$

where V and V_{max} are the volume and the maximum attainable volume of the dough, respectively. Parameter ϕ is the ratio of the initial dough volume increase to rate of the initial gas production rate. Comparison of the model with a typical set of experimental data is shown in Figure E.3.18. MATLAB® code E.3.18 shows the details of the computations.

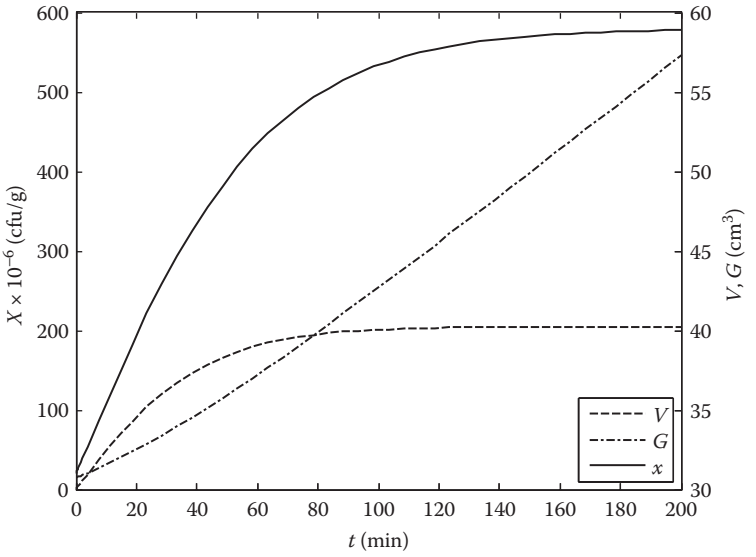


FIGURE E.3.18
Comparison of the model (Equations 3.35, 3.40, and E.3.19.1) with the experimental data of microbial growth, gas production and dough volume increase. (From Akdogan, H., and Özilgen, M., *Enzyme and Microbial Technology,* 14, 141–3, 1992.)

MATLAB® CODE E.3.18

Command Line:

```
clear all
close all

[t,x] = ode45('GasProd', 200, [31e6 15 0]);
plot(t, x(:,3), 'b-.'); hold on;
ylabel('x * 10-6 (cfu/g)')
xlabel('t (min)')
[AX,H1,H2] = plotyy(t, x(:,2), t,x(:,1)*(1e-6), 'plot'); hold on;
set(H1,'LineStyle','- -')
set(H2,'LineStyle','-')
legend('V','G', 'x', 'Location', 'SouthEast')
set(get(AX(2),'ylabel'), 'string', 'V, G (cm3)')
```

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M–Function:

```
function dx = GasProd(t,x)
% this function compute the gas production rates in the dough
mu = 0.031; Xmax = 59e6; a = 2.512e-8; B = 5.011e-8; o = 3.4; Vmax = 205;
dx1 = mu*x(1)*(1-(x(1)/Xmax));
dx2 = B*x(1) + a*dx1;
dx3 = o*(1-(x(3)/Vmax))*dx2;
dx = [dx1; dx2; dx3];
```

Figure E.3.18 will appear on the screen when we run the code.

Example 3.19: Kinetics of Microbial Growth and Lactic Acid Production by Mixed Cultures of *Streptococcus Thermophilus* and *Lactobacillus Bulgaricus* in Yogurt Production

Lactic acid production by mixed cultures of *Streptococcus thermophilus* and *Lactobacillus bulgaricus* is the most important chemical process involved in yogurt production. Interaction of these microorganisms in milk is favorable for both of the species, but not obligatory. Both numbers of the individual microorganisms and the total amounts of lactic acid produced by mixed cultures of these microorganisms are considerably higher than those obtained with pure cultures of each microorganism. In the mixed cultures, stimulation of growth of *S. thermophilus* was attributed to the production of certain amino acids (i.e., glycine, histidine, valine, leucine, and isoleucine) by *L. bulgaricus*. The *S. thermophilus* stimulates the growth of *L. bulgaricus* by producing formic acid. The logistic equation was modified to simulate the mixed culture growth of the microorganisms as (Ozen and Özilgen 1992)

$$\frac{dx_S}{dt} = \mu_S x_S \left(1 - \frac{\tau_S x_S + \tau_L x_L}{x_{S\max} + x_{L\max}}\right), \tag{E.3.19.1}$$

and

$$\frac{dx_L}{dt} = \mu_L x_L \left(1 - \frac{\tau_S x_S + \tau_L x_L}{x_{S\max} + x_{L\max}}\right), \tag{E.3.19.2}$$

where subscript *L* and *S* refer to *L. bulgaricus* and *S. thermophilus*, respectively. Some of the microbial species died at the end of the fermentation process, the death rates were simulated as (Ozen and Özilgen 1992)

$$\frac{dx}{dt} = -kx. \tag{E.3.19.3}$$

The Luedeking–Piret equation was modified to simulate lactic acid production by the mixed culture of the microorganisms as (Ozen and Özilgen 1992):

$$\frac{dc_{Pr}}{dt} = \alpha_S x_S + \alpha_L x_L + \beta_S \frac{dx_S}{dt} + \beta_L \frac{dx_L}{dt}. \tag{E.3.19.4}$$

Equations E.3.19.1 through E.3.19.4 are solved with MATLAB® code E.3.19 and compared with the experimental data.

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MATLAB® CODE E.3.19

Command Window:

```
clear all
close all

% MICROBIAL GROWTH KINETICS
% enter the data
tmo = [0 40 65 110 160 200 240 280 320 360 400];
lnxL = [15 16.3 17 18.6 19.5 20 20.05 20.01 19.45 19.15 18.9];
lnxS = [17 18.05 19.05 19.9 20.4 20.7 20.8 20.75 21 20.60 20.5];

% plot the data
plot(tmo,lnxL,'ro',tmo,lnxS,'rx'); hold on
legend('L. bulgaricus','S. thermophilus','Location', 'SouthEast')
ylabel('lnX (cfu cm3)')
xlabel('Time (min)')

% Search the beginning of the death phase of L. bulgaricus
j = 0; h = 0; intL = 0; intS = 0;

while intL < 1
    j = j + 1;
    if (lnxL(j)-lnxL(j + 1)) > 0
       intL = j*40;
    end
end

% Search the beginning of the death phase of S thermophilus
while intS < 1
    h = h + 1;
    if (lnxS(h)-lnxS(h + 1)) > 0
      intS = h*40;
    end
end

% plot the model
[t1,x1] = ode45('MixedGrowth', [0:1:intL], [exp(17) exp(15) 0]); %
growth of L. bulgaricus
[t2,x2] = ode45('LBdeath', [(intL):1:400], x1((intL + 1),2)); % death
of L. bulgaricus
[t3,x3] = ode45('MixedGrowth', [0:1:intS], [exp(17) exp(15) 0]); %
growth of S. thermophilus
[t4,x4] = ode45('STdeath', [(intS):1:400], x3((intS + 1),1)); % death
of S. thermophilus
plot(t1, log(x1(:,2)), 'b-.',t2, log(x2), 'b-.',t3, log(x3(:,1)),t4,
log(x4)); hold on

% KINETICS OF PRODUCT FORMATION
% enter the data
P = [0 0.08 0.1 0.25 0.60 0.87 1.35 1.42 1.55 1.58];
tp = [0 40 80 120 160 200 240 320 360 400];
```

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```
% model
[t,x] = ode45('MixedGrowth', [0:1:400], [exp(17) exp(15) 0]);

% plot the data and the model
figure
plot(tp,P,'r*',t, x(:,3), 'b-.') ;
ylabel('Lactic Acid (%)')
xlabel('Time (min)')
```

M-File1:

```
function dx = MixedGrowth(t,x)
% mixed culture growth and lactic acid production model for
Lactobacillus bulgaricus and Streptococcus thermophilus
muS = 0.028; muL = 0.035;tauL = 0.19; tauS = 1.34; alphaL = 1.1e-12;
alphaS = 1.1e-12; betaL = 6e-10; betaS = 6e-10; xLmax = 8e8; xSmax = 1.1e9;
dx1 = muS*x(1)*(1-((tauS*x(1) + tauL*x(2))/(xSmax + xLmax)));
dx2 = muL*x(2)*(1-((tauS*x(1) + tauL*x(2))/(xSmax + xLmax)));
dx3 = alphaS*x(1) + alphaL*x(2) + betaS*dx1 + betaL*dx2;
dx = [dx1; dx2; dx3];
```

M-File2:

```
function dx = STdeath(t,x)
% death phase model for Streptococcus thermophilus
kL = 9.4e-3; kS = 2e-3;
dx = -kS*x(1);
```

M-File3:

```
function dx = LBdeath(t,y);
% death phase model for Lactobacillus bulgaricus
kL = 9.4e-3; kS = 2e-3;
dx = -kL*y;
```

Figures E.3.19.1 and E.3.19.2 will appear on the screen when we run the code.

Example 3.20: Kinetics of Spontaneous Wine Production

The wine-making process may be analyzed in two phases: alcoholic fermentation and malolactic fermentation. During the alcoholic fermentation process, wine microorganisms consume the fermentable sugars and produce ethanol. A spontaneous wine production process is actually a mixed-culture and multi-product process, commenced by the natural microorganisms of the grapes. Natural grape microorganisms consists of various genera of molds, yeasts, and lactic acid bacteria. Generally wine yeast, *Saccharomyces cerevisiae*, is extremely low in population on the grapes. In the wine-making process it multiplies with a strong fermentative capacity, excludes most of the other microorganisms from the medium and eventually invades the raw grape juice.

In the alcoholic fermentation process, growth of the biomass may be simulated in three phases (Özilgen, Celik, and Bozoglu 1991):

$$\text{i. Exponential growth: } dx/dt = \mu x \tag{3.31b}$$

$$\text{ii. Stationary phase: } dx/dt = 0 \tag{3.31c}$$

$$\text{iii. Death phase: } dx/dt = -k_d x \tag{3.31d}$$

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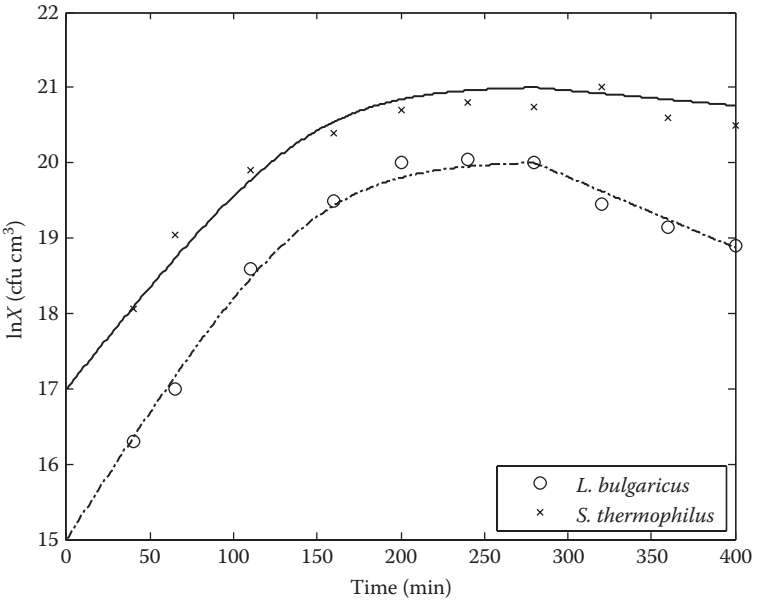


FIGURE E.3.19.1
Variation of the concentrations of *L. bulgaricus* and *S. thermophilus* in cultivations with 20% NFDM (nonfat dry milk) medium. (From Ozen, S., and Özilgen, M., *Journal of Chemical Technology and Biotechnology*, 54, 57–61, 1992.)

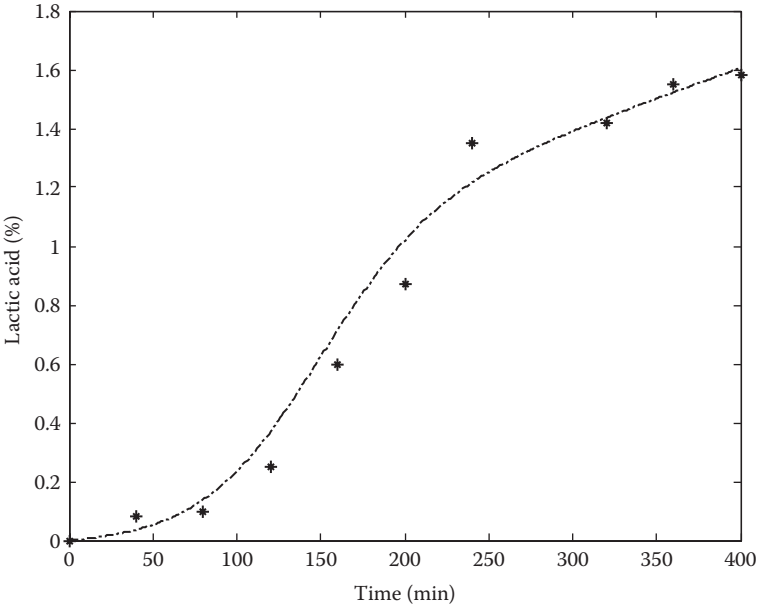


FIGURE E.3.19.2
Variation of the lactic acid concentration with time. (From Ozen, S., and Özilgen, M., *Journal of Chemical Technology and Biotechnology*, 54, 57–61, 1992.)

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Total biomass concentration, denoted by *x*, is actually a mixed culture and the microbial species contribute to *x* actually change with time. In spontaneous wine fermentations, as the process proceeds, alcohol-sensitive microorganisms are inhibited and the alcohol tolerant microorganisms dominate the culture. Alcohol-tolerant microorganisms are generally better alcohol producers, therefore parameter β of the Luedeking–Piret equation may be related with the ethanol concentration in the medium:

$$\beta = \beta_0 + \beta_1 c_{pr} + \beta_2 c_{pr}^2, \tag{E.3.20.1}$$

where β_0, β_1, and β_2 are constants. After substituting Equation E.3.20.1 in Equation 3.55:

$$\frac{dc_{Pr}}{dt} = \alpha x + (\beta_0 + \beta_1 c_{pr} + \beta_2 c_{pr}^2)\frac{dx}{dt}. \tag{E.3.20.2}$$

Substrate utilization in the exponential growth phase was

$$-\frac{dc_S}{dt} = \frac{1}{Y_{x/s}}\frac{dx}{dt} + \frac{1}{Y_{p/s}}\frac{dc_{Pr}}{dt}. \tag{E.3.20.3}$$

Lactic acid bacteria is the major species contributing to the total biomass concentration *x* in the malolactic fermentation phase, where lactic acid bacteria uses malic acid as a substrate to produce lactic acid. The logistic equation was employed to simulate microbial growth in the malolactic fermentation phase:

$$\frac{dx}{dt_M} = \mu_M x\left(1 - \frac{x}{x_{\max}}\right), \tag{E.3.20.4}$$

where t_M = time after commencement of the malolactic fermentation, and μ_M = specific growth rate of the malolactic fermentation.

Temperature changes in the fermentation vessel were modeled after making thermal energy balance:

$$-\sum_{i=1}^{n} U_i A_i (T - T_{\text{env}}) + \frac{V}{Y_\Delta}\frac{dx}{dt} = \frac{d(\rho c V T)}{dt}, \tag{E.3.20.5}$$

where the term $-\sum_{i=1}^{n} U_i A_i (T - T_{\text{env}})$ represents the energy loss from the fermentor surfaces, and the term $(V/Y_\Delta)(dx/dt)$ represents the thermal energy generation coupled with microbial growth. This term becomes zero after the end of the exponential growth in the alcoholic fermentation. The term $d(\rho c V T)/dt$ is thermal energy accumulation. Equation E.3.25.5 was rearranged after substituting Equation 3.44 for dx/dt:

$$\frac{dT}{dt} = K_1(T_{\text{env}} - T) + K_2 e^{\mu t}, \tag{E.3.20.6}$$

where $K_1 = \sum_{i=1}^{n}(U_i A_i/\rho c V)$ and $K_2 = (\mu x_0/Y_\Delta \rho c V)$. The numerical value of parameter K_2 was zero after the end of the exponential growth phase of the alcoholic fermentation. MATLAB® code E.3.20 compares the model with a typical set of experimental data in Figures E.3.20.1 and E.3.20.2.

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MATLAB® CODE E.3.20

Command Window:

```
clear all
close all

biomassD = [1.039,1.144,1.661,1.897,2.1872,2.1872,0.50,0.856,0.943,0.
971]; % microbal concentration
EthanolD = [0.143,0.251,0.373,0.822,1.099, 1.08 , 1.08, 1.08, 1.08,
1.08];
SugarD = [1.350,1.147,0.762, 0.025 , 0.025, 0.025, 0.025, 0.025,
0.025, 0.025];
tData = [25 55 70 120 150 170 200 240 260 280]; % times when
experimental data is obtained (h)
plot(tData,EthanolD,'+', tData,SugarD,'o'); hold on

% BIOMASS GROWTH MODEL
% exponential microbial growth during alcoholic fermentation
[t,y] = ode45('mgrw1',1:149,0.9); biomassM(1:149,1) = y;

% stationary microbial growth phase at the end of alcoholic
fermentation
[t,y] = ode45('mgrw2',150:174,2.1872);biomassM(150:174,1) = y;

% microbial death at the end of alcoholic fermentation
[t,y] = ode45('mgrw3',175:199,2.1);biomassM(175:199) = y;

% microbial growth in malo-lactic fermentation
[t,y] = ode45('mgrw4',200:300,0.5);biomassM(200:300) = y;
t = 1:1:300;

[AX,H1,H2] = plotyy(tData,biomassD, t, biomassM, 'plot'); hold on
set(H1,'LineStyle','d')
set(H2,'LineStyle','--')
set(get(AX(2),'ylabel'), 'string', 'x (OD_6_5_0)')
xlabel('Time (hours)')
ylabel('Ethanol (%), Reducing Sugar (%)')
legend('ethanol','sugar', 'biomass')

% ETHANOL
phase = 1 ; % growth phase
[t,y] = ode45(@(t,y) mgrw5(t,y,phase),0:150,[0.15 0 0]);
plot(t,y(:,2),'-');

phase = 2; % stationary phase
initial = y(end,2);
[t,y] = ode45(@(t,y) mgrw5(t,y,phase),150:300,[0 initial 0]);
plot(t,y(:,2),'-');

% REDUCING SUGAR
hold all;
phase = 1 ; % growth phase
[t,y] = ode45(@(t,y) mgrw5(t,y,phase),0:100,[0.085 0 1.8]);
plot(t,y(:,3),':');
```

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```
phase = 2; % after depletion of sugar
[t,y] = ode45(@(t,y) mgrw5(t,y,phase),100:300,[0 0 0.02123]);
plot(t,y(:,3),':');

% ENERGY BALANCE
time = [0 25 55 70 95 120 150 170 190 200 240 260 280];
Tdata = [20 22 24 28 29 31 30 30 29 28 28 25 25];
figure
plot(time,Tdata,'*'); hold on % plot the data
ylabel('Temperature (C)')
xlabel('Time (hours)')

% model
phase = 1 ; % growth phase
[t1,T1] = ode45(@(t,y) temp(t,y,phase), [0 130], 20);

phase = 2 ; % stationary phase
[t2,T2] = ode45(@(t,y) temp(t,y,phase), [130 300],T1(length(T1)));
plot(t1,T1,t2,T2)
```

M-File1:

```
function dx1 = mgrw1(t,x)
% exponential microbial growth during alcoholic fermentation
mu = 0.006;
dx1 = mu*x;
```

M-File2:

```
function dx2 = mgrw2(t,x)
% stationary microbial growth phase at the end of alcoholic
fermentation
dx2 = 0;
```

M-File3:

```
function dx3 = mgrw3(t,x)
% microbial death at the end of alcoholic fermentation
kd = 0.042;
dx3 = -kd*x;
```

M-File4:

```
function dx4 = mgrw4(t,x)
% microbial growth in malo-lactic fermentation
mu_m = 0.032;
xmax = 1.08;
dx4 = mu_m*x*(1-(x/xmax));
```

M-File5:

```
function dx = mgrw5(t,x,phase)
% product formation and substrate consumption models

format long g
mu = 0.006;
```

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```
alpha = 0.0045;
Yx = 0.04;
Yp = 10;

if phase = = 1 % exponential growth
    dxdt = mu * x(1);end
if phase = = 2; % stationary phase
    dxdt = 0;end

beta = (3.6 + 1.25 * x(2) + 0.004 *(x(2))^2);
dpdt = (alpha * x(1)) + (beta * dxdt);
dsdt = -(((1/Yx)*dxdt) + ((1/Yp)*dpdt));

dx = [dxdt;dpdt;dsdt];
```

M-File6:

```
function f = temp(t,T,phase)
if phase = = 1 % before depleting the sugar
% energy balance equation
K1 = 0.004;
K2 = 0.08;
Te = 18;
mu = 0.006;
 f = K1*(Te-T) + K2*exp(mu*t);
 f = f(:);
end

if phase = = 2; % after depleting the sugar
K1 = 0.004;
K2 = 0;
Te = 18;
mu = 0.006;
f = K1*(Te-T) + K2*exp(mu*t);
f = f(:);
end
```

Figures E.3.20.1 and E.3.20.2 will appear on the screen when we run the code.

Example 3.21: Kinetics of *Aspergillus Oryzae* Cultivations on Starch

Cultivation of *Aspergillus oryzae* on starch is described as a combination of two rate processes: starch hydrolysis and the uptake of some of the fermentable hydrolysis products for cellular activities, including growth, enzyme production, and maintenance. These processes are inter-related in a cyclic way and neither of them can be accomplished without the other (Figure E.3.21.1). The first link between these processes is starch hydrolyzing extracellular enzymes (i.e., glucoamylases and amylases). They are produced by the microorganism in the first process (i.e., with the cellular activities of the microorganism) and catalyze the second process (i.e., starch hydrolysis). The second link between these processes is the starch hydrolysis products. They are produced in the second process and consumed in the first process.

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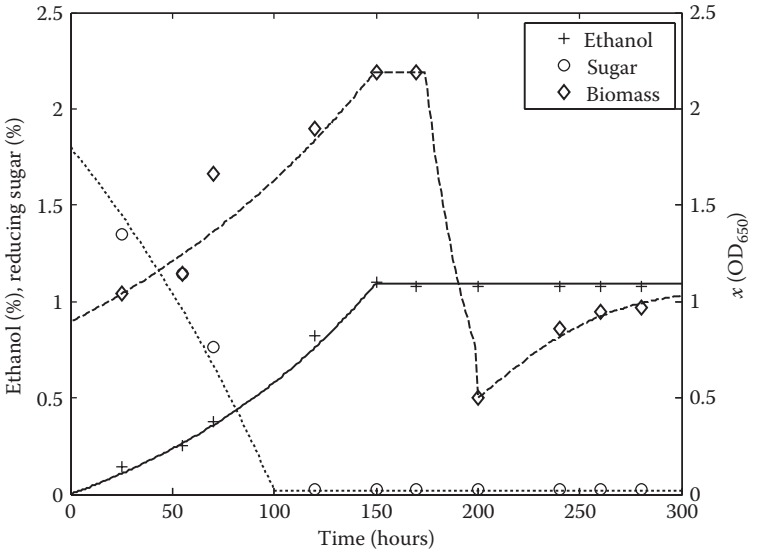


FIGURE E.3.20.1
Course of fermentation with slow fermented wine. Experimental data are shown in symbols. (From Özilgen, M., Celik, M., and Bozoglu, T. F., *Enzyme and Microbial Technology*, 13, 252–6, 1991.)

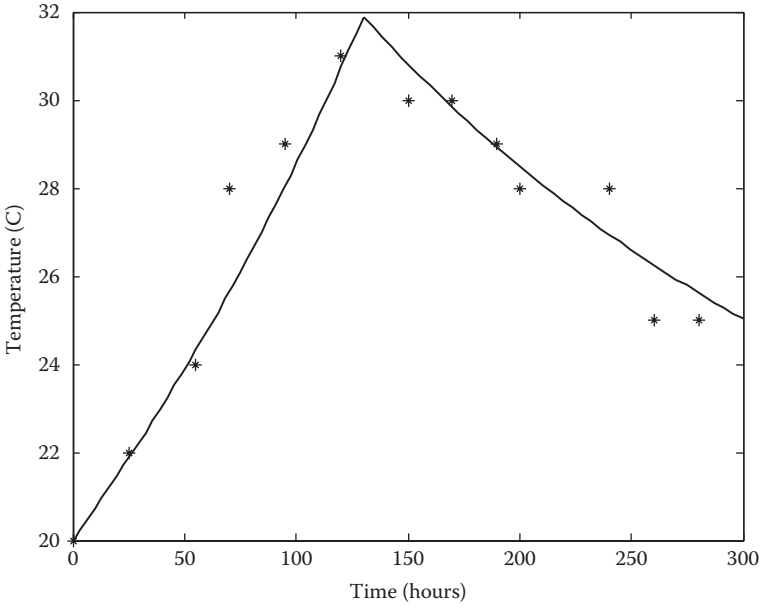


FIGURE E.3.20.2
Comparison of the model and the experimental temperatures. (From Özilgen, M., Celik, M., and Bozoglu, T. F., *Enzyme and Microbial Technology*, 13, 252–6, 1991.)

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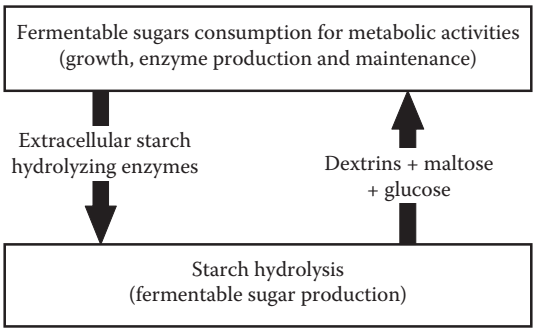


FIGURE E.3.21.1
Schematic description of the rate processes involved in *A. oryzae* cultivation on starch.

Biomass production was simulated with the logistic equation (Bayindirli, Özilgen, and Ungan 1991):

$$\frac{dx}{dt} = \mu x\left(1 - \frac{x}{x_{\max}}\right). \tag{3.34}$$

The total starch hydrolyzing enzyme production (Bayindirli, Özilgen, and Ungan 1991):

$$\frac{dc_E}{dt} = k_M \frac{dx}{dt} - k_N x, \tag{E.3.21.1}$$

where k_M and k_N are constants. The first term $k_M(dx/dt)$ indicates that the enzyme production rate was proportional to the growth rate of the microorganism. The second term $-k_N x$ shows that the microorganisms degrade the starch hydrolyzing enzyme in proportion with their own concentration. The *A. oryzae* produces extracellular proteases, which may be among the causes of the starch hydrolyzing enzyme degradation.

Starch hydrolyzing enzymes of *A. oryzae* are extracellular. If the microorganisms are separated from the broth during cultivation, the remaining enzymes will continue to degrade starch in the broth. When the total starch hydrolyzing enzyme activity is constant, the amount of starch degraded in time interval *dt* will be

$$-dc_S = k_S dt, \tag{E.3.21.2}$$

where k_S is the steady state starch degradation rate. If an additional enzyme is produced within this time interval, additional amounts of enzyme will be degraded in proportion with enzyme production (Bayindirli, Özilgen, and Ungan 1991):

$$-dc_S = k_S dt + k_U dc_E, \tag{E.3.21.3}$$

where k_U is a constant (i.e., grams of starch degraded per unit activity of enzyme produced). Equation E.3.26.3 may be rearranged (Bayindirli, Özilgen, and Ungan 1991):

$$-\frac{dc_S}{dt} = k_S + k_U \frac{dc_E}{dt}. \tag{E.3.21.4}$$

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The reducing sugar accumulation rates in the broth were (Bayindirli, Özilgen, and Ungan 1991)

$$\frac{dc_R}{dt} = k_R\left(-\frac{dc_S}{dt}\right) - \frac{1}{Y_{x/R}}\frac{dx}{dt} - k_R x, \tag{E.3.21.5}$$

where k_R is a proportionality constant; $Y_{x/R}$ is the biomass yield defined as grams of biomass produced per grams of starch used. Parameter k_R is the maintenance coefficient, defined as grams of starch used per gram of biomass in one hour to maintain vital activities other than growth. The term k_R (dc_S/dt) is the reducing sugar production rate in proportion to starch degradation. The terms $(1/Y_{x/R})(dx/dt)$ and $k_R x$ are the reducing sugar consumption rates for growth and maintenance, respectively.

Glucose constitutes only a fraction of the reducing sugars and its accumulation rates in the medium may be expressed similarly to the reducing sugar accumulation as

$$\frac{dc_G}{dt} = k_G\left(-\frac{dc_S}{dt}\right) - \frac{1}{Y_{x/G}}\frac{dx}{dt} - k_G x, \tag{E.3.21.6}$$

where the model constants had similar meanings to those of Equation E.3.21.5. MATLAB® code E.3.21 was used to compare the model with the experimental data.

MATLAB® CODE E.3.21

Command Window:

```
clear all
close all

TimeD = [5 10 20 45 50 70 75 90 100 120];
BiomassD = [0.344 0.443 0.162 3.579 5.190 10.916 11.754 12.623 12.427
12.677];
StarchD = [27.713,26.788,26.109,16.834,13.844,3.648,2.131,0.170,0.001
17,-1.244];

[t,x] = ode45('GrowthOnStarch', 0:1:120, [0.01 4900 29 0 0]);
ylbl = {'Biomass (g/L)','Enzyme (u/L)','Starch (g/L)','Reducing Sugar
(g/L)','Glucose (g/L)'};

% prepare the first figure
figure
 [AX,H1,H2] = plotyy(TimeD,BiomassD,TimeD,StarchD,'plot'); hold on
set(H1,'LineStyle','*')
set(H2,'LineStyle','+')
legend('Biomass','Starch',2,'Location','East')

set(get(AX(2),'ylabel'), 'string', 'Starch (g/L)')
xlabel('Time (hour)');
ylabel('Biomass (g/L)');
[AX,H3,H4] = plotyy(t,x(:,1),t,x(:,3),'plot'); hold on
```

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```
set(H3,'LineStyle','- -')
set(H4,'LineStyle','-')

% Enter the enzyme, reducing sugar and glucose data
EnzymeD = [1103,1403,-
599,11234,16122,31758,33374,32466,29330.729,25076];
ReducingSD = [0.783,1.814,3.6231,6.456,6.7293,7.002,6.9134,6.485,6.24
43,6.668];
GlucoseD = [0.299,0.707,1.406,2.427,2.513,2.543,2.493,2.294,2.189,2.3
53];

% prepare the second figure
figure
[AX,H1,H2] = plotyy(TimeD,ReducingSD, TimeD,EnzymeD,'plot'); hold on
set(H1,'LineStyle','*')
set(H2,'LineStyle','+')
set(get(AX(2),'ylabel'), 'string', 'Enzyme (u/L)')
plot(TimeD,GlucoseD,'d') ; hold on
xlabel('T (hour)');
legend('Reducing Sugar','Glucose','Enzyme',3,'Location','East')

plot(t, x(:,5), 'k-',t, x(:,4), 'k-'); hold on
ylabel('Reducing Sugar, Glucose (g/L)');
[AX,H3,H4] = plotyy(t,x(:,4),t,x(:,2),'plot'); hold on
set(H3,'LineStyle','- -')
set(H4,'LineStyle','-')
```

M-File:

```
function dx = GrowthOnStarch(t,x)
u = 13.3e-2; Xmax = 12.5;
kM = 3.3e3; kN = 20;
ks = 15.8e-2; kv = 45e-5;
kR = 1.09; Yr = 0.55; BR = 4.5e-3;
kG = 0.42; Yg = 1.4; BG = 1.8e-3;

 % Biomass growth Model
dx1 = u*x(1)*(1-(x(1)/Xmax));

% Starch Hydrolyzing Enzyme Production Model
dx2 = kM*dx1 - kN*x(1);

% Concentration of Remaining Starch
dx3 = -ks - kv*dx2;

% Concentration of Remaining Reducing Sugar
dx4 = -kR*dx3 - (1/Yr)*dx1 - BR*x(1);

% Concentration of Remaining Glucose
dx5 = -kG*dx3 - (1/Yg)*dx1 - BG*x(1);

dx = [dx1; dx2; dx3; dx4; dx5];
```

When we run the code Figures E.3.21.2 and E.3.21.3 will appear in the screen.

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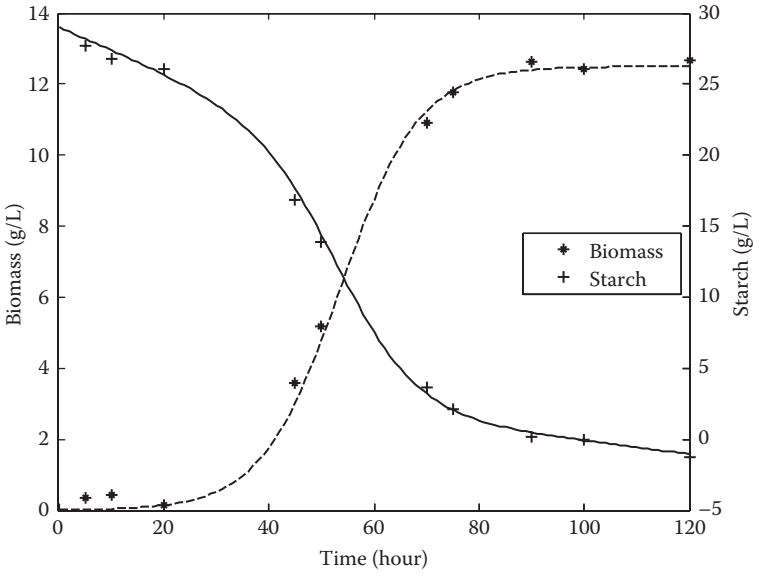


FIGURE E.3.21.2
Time course of *A. oryzae* growth and starch consumption. (Original data (shown with symbols) from Bayindirli, A., Özilgen, M., and Ungan, S., *Biocatalysis*, 5, 71–8, 1991.)

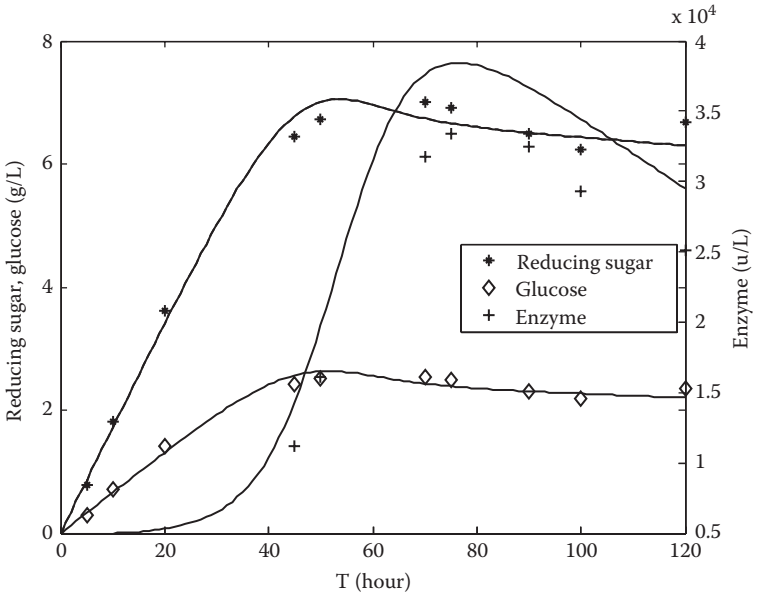


FIGURE E.3.21.3
Variation of enzyme activity, reducing sugar, and glucose concentrations during the course of the growth of *A. oryzae* on starch. (Original data (shown with symbols) from Bayindirli, A., Özilgen, M., and Ungan, S., *Biocatalysis*, 5, 71–8, 1991.)

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3.10 Kinetics of Microbial Death

Microbial death kinetics has a significant importance in food processing since it is among the major phenomena occurring during pasteurization and sterilization processes. Microbial death is generally described in analogy with unimolecular, irreversible, first-order rate expression:

$$x(\text{live microoganism}) \xrightarrow{k_d} x_d\,(\text{dead microoganism})$$

$$\frac{dx}{dt} = -k_d x. \tag{3.33}$$

An alternative expression for Equation 3.33 is

$$\frac{d(\log x)}{dt} = -\frac{1}{D_T}, \tag{3.57a}$$

with

$$D_T = \frac{2.303}{k_d}. \tag{3.58b}$$

The D_T value is defined as the heating time at constant temperature T to reduce microbial population by one log cycle, or 10% of its initial value. The z value is defined as the temperature difference required to change the D_T value by a factor of 10, or one log cycle:

$$\frac{d(\log D_T)}{dT} = -\frac{1}{z}. \tag{3.57c}$$

Equation 3.54 may be rearranged and integrated as

$$D_T = D_{T\text{ref}}\,10^{(T_{\text{ref}}-T)/z}. \tag{3.57d}$$

The z value is related with the activation energy of the Arrhenius expression:

$$z = \frac{2.303RTT_{\text{ref}}}{E_a}. \tag{3.58}$$

During thermal processing of the foods, microbial death and inactivation of the enzymes are always accompanied with a loss of nutrients due to thermal degradation, since they share the same medium. Although death of the microorganisms and destruction of the enzymes and toxins are desired, loss of the nutrients is not desired. The range of the kinetic constants describing the resistance of the food components to thermal processing are given in Table 3.6.

In most processes, spores, vegetative cells, and enzymes are destroyed while color, flavor, and vitamins are desired to survive. Among the constituents to be destroyed enzymes usually have the highest D_{121} (Table 3.6) values, therefore enzyme inactivation is almost the most difficult task to achieve in thermal processing.

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TABLE 3.6

Kinetic Constants Describing the Resistance of the Food Constituents to Thermal Processing

Constituent	z (°C)	E_a (Joules/mol)	D_{121} (min)
Vitamins	20–30	$8.4 \times 10^4 - 12.5 \times 10^4$	100–1000
Color, texture, flavor	25–45	$4.2 \times 10^4 - 12.5 \times 10^4$	5–500
Enzymes	12–56	$5.0 \times 10^4 - 41.8 \times 10^4$	1–10
Vegetative cells	4–7	$41.8 \times 10^4 - 50.2 \times 10^4$	0.002–0.02
Spores	7–12	$22.2 \times 10^4 - 34.7 \times 10^4$	0.1–5.0
Cooking value (overall quality estimation)	15–45	$5.5 \times 10^4 - 17.0 \times 10^4$	1.2–12.5

Source: Lund, D., *Food Technology,* 31, no. 2, 71–78, 1977; Hallström, B., Skjöldebrand, C., and Trägårdh, C., *Heat Transfer & Food Products.* Elsevier Applied Science Publishers, London, 1988.

Example 3.22: MATLAB® Code for Conversion of the D_T and z Values into k_d and E_a and the Kinetic Compensation Relations for Microbial Death

The relation between the D_T value and the thermal death rate reaction rate constant k_d is

$$D_T = \frac{2.303}{k_d}. \tag{3.58}$$

The D_T values reported by Rodrigo et al. (1993) for destruction of *Clostridium sporogenes* PA3679 spores in the mushroom extract at different pH values and temperatures is the data, D matrix, of the MATLAB code E.3.22.a, where the D values are converted into the thermal death rate constants k_d.

MATLAB® code E.3.22.b converts the thermal death rate constants back into the D_T values.

Temperature effects on the death rate constants were given with the Arrhenius expression:

$$k = k_0 \exp\left\{-\frac{E_a}{RT}\right\}. \tag{3.5}$$

Equation 3.5 may be linearized as

$$\ln(k_d) = \ln(k_{d0}) - \frac{E_a}{RT}.$$

MATLAB® code E.3.22.c determines the parameters $\ln(k_{d0})$ and E_a.

The compensation relation is

$$\ln(k_{d0}) = -3.29 + 3.03 \times 10^{-4} E_a. \tag{E.3.22.1}$$

MATLAB® code E.3.22.d determines the compensation relation by using the ln (k_{d0}) and E_a values. MATLAB® code E.3.22.e converts E_a values to z values. MATLAB® code E.3.22.f converts the z values back into E_a values.

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MATLAB® CODE E.3.22.a

Command Window:

```
clear all
close all

% enter the data
D = [1.5 0.63 0.27 0.086 0.029; 1.64 0.87 0.31 0.098 0.030; 1.774
0.86 0.32 0.091 0.027; 1.72 0.68 0.19 0.059 0.02];
pH = [6.65 6.22 5.34 4.65];

% calculate the thermal death reaction rate constants
k = 2.303./(D*60);

% tabulate the results:
fprintf('\n     Thermal death rate constants kd (1/s)\n')
fprintf('pH   394(K)  398(K)  403(K)  408(K)  413(K)\n')
pH2 = pH';
for i = 1:4
fprintf('%2.2f%9.4f%9.4f%9.4f%9.4f%9.4f\
n',pH2(i),k(i,1),k(i,2),k(i,3), k(i,4),k(i,5))
end
```

When we run the code the following will appear on the screen:

```
       Thermal death rate constants kd (1/s)
pH    394(K)  398(K)  403(K)  408(K)  413(K)
6.65  0.0256  0.0609  0.1422  0.4463  1.3236
6.22  0.0234  0.0441  0.1238  0.3917  1.2794
5.34  0.0216  0.0446  0.1199  0.4218  1.4216
4.65  0.0223  0.0564  0.2020  0.6506  1.9192
```

MATLAB® CODE E.3.22.b

Command Window:

```
clear all
close all

% enter the data
k = [0.0256 0.0609 0.1422 0.4463 1.3236; 0.0234 0.0441 0.1238 0.3917
1.2794; 0.0216 0.0446 0.1199 0.4218 1.4216; 0.0223 0.0564 0.2020
0.6506 1.9192];
pH = [6.65 6.22 5.34 4.65];

% calculate the D values
D = 2.303./(k*60);

% tabulate the results:
fprintf('\n     D values (min)\n')
fprintf('pH   394(K)  398(K)  403(K)  408(K)  413(K)\n')
pH2 = pH';
```

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```
for i = 1:4
fprintf('%2.2f%9.4f%9.4f%9.4f%9.4f%9.4f\
n',pH2(i),D(i,1),D(i,2),D(i,3), D(i,4),D(i,5))
end
```

When we run the code the following will appear on the screen:
D values (min)

```
pH   394(K)  398(K)  403(K)  408(K)  413(K)
6.65  1.4993  0.6303  0.2699  0.0860  0.0290
6.22  1.6403  0.8704  0.3100  0.0980  0.0300
5.34  1.7770  0.8606  0.3201  0.0910  0.0270
4.65  1.7212  0.6806  0.1900  0.0590  0.0200
```

MATLAB® CODE E.3.22.c

Command Window:

```
clear all
close all

% enter the data
T = [121 125 130 135 140];
D = [1.5 0.63 0.27 0.086 0.029; 1.64 0.87 0.31 0.098 0.030; 1.774
0.86 0.32 0.091 0.027; 1.72 0.68 0.19 0.059 0.02];
pH = [6.65 6.22 5.34 4.65];
R = 8.314;
Tref = 121;

  % compute ln(kd)
for i = 1:5
    L(i) = -1/(R*(T(i) + 273));
    for j = 1:4
       lnkd(j,i) = log(2.303/(D(j,i)*60));
    end
end

% compute ln(kd0) and Ea
for i = 1:4
    f = polyfit(L, lnkd(i,:),1);
    Ea(i) = f(1);
    lnkd0(i) = f(2);
    rmatrix = corrcoef(lnkd(i,:),L);
    r(i) = rmatrix(1,2);
end

% tabulate the results:
fprintf('\n pH    Ea (J/mol)   lnkd0       r\n')
pH2 = pH';
for i = 1:4
fprintf('%2.2f%14.1f%14.5f% 14.5f \n',pH2(i),Ea(i),lnkd0(i),r(i))
end
```

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When we run the code the following will appear on the screen:

```
pH     Ea (J/mol)    lnkd0        r
6.65    278498.2    81.31450    0.99842
6.22    287546.4    83.87150    0.99677
5.34    299594.0    87.48260    0.99678
4.65    319939.2    93.85763    0.99981
```

MATLAB® CODE E.3.22.d

Command Window:

```
clear all
close all

Ea = [278498.2 287546.4 299594.0 319939.2];
lnkd0 = [81.31450 83.87150 87.48260 93.85763];
xlabel('Ea');
ylabel('lnk_d_0')
hold on,
plot(Ea,lnkd0,'k*');
f = polyfit(Ea,lnkd0,1);
y = polyval(f,Ea);
plot(Ea, y);
rm = corrcoef(Ea,lnkd0);
for i = 1:length(Ea);
d(i) = ((lnkd0(i))-(f(2) + f(1)*Ea(i)))^2;
end;
r = rm(1,2)
se = sqrt(sum(d)/length(Ea))
fprintf('kinetic compensation relation is')
fprintf('\nlnkd0 = %.2gEa %2g\n',f(1), f(2))
```

The following lines and Figure E.3.22 will appear on the screen after running the code:

```
r =
    0.9998
se =
    0.0994

kinetic compensation relation is
lnkd0 = 0.0003Ea -3.36036
```

Example 3.23: Kinetics of the Death of Spores When Subjected to Dynamic Lethal Temperatures

Sapru et al. (1993) suggested that when a population of dormant spores are subjected to dynamic lethal temperatures, a fraction of the population die without activation and the other fraction are activated first and then die:

$$\text{dormant spores } (x) \xrightarrow{k_d} \text{dead spores}, \tag{E.3.23.1}$$

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MATLAB® CODE E.3.22.e

Command Window:

```
clear all
close all

% enter the data
R = 8.314;
Tref = 394;
pH = [6.65 6.22 5.34 4.65];
Ea = [278498.2 287546.4 299594.0 319939.2];

% convert Ea to z
T = 394;
for i = 1:length(Ea);
z(i) = 2.303*R*T*Tref./Ea(i);
end;

% tabulate the results:
fprintf('\n pH     z (C)\n')
pH2 = pH';
for i = 1:4
fprintf('%2.2f%14.1f\n',pH2(i),z(i))
end
```

When we run the code the following will appear on the screen:

```
pH      z (C)
6.65     10.7
6.22     10.3
5.34      9.9
4.65      9.3
```

MATLAB® CODE E.3.22.f

Command Window:

```
clear all
close all

% enter the data
z = [10.7 10.3 9.9 9.3];
R = 8.314;
Tref = 394;

% convert Ea to z
for i = 1:length(Ea);
Ea(i) = 2.303*R*T*Tref/z(i);
end

% tabulate the results:
fprintf('\n pH    Ea(J/mole)\n')
```

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```
pH2 = pH';
for i = 1:4
fprintf('%2.2f%14.1f\n',pH2(i),Ea(i))
end
```

When we run the code the following will appear on the screen:

```
 pH     Ea(J/mole)
6.65    277787.5
6.22    288575.3
5.34    300234.9
4.65    319604.9
```

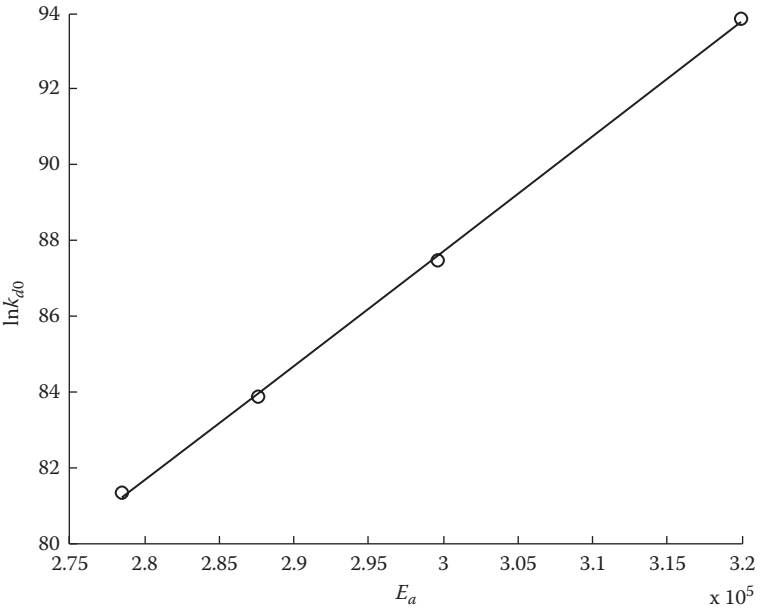


FIGURE E.3.22
Comparison of the experimental data with Equation E.3.22.1.

$$\text{dormant spores } (x) \xrightarrow{k_a} \text{activated spores } (x_a), \tag{E.3.23.2}$$

$$\text{activated spores } (x_a) \xrightarrow{k_{ad}} \text{dead spores.} \tag{E.3.23.3}$$

Equation E.3.23.1 refers to the fraction that die without activation; Equations E.3.23.2 and E.3.23.3 refer to the other fraction. The process may be described as

$$\frac{dx}{dt} = -(k_d + k_a)x, \tag{E.3.23.4}$$

$$\frac{dx_a}{dt} = k_a x - k_{ad} x_a. \tag{E.3.23.5}$$

MATLAB® code E.3.23 tests the validity of the model.

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MATLAB® CODE E.3.23

Command Window:

```
clear all
close all

% introduce the data
TimeDlnx = [0 5 15 21 30 41 45 50 51 52 54];
lnxD = [20.4 22 20 19.7 18.8 19 19 17 16 13.9 10.9];
TimeDT = [0:1:56];
T = [100 102 103.5 106 108.2 109.5 110 110 109.9 110 110 110 110 111
111.6 111.8 112.2 112.5 113.8 113.9 114 114.5 115 114.5 115.2 112.5
112 110 108.6 107 106 105 104.6 105 106.8 106.8 106.9 108 108 108
108 108 108 108 108 110.5 113.5 116 118.4 119 120.4 119 118 117
118.6 118 120]; % temperature data (oC)

% constants of the model
Ead = 3.541e5; % J/mole
Eaa = 5.0e5; % J/mole
Eaad = 3.6e5; % J/mole
kd0 = 5e46; % 1/min
ka0 = 6e45; % 1/min
kad0 = 7e48; % 1/min
R = 8.314; % J/moleK

% model
x(1) = 33e8; % spores/mL
xa(1) = 2.3e8; % spores/mL
deltaTime = 2; % min
for i = 2:1:length(TimeDT);
k = i-1;
kd(k) = kd0*exp(-Ead/(R*(T(k) + 273)));
ka(k) = ka0*exp(-Eaa/(R*(T(k) + 273)));
kad(k) = kad0*exp(-Eaad/(R*(T(k) + 273)));
x(i) = x(k) - ((kd(k) + ka(k))*x(k))*deltaTime;
if x(i) < 1
x(i) = 1;
end
if xa(k) = = 1
xa(i) = 1;
end

xa(i) = xa(k) + (ka(k)*x(k) - kad(k)*xa(k))*deltaTime;
if xa(i) < 1
xa(i) = 1;
end
if xa(k) = = 1
xa(i) = 1;
end
xTotal(i) = xa(i) + x(i);
end
```

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```
logxTotal = log(xTotal);
plot(TimeDT,logxTotal,'-'); hold on

% plot the data
[AX,H1,H2] = plotyy(TimeDlnx,lnxD,TimeDT,T); hold on
set(H1,'LineStyle','*')
set(H2,'LineStyle',':')
xlabel('Time (min)');
ylabel('ln(x) (survivors/mL)');
set(get(AX(2),'ylabel'), 'string', 'Temperature (\circC)')
legend('model','survivor data','temperature',3,'Location','NorthEast')
```

When we run the code Figure E.3.23 will appear in the screen.

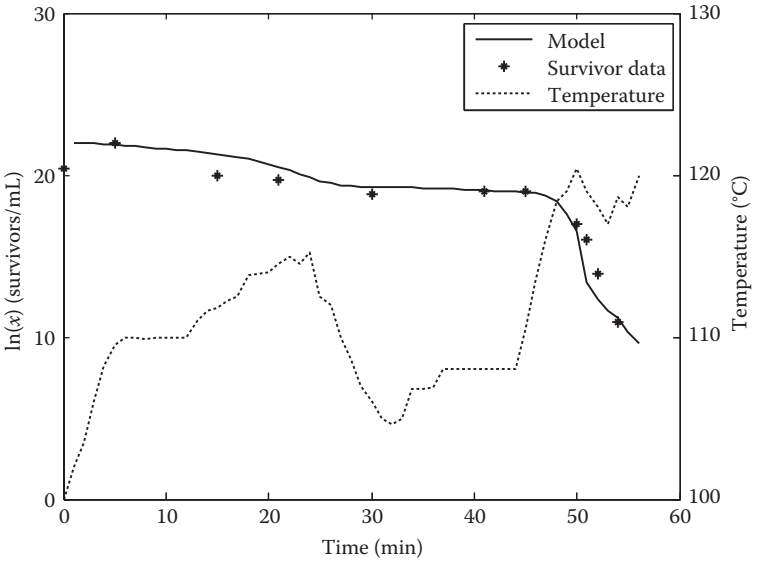


FIGURE E.3.23
Comparison of the model with the experimental data obtained with *Bacillus stearothermophilus* spores subjected to dynamic lethal temperatures. (Adapted from Sapru, V., Smerage, G. H., Teixeira, A. A., and Lindsay, J. A., *Journal of Food Science,* 223–8, 1993.)

Example 3.24: Kinetics of Ultraviolet Inactivation Processes

The *Series-event model* (Severin, Suidan, and Engelbrecht 1983) may be used to describe the ultraviolet inactivation processes. An event is assumed to be a unit of damage. The event occurs in a stepwise fashion:

$$M_0 \xrightarrow{kI} M_1 \xrightarrow{kI} M_2 \xrightarrow{kI} \ldots\ldots M_{n-1} \xrightarrow{kI} M_n, \tag{E.3.24.1}$$

where k = constant, I = total point ultraviolet intensity, and M_i = an organism that has reached event level i. The rate at which an organism passes from one event level to the next is first order with respect to the ultraviolet intensity and independent of the event level occupied by the organism. As long as an organism is exposed to the ultraviolet collects damage. An event threshold exists such that an organism that collects damage greater than the tolerable event threshold is deactivated. The threshold may vary depending on the species, strain, or culturing conditions; however, for a given set of conditions the threshold level is constant.

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For a well-mixed, flat, thin-layered, closed batch reactor the rate at which the organisms pass through event level i is

$$R_{xi} = kIx_{i-1} - kIx_i. \tag{E.3.24.2}$$

Equation E.3.24.2 may be incorporated in Equation 3.57 written for species at damage level i in a batch reactor as

$$\frac{dx_i}{dt} = kIx_{i-1} - kIx_i. \tag{E.3.24.3}$$

With $i = 0$ (x_0 = concentration of the undamaged microorganisms) Equation E.3.24.3 is rewritten as

$$\frac{dx_0}{dt} = -kIx_0. \tag{E.3.24.4}$$

The solution to Equation E.3.24.3 is

$$x_0 = x_{\text{initial}}\ e^{-kIt}. \tag{E.3.24.5}$$

Equation E.3.24.5 describes the variation of the concentration of the undamaged microorganisms with time, where x_{initial} is the initial concentration of the microorganisms before being subjected to UV radiation.

Equation E.3.24.3 may be rewritten and solved sequentially from $i = 0$ to $i = n–1$ (i.e., when $i = 1$ we have)

$$\frac{dx_1}{dt} = kIx_0 - kIx_1. \tag{E.3.24.6}$$

After substituting Equation E.3.24.5 in Equation E.3.24.6 and rearranging

$$\frac{dx_1}{dt} + kIx_1 = kIx_{\text{initial}}\ e^{-kIt}. \tag{E.3.24.7}$$

The solution to Equation E.3.24.7 is

$$x_1 = x_{\text{initial}}\, e^{-kIt} kIt. \tag{E.3.24.8}$$

The general expression for time varying density of organisms at any level i is

$$x_i = \frac{x_{\text{initial}}(kIt)^i}{i!} e^{-kIt}. \tag{E.3.24.9}$$

The total fraction of the surviving organisms between any level 0 and $n–1$ is

$$\frac{x}{x_{\text{initial}}} = \sum_{i=0}^{n-1} \frac{x_i}{x_{\text{initial}}} = \exp(-kIt) \sum_{i=0}^{n-1} \frac{(kIt)^i}{i!}, \tag{E.3.24.10}$$

where n = threshold number of the damaged sites required for inactivation. MATLAB® code E.3.24 simulates the inactivation processes through Equation E.3.24.10.

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MATLAB® CODE E.3.24

Command Window:

```
clear all
close all
% enter the constants
k = [1.538e-3 0.891e-3 0.0724e-3];
n = [9 15 1];
I = 300;

% start the figure
figure; hold on;
xlabel('Contact Time (sec)');
ylabel('Surviving Fraction');

% compute the model
for i = 1:3;
     for t = 0:200;
       clear S
         for j = 0:n(i);
             S(j + 1) = (k(i)*I*t)^(j)/factorial(j);
         end
             time(t + 1) = t;
             FS(t + 1) = exp(-k(i)*I*t)*sum(S);
       end
% plot the model
          if i = = 1; plot(time,FS, '-'); end
          if i = = 2; plot(time,FS, ':'); end
          if i = = 3; plot(time,FS, '--'); end
end

legend('k = 1.538e-3 1/s', 'k = 0.891e-3 1/s', 'k = 0.0724e-3 1/s',
'Location','NorthEast')
grid on
```

Figure E.3.24 will appear on the screen when we run the code.

Example 3.25: Weibull Model of Microbial Inactivation

The Weibull distribution model is often used in the industry with mechanical or electrical devices to estimate the probability of the failure $p(t)$ at a given time t (Weibull 1951):

$$p(t) = e^{-[(t-\gamma)/\delta]^n}. \tag{E.3.25.1}$$

Parameters n, γ, and δ are referred to as the shape factor, location parameter, and the characteristic life, respectively. The Weibull distribution model has three adjustable parameters, so it is commonly used in the industry to model a surviving fraction of the commodities that may not be represented with the other models. The location factor $\gamma = 0$ if failures may start at $t = 0$, then the Weibull model becomes

$$p(t) = e^{-(t/\delta)^n}. \tag{E.3.25.2}$$

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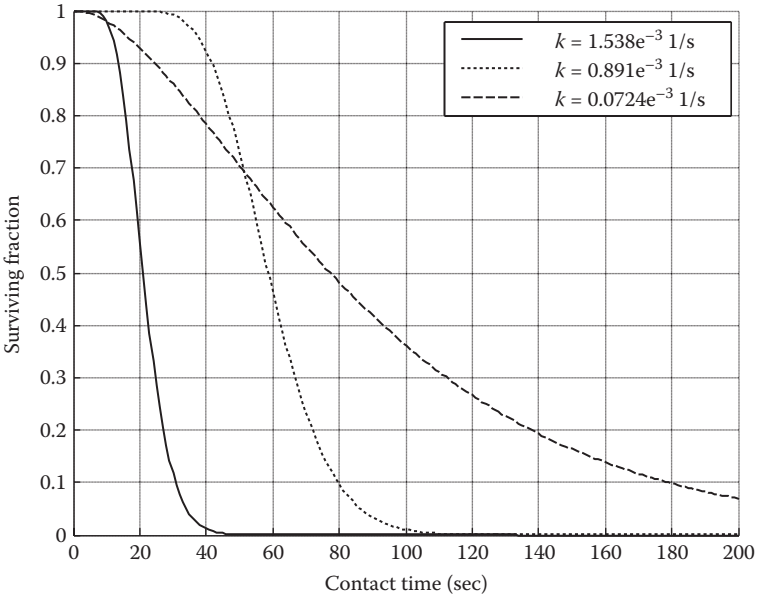


FIGURE E.3.24
Inactivation processes as described by Equation E.3.23.10. Kinetic parameters, which simulate the data very closely (From Severin, B. F., Suidan, M. T., and Engelbrecht, R. S., *Water Research,* 17, 1669–78, 1983.) *for individual species as: Escherichia coli* $n = 9, k = 1.538 \times 10^{-3}$ cm²/mW s; *Candida parasilosis* $n = 15, k = 0.891 \times 10^{-3}$ cm²/mW s; f2 bacterial virus $n = 1, k = 0.0724 \times 10^{-3}$ cm²/mW s.

Equation E.3.25.2 may be used to estimate the fraction of the surviving microorganisms $x(t)/x_0$ in a sterilization process as

$$\ln\left(\frac{x(t)}{x_0}\right) = -\left(\frac{t}{\delta}\right)^n, \tag{E.3.25.3}$$

where parameters δ and n varies with the experimental conditions. The differential form of Equation E.3.25.3 is

$$\frac{dx}{dt} = -k_{app}x, \tag{E.3.25.4}$$

with the time-dependent apparent rate constant:

$$k_{app} = \frac{n}{t}\left(\frac{t}{\delta}\right)^n \tag{E.3.25.5}$$

(van Boekel 2002), after modeling 55 sets of thermal processing data from the literature with the Weibull Equation E.3.25.3, concluded that when $n < 1$ the upward concave survival curve implies that the cells have the ability to adapt thermal stress and become more resistant to temperature effects. When $n > 1$, the downward concave survival curve implies that the cells are accumulating the damage and becoming increasingly heat sensitive.

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Buzrul et al. (2008) employed Equation E.3.25.3 for modeling microbial inactivation in high pressure processing, where parameter δ was analogous to parameter D_T of thermal processing operations. A variation of δ with pressure is:

$$\frac{d(\log\delta)}{dP} = -\frac{1}{z_p}. \tag{E.3.25.6}$$

MATLAB® code E.3.25.a prepares Figure E.3.25.1 to depict a variation of parameter δ with pressure. MATLAB code E.3.25.b computes the fraction of the microorganisms surviving the process (Figure E.3.25.2).

MATLAB® CODE E.3.25.a

Command Window:

```
clear all
close all
format compact

% data for variation of delta with pressure
pData = [400 450 500 550 600]; % Pressure (MPa)
deltaD = [10.5 5.4 3.2 1.8 1.2];

% plot the data
semilogy(pData, deltaD,'d'); hold on
xlabel('Pressure (MPa)'); hold on
ylabel('log(delta)'); hold on
grid on
ylim([1 12])

% modeling
LogDelta = log(deltaD);
f = polyfit(pData,LogDelta,1)
y = polyval(f,pData);
y1 = exp(y);

% plot the model
semilogy(pData,y1,'-'); hold on

% determine the correlation coefficient
rm = corrcoef(pData,LogDelta); % correlation coefficients matrix
r = rm(1,2) % correlation coefficient

% determine the standard error
for i = 1:length(pData);
      d(i) = ((LogDelta(i))-(f(2)+f(1)*pData(i)))^2;
end;
se = sqrt(sum(d)/length(pData))

fprintf('equation of the best fitting line is ')
fprintf('log(delta) = %.f%.4fP',f(2), f(1))
zp = -1/f(1);
fprintf('\n\nzp = %.f 1/MPa\n', zp)
```

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The following lines and Figure E.3.25.1 will appear on the screen when we run the code:

```
f =
   -0.0109   6.6309
r =
   -0.9969
se =
    0.0602
equation of the best fitting line is log(delta) = 7-0.0109P

zp = 92 1/MPa
```

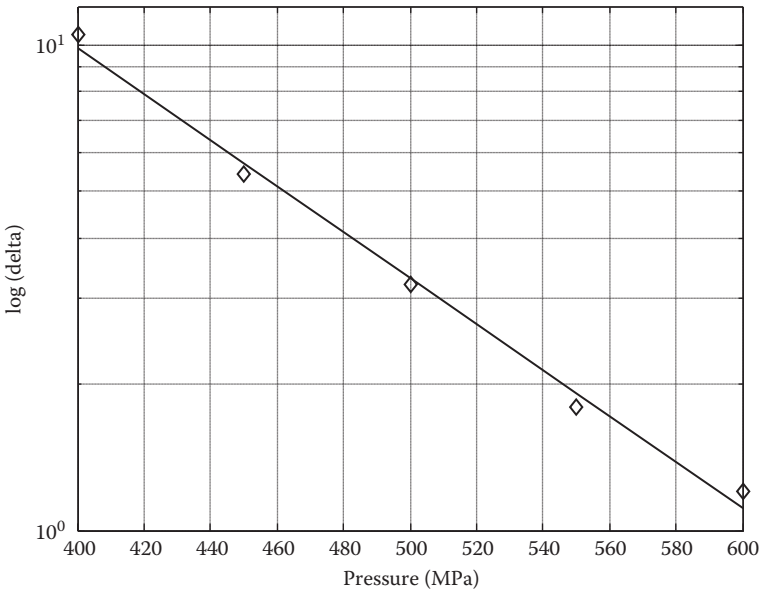


FIGURE E.3.25.1
Variation of the characteristic life δ with pressure during high pressure inactivation of *E. coli* in whole milk. (Adapted from Buzrul, S., Alpas, H., Largeteau, A., and Demazeau, G., *European Food Research and Technology*, 227, 443–8, 2008.)

Gomez et al. (2005) employed Equation E.3.25.3 for modeling microbial inactivation by pulsed electric fields. MATLAB code E.3.25.c computes the fraction of the microorganisms surviving the process (Figure E.25.3).

3.11 Ideal Reactor Design

Vessels used to conduct chemical reactions are called reactors. There are three basic types of ideal reactors: *Batch*, *Continuously Stirred Tank* (*CSTR*), and *Plug Flow* (*PF*). A batch reactor is a closed vessel with no input and output streams. Reactants are charged into the reactor,

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MATLAB® CODE E.3.25.b

Command Window:

```
clear all
close all

% survival data of E. coli at 400 MP
TimeD1 = [0 4 11 17 22 32 41 60 80];
xRatioData1 = [0 -0.4 -0.7 -0.9 -1.2 -1.8 -2.8 -3.7 -5];
f = [ -0.0109  6.6309];
plot(TimeD1,xRatioData1,'o'); hold on % plot the 400 MPa data
grid on

% survival data of E. coli at 500 MP
TimeD2 = [0 8 11 18 22 30 37 40];
xRatioData2 = [0 -1.3 -2.8 -3 -4 -6 -6.3 -7.5];
plot(TimeD2,xRatioData2,'*'); hold on % plot the 500 MPa data
legend('400 MPa', '500 MPa', 2,'Location','SouthWest')

% Weibull Model Parameters
Pexp = [400 500];
LogDeltaExp = f(2) + f(1)*Pexp;
delta = exp(LogDeltaExp);
n = 0.78;
t = [0 10 20 30 40 50 60 70 80; 0 10 20 30 40 50 60 70 80];

for i = 1:2;
    for j = 1:9;
      Delta = delta(i);
      y(i,j) = -(t(i,j)./Delta).^n;
     end
end

% model
plot(t(1,:),y(1,:), ':', t(2,:),y(2,:), ':'), hold on % plot the model
xlabel('Time (min)')
ylabel('log[x(t)/x_0]')
```

The following lines will appear on the screen when we run the code:

```
r =
   -0.9969
se =
    0.0602
equation of the best fitting line is log(delta) = 7-0.0109P
zp = 92 1/MPa
```

left for a certain period to be well mixed, and then removed when the required conversion is achieved. A CSTR reactor is equipped with input and output streams. Due to the well mixing, every point in the reactor and just at the exit are expected to have the same concentration. Plug flow reactors are tubular flow reactors, there is no velocity gradient in radial direction, and composition of the fluid varies in the flow direction only.

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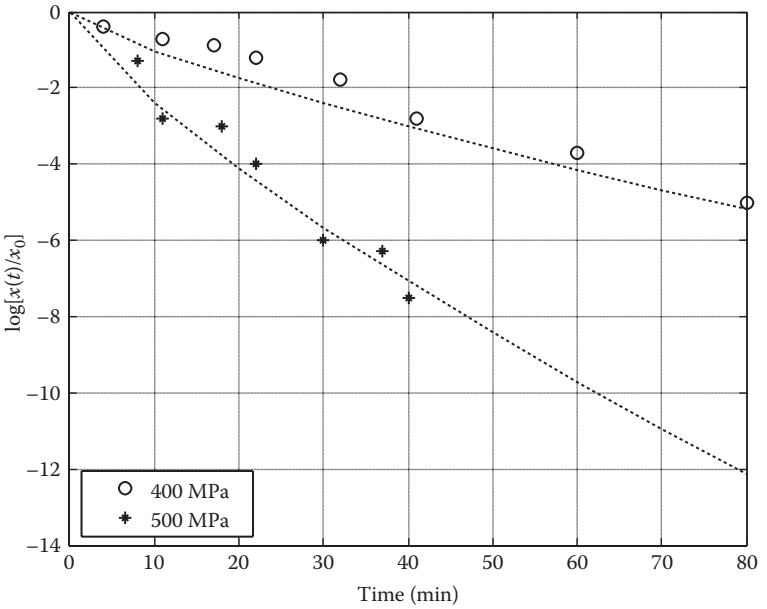


FIGURE E.3.25.2
Comparison of the Weibull model with the experimental data obtained during high pressure inactivation of *E. coli* in whole milk. (Adapted from Buzrul, S., Alpas, H., Largeteau, A., and Demazeau, G., *European Food Research and Technology,* 227, 443–8, 2008.)

MATLAB® CODE E.3.25.c

Command Window:

```
clear all
close all

% survival data of L. monocytogenes treated at pH=3.5 and 22 kV/cm
TimeD1=[0 10 20 120 200 400 600 800 1000]; % microseconds
lnxRatioData1=[0 -1.4 -2.8 -5.5 -7.4 -9.9 -12.2 -13.1 -13.4];
plot(TimeD1,lnxRatioData1,'o'); hold on
TimeModel=[1:10:1000];

% survival data of L. monocytogenes treated at pH=5 and 28 kV/cm
TimeD2=[0 5 10 120 200 400 600 800 1000];
lnxRatioData2=[0 -1.2 -2.8 -5.1 -6.2 -7.4 -8.5 -8.8 -9.7];
plot(TimeD2,lnxRatioData2,'*'); hold on
legend('pH=3.5 and 22 kV/cm', 'pH=5.0 and 28 kV/cm',
2,'Location','NorthEast')

% Model
n=[0.38 0.39];
delta=[2.30 1.20];
for i=1:length(TimeD1)
lnxRatioModel1=-(TimeModel./delta(1)).^n(1);
end
```

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```
plot(TimeModel,lnxRatioModel1,'-'); hold on
for i=1:length(TimeD2)
lnxRatioModel2=-(TimeModel./delta(2)).^n(2);
end
plot(TimeModel,lnxRatioModel2,'-'); hold on
xlabel('Treatment Time (microseconds)')
ylabel('ln[x(t)/x_0]')
grid on
```

Figure E.3.25.3 will appear on the screen when we run the code.

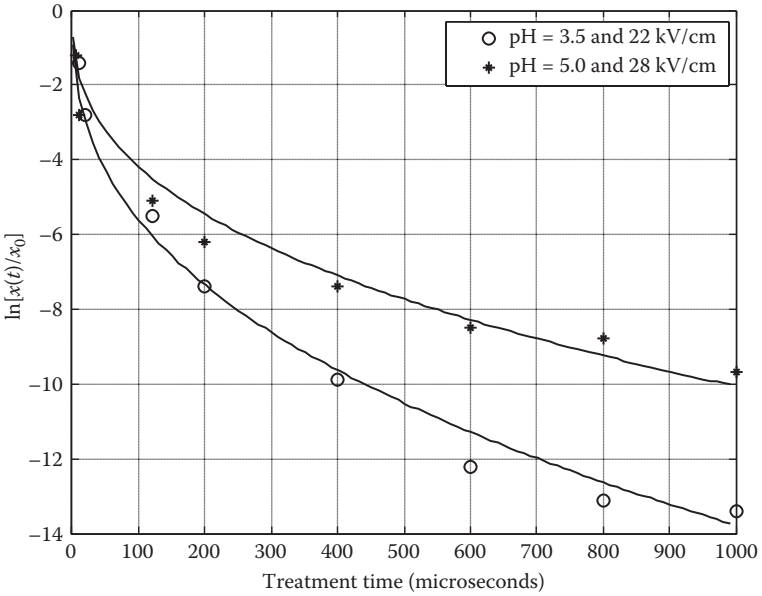


FIGURE E.3.25.3
Comparison of the Weibull model with the experimental data obtained during inactivation of *Listeria monocytogenes* by pulsed electric fields. (Adapted from Gomez, N., Garcia, D., Alvarez, I., Condon, S., and Raso, J., *International Journal of Food Microbiology,* 103, 199–206, 2005.)

Material for a specific chemical balance around batch or CSTR reactor requires

$$\begin{pmatrix}\text{input rate}\\ \text{into the}\\ \text{reactor}\end{pmatrix}-\begin{pmatrix}\text{output rate}\\ \text{from the}\\ \text{reactor}\end{pmatrix}+\begin{pmatrix}\text{generation}\\ \text{rate in the}\\ \text{reactor}\end{pmatrix}=\begin{pmatrix}\text{accumulation}\\ \text{rate in the}\\ \text{reactor}\end{pmatrix}. \tag{3.59a}$$

In a batch reactor where reaction $A \rightarrow k$ products is occurring, with the rate expression $R_A = -kc_A$ we have

$$\begin{pmatrix}\text{input rate}\\ \text{into the}\\ \text{reactor}\end{pmatrix}=\begin{pmatrix}\text{output rate}\\ \text{from the}\\ \text{reactor}\end{pmatrix}, \tag{3.59b}$$

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$$\text{generation of } A \text{ rate in the reactor} = R_A V, \tag{3.59c}$$

$$(\text{accumulation rate of } A \text{ in the reactor}) = \frac{d(c_A V)}{dt}. \tag{3.59d}$$

With a constant reactor volume V, after substituting Equations 3.59b through d into Equation 3.57 we will obtain

$$\frac{dc_A}{R_A} = R_A. \tag{3.59e}$$

After rearranging Equation 3.59e, we may calculate the time required to achieve a certain final reactant concentration c_{Af} after starting with the initial concentration c_{A0} as

$$t = \int_{c_{A0}}^{c_{Af}} \frac{dc_A}{R_A}. \tag{3.60}$$

Example 3.26: Acid Hydrolysis of Lactose in a Batch Reactor

Large amounts of lactose are produced in the cheese industry. It is not a good food ingredient because of its low solubility and limited sweetness. It is a pollutant when disposed into the environment. Lactose hydrolysis is generally achieved with an enzymatic process. Resin catalyzed hydrolysis may be preferred over enzymatic processes in some applications because of the higher temperature and conversion rates, and lower pH that prevents microbial contamination. Chen and Zall (1983) have shown that resin catalyzed lactose hydrolysis may be expressed with an irreversible first-order apparent rate expression as

$$\text{Lactose} \xrightarrow{k} \text{products}. \tag{E.3.26.1}$$

The major products, glucose and galactose, have higher solubility and sweetness. An Arrhenius type of rate expression was suggested to express the temperature effects on the apparent rate constant k with $k_0 = 2.54 \times 10^{21}$ h^{-1} and $E_a = 1.543 \times 10^5$ J/mole. A batch reactor will be used to convert a 10% (w/w) lactose solution to obtain $c_{Af}/c_{A0} = 0.60$. Initial temperature of the reactor will be 95°C. Chen and Zall (1983) observed formation of browning products during their studies; therefore, a linearly decreasing temperature profile,

$$T = T_0 - \alpha t, \tag{E.3.26.2}$$

will be used during the hydrolysis experiments to reduce the formation of the browning reactions ($T_0 = 95$°C, α = constant). Parameter α will be chosen such that the temperature of the reactor will be 75°C at the end of the process. What should the process time and parameter α be?

Solution: The reaction rate expression is

$$\frac{dc_A}{dt} = R_A, \tag{E.3.26.3}$$

where

$$R_A = kc_A = k_0 c_A \exp\{-E_a/RT\}. \tag{E.3.26.4}$$

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After combining Equation E.3.26.4 and Equation E.3.26.2 and substituting values of constants we will obtain

$$\frac{dc_A}{dt} = 2.54\times10^{21} c_A \exp\left\{-\frac{18559}{T}\right\}, \tag{E.3.26.5}$$

we may use Equation E.3.26.2 to calculate the derivative

$$\frac{dT}{dt} = -\alpha, \tag{E.3.26.6}$$

after combining Equations E.3.26.5 and E.3.26.6 and rearranging we will obtain

$$\int_{c_{A0}}^{0.6c_{A0}} \frac{dc_A}{c_A} = -\int_{368}^{348} \frac{2.54\times10^{21}}{a} \exp\left\{\frac{18559}{T}\right\} dT. \tag{E.3.26.7}$$

We may define the integral as

$$I = \int_{368}^{348} \exp\left\{-\frac{18559}{T}\right\} dT,$$

and use the Simpson's method to calculate it with $\Delta T = 2K$, $N = (368–348)\Delta T = 10$:

$$I = \frac{2}{3}\left\{f_0 + 4\left(f_1 + f_3 + f_5 + f_7 + f_9\right) + 2\left(f_2 + f_4 + f_6 + f_8\right) + f_{10}\right\},$$

where

$$f_0 = \exp\left\{-\frac{18559}{368}\right\} = 1.25\times10^{-22}, \quad f_1 = \exp\left\{-\frac{18559}{366}\right\} = 9.5\times10^{-23},$$

$$f_2 = \exp\left\{-\frac{18559}{364}\right\} = -7.19\times10^{-23}, \quad f_3 = \exp\left\{-\frac{18559}{362}\right\} = 5.42\times10^{-23}.$$

After substituting the numbers in Equation E.3.26.7, we will calculate that $\alpha = 4.15$, therefore the temperature profile should be $T = 368–4.15t$. Since the final temperature is required to be 348 K the reaction time should be 4.8 hours. MATLAB® code E.3.26 shows the details of the computations.

In a CSTR (Figure 3.7) with input and output flow rates of F, where reaction $A \xrightarrow{k}$ products is occurring (rate expression $R_A = -kc_A$) we have

$$\text{input rate of } A \text{ into the reactor} = Fc_{A0}, \tag{3.61a}$$

$$\text{output rate from the reactor} = Fc_A, \tag{3.61b}$$

$$\text{generation of } A \text{ rate in the reactor} = R_A V, \tag{3.61c}$$

$$\text{accumulation rate of } A \text{ in the reactor} = \frac{d(c_A V)}{dt}, \tag{3.61d}$$

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MATLAB® CODE E.3.26

Command Line:

```
clear all
close all
format short g

Ti = 368; % initial temperature (K)
T = 348; % temperature (K)
F = @(x)exp(-18559./x);
% quad numerically evaluates integral with adaptive Simpson
quadrature, where F = function to be integrated, 368 and 348 are the
limits of the integral
I = quad(F,368,348);
F = @(y)1./(y);
C = quad(F,0.1,0.06);
alfa = (2.54e21)*I/C
time = (T - Ti)/(-alfa)
```

The following will appear on the screen after running the code:

```
alfa =
    4.1568
time =
    4.8114
```

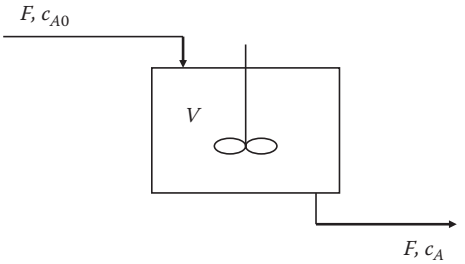


FIGURE 3.7
A continuously stirred tank reactor (CSTR).

after substituting Equations 3.61a through d into Equation 3.57 we will obtain

$$Fc_{A0} - Fc_A + R_A V = \frac{d(c_A V)}{dt}. \tag{3.62}$$

With a constant reactor volume V, under steady state conditions; that is, $d(c_A V)/dt = 0$, Equation 3.62 may be rearranged as

$$\frac{V}{F} = -\frac{c_{A0} - c_A}{R_A}. \tag{3.63}$$

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The ratio $V/F = \tau$ is called the residence time. It is the average time spent by the entering liquid in the reactor.

Example 3.27: Acid Hydrolysis of Lactose in a CSTR

The lactose hydrolysis process described in Example 3.26 will be conducted in two series CSTRs (Figure E.3.27). The first reactor has a volume of 1 m^3 and operated at 95°C. The second reactor has a volume of 3 m^3 and operated at 50°C. What should be the volumetric flow rate F (m^3/h) to obtain $c_{A2}/c_{A0} = 0.60$?

Solution: Under the steady state conditions, the lactose balance around the first reactor is performed similarly as Equation 3.62 to obtain

$$Fc_{A0} - Fc_{A1} - k_1 c_{A1} V_1 = 0. \tag{E.3.27.1}$$

A similar balance is performed for the second reactor:

$$Fc_{A1} - Fc_{A2} - k_2 c_{A2} V_2 = 0. \tag{E.3.27.2}$$

After rearranging Equation E.3.27.1 we will obtain

$$c_{A1} = \frac{Fc_{A0}}{F + k_1 V_1}. \tag{E.3.27.3}$$

Equation E.3.27.3 is substituted in Equation E.3.27.2 to obtain

$$F^2 \frac{c_{A0}}{F + k_1 V_1} - Fc_{A2} - k_2 c_{A2} V_2 = 0. \tag{E.3.27.4}$$

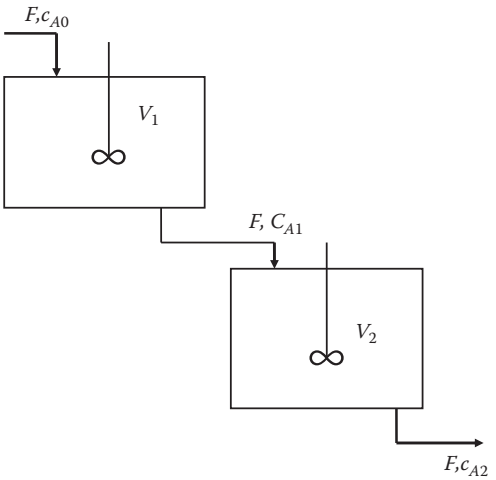


FIGURE E.3.27
The lactose hydrolysis process.

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All the terms of Equation E.3.27.4 will be divided in c_{A0} to obtain

$$F^2 \frac{1}{F + k_1 V_1} - \frac{c_{A2}}{c_{A0}} F - k_2 V_2 \frac{c_{A2}}{c_{A0}} = 0. \tag{E.3.27.5}$$

The Arrhenius expression is

$$k = k_0 \exp\left\{-\frac{E_a}{RT}\right\}. \tag{3.5}$$

After substituting the numbers in Equation 3.5 we will calculate the reaction rate constant as 0.317 h^{-1} at 95°C and at 2.82×10^{-4} h^{-1} 50°C. After substituting $c_{A2}/c_{A0} = 0.6$ and values of the rate constants and the reactor volumes in Equation E.3.27.5 we will calculate $F = 0.44$ m^3/h. Details of the computations are available in MATLAB® code E.3.27.

In a PF reactor where reaction $A \rightarrow k$ products is occurring, with the rate expression $R_A = -kc_A$, the material described in Equation 3.57 may be done around a volume element of a PF reactor as described in Figure 3.8.

Each term appearing in the material may be written as follows:

$$(\text{input rate of } A \text{ into the volume element}) = \left[Fc_A\right]_z, \tag{3.64a}$$

MATLAB® CODE E.3.27

Command Line:

```
clear all
close all

T = [95 50]; % enter the temperatures

% compute the reaction rate constants
k(1) = (2.54e21)*exp(-18559/(T(1) + 273));
k(2) = (2.54e21)*exp(-18559/(T(2) + 273));

F = 1e-8; % flow rate (m3/h)

f = (F^2)/(F + (k(1))*1)-0.6*F-(k(2))*3*0.6;

while f < 1e-10
    F = F + 1e-8;
    f = (F^2)/(F + (k(1))*1)-0.6*F-(k(2))*3*0.6;
end

FLOW_RATE = F
```

The following will appear on the screen after running the code:

```
FLOW_RATE =

    0.4792
```

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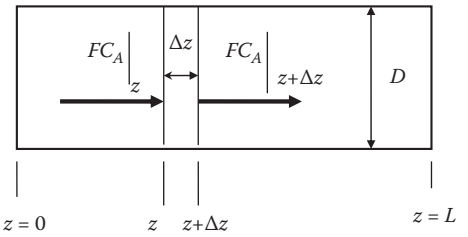


FIGURE 3.8
The volume element in a PF reactor used for material balance.

$$(\text{output rate of } A \text{ from the volume element}) = \left[Fc_A\right]_{z+\Delta z}, \tag{3.64b}$$

$$\left(\text{generation rate of } A \text{ in the volume element}\right) = R_A \Delta z S, \tag{3.64c}$$

where S = cross-sectional area of the PF reactor:

$$(\text{accumulation rate of } A \text{ from the volume element}) = \frac{d\left(c_A \Delta z S\right)}{dt}. \tag{3.64d}$$

Under steady state conditions; that is, $d(c_A \Delta z S)/dt = 0$, after substituting Equations 3.64a through d into Equation 3.57 we will obtain

$$\left[Fc_A\right]_z - \left[Fc_A\right]_{z+\Delta z} + R_A \Delta z S = 0. \tag{3.65}$$

Equation 3.65 may be rearranged as

$$F\frac{[c_A]_z - [c_A]_{z+\Delta z}}{\Delta z} = R_A S. \tag{3.66}$$

After taking the limit of the left-hand side of Equation 3.66 as $\lim \Delta z \to 0$ we will obtain

$$F\frac{dc_A}{dz} = R_A S. \tag{3.67}$$

We may calculate the reactor length (L) for required conversion after rearranging and integrating Equation 3.67:

$$L = \frac{F}{S}\int_{c_{A0}}^{c_{Af}} \frac{dc_A}{R_A}. \tag{3.68}$$

Example 3.28 Acid Hydrolysis of Lactose in a Plug Flow Reactor

The lactose hydrolysis process described in Example 3.26 will be conducted in a PF reactor. The temperature is 95°C at the inlet of the reactor and will decrease linearly as $T = T_0 - \beta z$ along the reactor and will be 75°C at the exit. What should S/F ratio in (h/m) to obtain $c_{Af}/c_{A0} = 0.60$ in a 2 m long reactor?

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Solution: Under the steady state conditions, the lactose balance around a shell element of the reactor is performed similarly to Equation 3.67 to obtain

$$F\frac{dc_A}{dz} = -kc_A S. \tag{E.3.28.1}$$

The data implies that $\beta = 10°C/m$ and the temperature profile along the reactor is

$$T = 95 - 10z. \tag{E.3.28.2}$$

The reaction rate constant is expressed in terms of the Arrhenius expression as

$$k = 2.54 \times 10^{21} \exp\left\{-\frac{18559}{273 + (95 - 10z)}\right\}. \tag{E.3.28.3}$$

After combining Equations E.3.28.1 and E.3.28.3 and rearranging we will obtain

$$-\frac{1}{2.54 \times 10^{21}} \int_{c_{A0}}^{c_{Af}} \frac{dc_A}{c_A} = \frac{S}{F} \int_0^2 \exp\left\{-\frac{18859}{368 - 10z}\right\} dz. \tag{E.3.28.4}$$

The integral appearing on the right-hand side needs to be evaluated numerically, similarly as that of Example 3.26. After substituting the numbers in Equation E.3.28.4, we will calculate $S/F = 2.4$ h/m. Details of the computations are given in MATLAB® code E.3.28.

MATLAB® CODE E.3.28

Command Line:

```
clear all
close all

% enter the data
Ti = 95; % inlet temperature (K)
T = 75; % exit temperature (K)
z = 2; % length of the reactor (m)

B = (95-75)/z;
F = @(z)exp(-18559./(368-B*z));
I = quad(F,0,2);
F = @(y)1./(y);
C = quad(F,0.1,0.06);
SF_Ratio = -C/((2.54e21)*I)
```

The following will appear on the screen after running the code:

```
SF_Ratio =
    2.4057
```

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Example 3.29: Acid Hydrolysis of Lactose With Immobilized β-Galactosidase in CSTR and Plug Flow Reactors

a. Kinetic constants for lactose hydrolysis by β-galactosidase from *Escherichia coli* were reported as $K_M = 1.9$ moles/m^3 and $v_{max} = 6.55 \times 10^{-6}$ moles/(min mg enzyme) at 20°C and pH = 7.6 (Whitaker 1994). If this enzyme should be immobilized on a nonporous support to obtain 10 mg enzyme/cm^3 of the reactor with $\eta = 0.8$, what should be the volumetric input flow rate of 50 moles/m^3 lactose solution to a 0.7 m^3 CSTR to achieve $c_{exit}/c_0 = 0.30$?

Solution: It is required that $c_{A0} = 50$ moles/m^3 and $c_A = 15$ moles/m^3. The apparent reaction rate is

$$R_{App} = -h\frac{c_A V_{max}}{K_M + c_A}. \tag{E.3.29.1}$$

After substituting the numbers, we will calculate that $R_{App} = -4.65 \times 10^{-6}$ moles/min mg enzyme. Since we have 10 mg enzyme/cm^3 of a reactor, the apparent rate may be expressed in terms of the reactor volume as $R_{App} = -46.5$ moles/min m^3. The lactose balance around the reactor under steady state conditions requires

$$Fc_{A0} - Fc_A + R_{App}V = 0. \tag{E.3.29.2}$$

Equation E.3.29.2 will be rearranged as

$$F = -V\frac{R_{App}}{c_{A0} - c_A}. \tag{E.3.29.3}$$

After substituting the numbers in Equation E.3.29.3 we will obtain $F = 0.93$ m^3/min.

b. The same enzyme immobilized support is filled into a packed bed PF reactor (reactor diameter = 10 cm). What should be the reactor length to achieve the same conversion as in section (a)?

Solution: The lactose balance around the reactor under steady state conditions requires

$$L = \frac{F}{S}\int_{c_{A0}}^{c_{Af}} \frac{dc_A}{R_{App}}. \tag{3.68}$$

We have already calculated that $F = 0.93$ m^3/min, it is also known that $c_{A0} = 50$ moles/m^3 and $c_A = 15$ moles/m^3 and the cross-sectional area of the reactor is $S = \pi$(reactor radius)$^2 = 7.85 \times 10^{-3}$ m^2. The apparent reaction rate is $R_{App} = -52.4c_A/1.9 + c_A$ moles/min m^3. After substituting the numbers in Equation 3.68 we will obtain

$$L = -\frac{0.93 m^3/\text{min}}{7.85 \times 10^{-3} m^2}\int_{50}^{15} \frac{1}{\frac{52.4c_A}{1.9 + c_A}} dc_A = 84.3\,\text{m}.$$

The volume of the reactor = $(L)(S) = 0.66$ m^3 and the smaller reactor volume required for the same conversion in a CSTR.

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c. If the immobilized enzyme loses 10% of its activity after 24 hours of operation with reaction:

$$\underset{\text{active enzyme}}{E} \rightarrow \underset{\text{inactive enzyme}}{E_i}$$

what will be the c_{Af}/c_0 ratio after 3 days of operation with both CSTR and PF reactors?

Solution: We have already described the enzyme inactivation rate as

$$\frac{dc_E}{dt} = -k_d c_E. \tag{3.20}$$

After integrating and rearranging Equation 3.20 we will have

$$k_d = -\frac{1}{t}\ln\left(\frac{c_E}{c_{E0}}\right). \tag{E.3.29.4}$$

Since $c_E/c_{E0} = 0.90$ when $t = 24$ hours we may use Equation E.3.29.4 to calculate $k_d = 4.4 \times 10^{-3}$ h^{-1}. Equation E.3.29.4 may be rearranged to calculate the fraction of the remaining enzyme activity after 3 days (72 hours) of operation as

$$\frac{c_E}{c_{E0}} = \exp(-k_d t) = 0.72$$

The initial maximum enzyme activity v_{max} was defined as

$$v_{max} = k_3 c_{E0}. \tag{3.9}$$

The remaining maximum enzyme activity after 3 days is
$v_{max}^{3days} = (k_3 c_{E0})(c_E/c_{E0}) = (6.55 \times 10^{-6})(0.72) = 4.72 \times 10^{-6}$ moles/(min mg enzyme) since we have initially 10 mg enzyme immobilized/cm^3 of reactor $v_{max}^{3days} = 47.2$ moles/min m^3.

i. The c_{Af}/c_0 ratio after 3 days of operation with CSTR

We will substitute v_{max}^{3days} in Equation E.3.18.1 for v_{max} to calculate R_{App}. Under these conditions Equation E.3.18.2 will be rewritten as

$$Fc_{A0} - Fc_A - \eta v_{max}^{3days}\frac{c_A}{K_M + c_A}V = 0. \tag{E.3.29.5}$$

After substituting the numbers, we will calculate $c = 23.7$ moles/m^3 from Equation E.3.29.5, implying that $c_{Af}/c_0 = 0.474$.

ii. The c_{Af}/c_0 ratio after 3 days of operation with PF reactor

We will substitute v_{max}^{3days} in Equation E.3.18.1 for v_{max} to calculate R_{App}. Under these conditions Equation 3.68 will be rewritten as

$$84.3\,m = -\frac{0.93\,m^3/\text{min}}{7.85\times10^{-3}m^2}\int_{50}^{c_{Af}}\frac{1}{\dfrac{37.7c_A}{1.9+c_A}}dc_A. \tag{E.3.29.6}$$

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Equation E.3.29.6 will be simplified as

$$16.7 = \ln(c_{Af}) + 0.54c_{Af}. \tag{E.3.29.7}$$

After solving Equation E.3.29.7 we will obtain $c_{Af} = 23.8$ moles/m^3, implying that $c_{Af}/c_{A0} = 0.474$.

The computations are also carried out by MATLAB® code E.3.29.

MATLAB® CODE E.3.29

Command Window:

```
clear all
close all
format compact

% constants
Ca0 = 50; Ca = 15; Vmax = 6.55e-6; Km = 1.9; n = 0.8; V = 0.7; S = pi*0.05^2
Va = 10e6; % unit converted

Rapp = -n*Ca*Vmax/(Km + Ca) % apparent reaction rate
F = -(V*Va)*Rapp/(Ca0-Ca) % volumetric flow rate
% compute the reactor volume
Y = @(x)(1.9 + x)./(52.4*x);
I = quad(Y,50,15)
L = -(F/S)*I
Reactor_Volume = L*S

% compute the remaining enzyme activity
kd = (-1/24)*log(0.9)
Remaining_Enzyme_Activity = exp(-kd*72)
```

The following will appear on the screen when we run the code:

```
S =
    0.0079
Rapp =
   -4.6509e-006
F =
    0.9302
I =
   -0.7116
L =
   84.2769
Reactor_Volume =
    0.6619
kd =
    0.0044
Remaining_Enzyme_Activity =
  0.7290
```

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Example 3.30: Reactors-in-Series Model for Digestion in Stomach and Intestines

The Eyriés (2003) model simulates stomach and intestines as a combination of ideal reactors as depicted in Figure E.3.30.1. Taking a caplet of medication may be regarded as an impulse passing through the stomach and the intestine. The degradation rate of the drug may be simulated as

$$R_{\text{digestion}} = -kC. \tag{E.3.30.1}$$

The medication balance around the first CSTR is

$$Fc_0\delta(t) - Fc_1(t) - kc_1(t)V_1 = \frac{d\left[c_1(t)V_1\right]}{dt}. \tag{E.3.30.2}$$

Where V_1 is the volume of CSTR1; the medication concentrations are depicted with $c_0(t)$ before entering and with $c_1(t)$ after leaving CSTR1. After substituting $\tau = V_1/F$ = constant Equation E.3.30.2 is rearranged as

$$\tau\frac{dc_1(t)}{dt} = c_0\delta(t) - c_1(t) - k\tau c_1(t). \tag{E.3.30.3}$$

The Laplace transform of Equation E.3.30.3 is

$$sc_1(s) - c_1(0) = \frac{c_0}{\tau} - \left(k + \frac{1}{\tau}\right)c_1(s), \tag{E.3.30.4}$$

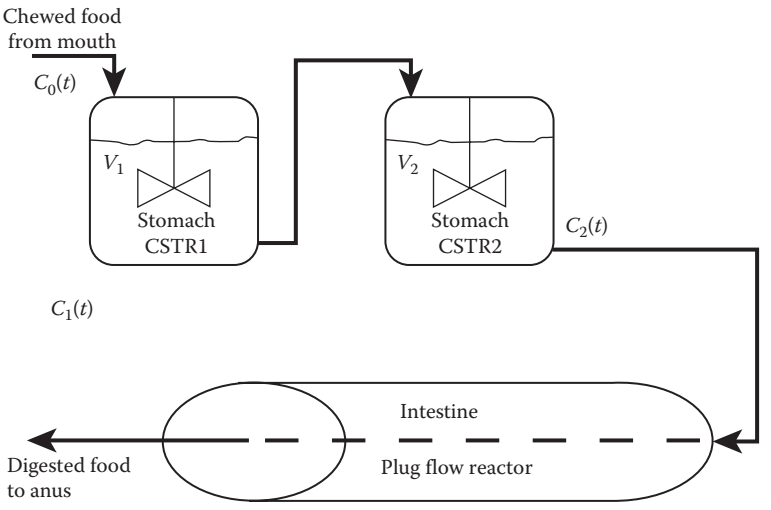


FIGURE E.3.30.1
Stomach (two CSTRS in series) and intestines (a plug flow reactor) as described by the Eyriés model. (From Eyriés, P., A Distributed-Parameter Modeling Approach for Performance Monitoring of Oral Drug Delivery Systems, Master of Science Thesis, Chemical Engineering Department, Worcester Polytechnic Institute, Worcester, Massachusetts, 2003.) The model considers the stomach as a nonideal CSTR, which behaves in-between an ideal CSTR and a plug flow reactor. The nonideality is described by replacing the single CSTR with a cascade of ideal CSTRs. The intestine is modeled as a single cylindrical plug flow reactor surrounded with a wall of constant width.

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since $c_1(0) = 0$ we will calculate $c_1(s)$ as

$$c_1(s) = \frac{c_0/\tau_1}{s + (1 + k/\tau_1)}. \tag{E.3.30.5}$$

The back transform of Equation E.3.30.3 is (Table 2.20)

$$c_1(t) = \frac{c_0}{\tau} \exp\left\{-\left(k + \frac{1}{\tau}\right)t\right\}. \tag{E.3.30.6}$$

When $\tau_1 = \tau_2$ concentration of the medication at the exit of the second CSTR may be calculated with a similar procedure as

$$c_2(t) = \frac{c_0 t}{\tau^2} \exp\left\{-\left(k + \frac{1}{\tau}\right)t\right\}. \tag{E.3.30.7}$$

The exit concentration of the nutrient from the cascade of j CSTRs may be expressed as

$$c_j(t) = \frac{c_0 t^{j-1}}{(j-1)!\tau^j} \exp\left\{-\left(k + \frac{1}{\tau}\right)t\right\}. \tag{E.3.30.8}$$

MATLAB® code E.3.30.a carries out the computations to determine the variation of the normalized drug concentration, $c_2(t)/c_0$, with time by using the "*two CSTRs in series*" stomach model with $k = 1.66 \times 10^{-4}$ s^{-1} and $\tau = 900$ s.

MATLAB® CODE E.3.30.a

Command Window:

```
clear all
close all

% cratio(i) = c2(i)/c0
c0 = 1;
t = [0:100:8000];
tau = 900;
k = 1.66*10^(-4);
i = 1;
while i < 82;
cratio(i) = (t(i)/tau^2)*exp(-(k + 1/tau)*t(i));
i = i + 1;
end
plot(t,cratio)
xlabel('time (seconds)')
ylabel('c2(t)/c0')
```

When we run the code Figure E.3.30.2 will appear on the screen.

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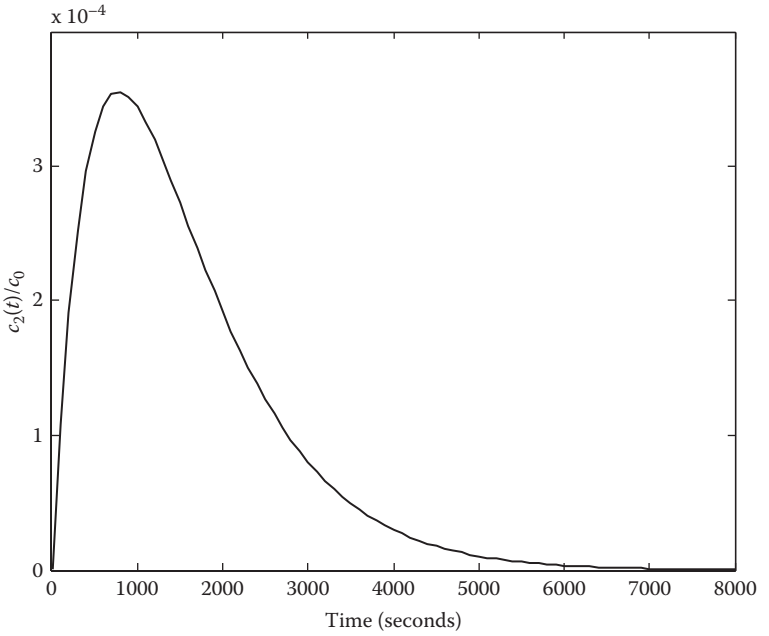


FIGURE E.3.30.2
Variation of the normalized drug concentration, $c_2(t)/c_0$, with time at the exit of the stomach, which is simulated as a cascade of two CSTRs.

The medication is ingested in the intestine while transported by convection through the lumen. The equation of continuity describes it as

$$\frac{\partial c}{\partial t}+\left(\frac{1}{r}\frac{\partial\left(rN_r\right)}{\partial r}+\frac{1}{r}\frac{\partial N_\theta}{\partial \theta}+\frac{\partial N_x}{\partial x}\right)=R. \tag{2.13}$$

Mass transport does not occur in r and θ directions in a plug flow reactor, implying that $N_r = N_q = 0$. We also have

$$N_{\text{drug}} = x_{\text{drug}}\left(N_{\text{drug}} + N_{\text{lumen fluid}}\right) - D_{\text{drug}}\frac{dc_{\text{drug}}}{dx}. \tag{E.3.30.9}$$

In a PF reactor, mass transfer with diffusion is negligible when we compare it with that of convection and $x_{\text{drug}}(N_{\text{drug}} + N_{\text{lumen fluid}}) = vc_{\text{drug}}$, where v is the constant flow velocity in the intestine through the lumen. After substituting Equation E.3.30.1 in Equation 2.13 we will have

$$\frac{\partial c(t,x)}{\partial t} = -v\frac{\partial c(t,x)}{\partial x} - kc(t,x). \tag{E.3.30.10}$$

The drug concentration at the inlet of the intestine (PF reactor) is the same as that of the jth CSTR of the stomach, implying a BC for Equation E.3.30.10 as

$$\text{BC } c(0,t) = c_j(t) \tag{E.3.30.10a}$$

$$\text{IC } c(x,0) = 0. \tag{E.3.30.10b}$$

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The Laplace transform of Equation E.3.30.7 is

$$sc(s) - c(0) = -v\frac{dc(s)}{dx} - kc(s). \tag{E.3.30.11}$$

When $j = 2$ and we use transformation $L\{t^n e^{-\alpha t}\} = n!/(s+\alpha)^{n+1}$ (Table 2.19) boundary condition of Equation E.3.30.8 will be $c_0(s) = c_2(s) = c_0/\tau^2/[s + (k + 1/\tau)]^2$. Equation E.3.30.8 may be rearranged as $\int dc(s)/c(s) = -\int k + s/v\, dx + \kappa$, where κ is the integration constant. Upon integration we will have $\ln(c(s)) = -(k + s/v)x + \kappa$ or $c(s) = \kappa_1 \exp(-k + s/vx)$ where $\kappa_1 = \exp(\kappa)$. When $x = 0$ $c_0(s) = c_2(s) = c_0/\tau^2/[s + (k + 1/\tau)]^2 = \kappa_1$, then we will have

$$c(s) = \frac{c_0/\tau^2}{\left[s+\left(k+1/\tau\right)\right]^2}\exp\left\{-\frac{k+s}{v}x\right\} = \left(\frac{c_0}{\tau^2}e^{-kx/v}\right)\frac{e^{-(x/v)s}}{\left[s+\left(k+1/\tau\right)\right]^2}. \tag{E.3.30.12}$$

We will use the "*delayed n*th *power frequency shift*" back transformation formula

$$L^{-1}\left\{\frac{e^{-\beta s}}{(s+\alpha)^{n+1}}\right\} = \frac{(t-\beta)^n}{n!}e^{-\alpha(t-\beta)}$$

to obtain

$$c(t) = \left(t+\frac{x}{v}\right)\frac{c_0}{\tau^2}\exp\left\{-\frac{kx}{v}\right\}\exp\left\{-\left(k+\frac{1}{\tau}\right)\left(t+\frac{x}{v}\right)\right\}. \tag{E.3.30.13}$$

It should be noticed that [E.3.30.13] predicts $c(t) = c_2(t)$ when $x = 0$. MATLAB® code E.3.30.b computes variation of the normalized drug concentration with time and position along the intestine.

MATLAB® CODE E.3.30.b

Command Window:

```
clear all
close all

% constants
v=1.1*(10^-5); % m/s
k=1.66*10^(-4);
tau=900;
t=[0:2:4000];
x=[0:0.02:0.1];
L=2; % m
e=x/L; % dimensionless position
[e,t]=meshgrid(e,t); % transforms e and t into arrays to prepare
3-D mesh/surface plots
cratio=((t+e./v)/tau^2).*exp(-k.*e./v).*exp(-1*(k+1/
tau).*(t+e./v)); % cratio(i)=c(i)/c0
mesh(t,e,cratio); % cratio=c(t)/c0
ylabel('dimensionless position')
xlabel('time')
zlabel('cratio')
```

When we run the code Figure E.3.30.3 will appear on the screen.

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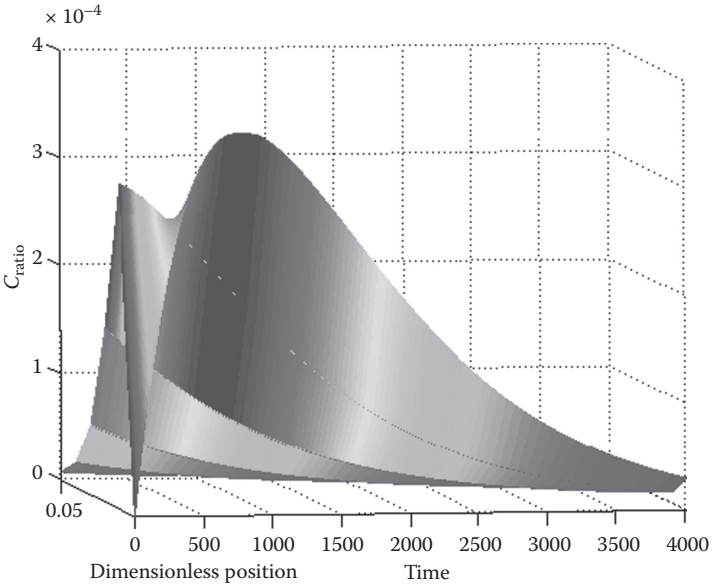


FIGURE E.3.30.3
Variation of the normalized drug concentration, $c(t)/c_0$, with time (seconds) and dimensionless position along the intestine. Arrival of the drug to the inlet of the intestine (where the dimensionless position is zero) is described with a very nice peak as a function of time. Depletion of the drug along the intestine (as a function of time) is also seen clearly.

Example 3.31: A Model for Pasteurization With Microwaves in a Tubular Flow Reactor

In most microwave ovens, the microwaves change their polarization 2450 times in 1 second. Polar molecules try to align themselves according to the polarity of the microwave field. Their rapid movement causes tremendous intermolecular collisions, which heats up the medium that may be used to pasteurize the liquid foods. A section of an experimental microwave PF pasteurization reactor is shown in Figure E.3.31.1.

At a constant temperature, the thermal death rate of the microorganisms is

$$\frac{dx}{dt} = -k_d x. \tag{3.31d}$$

Temperature effects on the death rate constant k_d may be expressed with the Arrhenius equation:

$$k_d = k_{d0} \exp\left\{-\frac{E_a}{RT}\right\}. \tag{3.5}$$

Heating of a stagnant fluid via microwave absorption may be expressed as

$$p = \omega \varepsilon_0 E^2 \kappa, \tag{E.3.31.1}$$

where p = absorbed microwave power, ω = angular frequency, ε_0 = dielectric constant of free space, E = electric field intensity coupled by matched load, and κ = relative dielectric loss factor.

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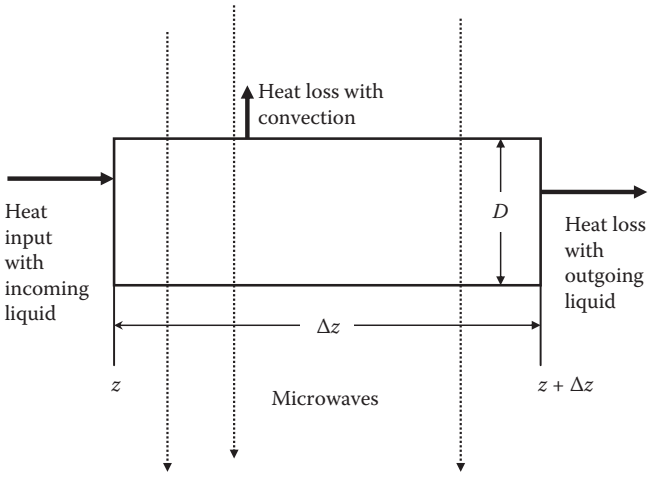


FIGURE E.3.31.1
Shell element of a pasteurization reactor.

The constant κ is the overall measure of the ability of the material to respond to the microwave field. Temperature effects on κ may be expressed as

$$\kappa = \phi \exp(-\beta T), \tag{E.3.31.2}$$

where β = constant. Heating of a stagnant liquid may be expressed after combining Equations E.3.31.1 and E.3.31.2 as

$$p = \alpha \exp(-\beta T), \tag{E.3.31.3}$$

where $\alpha = \omega \varepsilon_0 E^2 \phi$ = constant. Thermal energy balance around an infinitely small shell element of the pasteurization reactor as depicted in Figure E.3.31.1 requires

$$\begin{pmatrix}\text{input rate}\\ \text{into the}\\ \text{shell}\\ \text{element}\end{pmatrix} - \begin{pmatrix}\text{output}\\ \text{rate from}\\ \text{the shell}\\ \text{element}\end{pmatrix} + \begin{pmatrix}\text{generation}\\ \text{rate in}\\ \text{the shell}\\ \text{element}\end{pmatrix} = \begin{pmatrix}\text{accumulation}\\ \text{rate in}\\ \text{the shell}\\ \text{element}\end{pmatrix}. \tag{E.3.31.4}$$

After assuming no radial temperature distribution, we may convert Equation E.3.31.4 in mathematical terms as (Özilgen and Özilgen 1991)

$$\frac{\pi D_r^2 v \rho c}{4}\left[T - T_{\text{ref}}\right]_z - \frac{\pi D_r^2 v \rho c}{4}\left[T - T_{\text{ref}}\right]_{z+\Delta z} - \pi D_r \Delta z U\left(T - T_{\text{env}}\right) + \frac{\pi D_r^2 \Delta z \alpha e^{-\pi T}}{4}$$
$$= \frac{\pi D_r^2 \Delta z \rho c}{4}\frac{dT}{dT}, \tag{E.3.31.5}$$

where D_r is the diameter of the reactor, v, c, and ρ are the velocity, specific heat, and density of the liquid. The term $\left(\pi D_r^2 v \rho c/2\right)\left[T - T_{\text{ref}}\right]_z$ is the enthalpy of the liquid entering into the shell element at distance z from the entrance of the heating section of the reactor. It should be noticed that the

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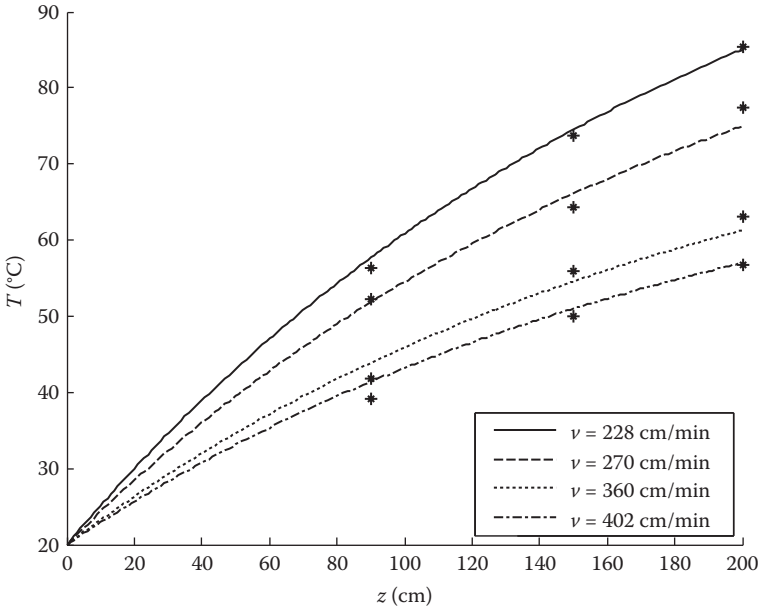


FIGURE E.3.31.2
Comparison of the model and the experimentally determined temperatures along the flow reactor. (Adapted from Özilgen, S., and Özilgen, M., *Enzyme and Microbial Technology*, 13, 419–23, 1991.)

enthalpy is calculated with respect to an arbitrarily chosen reference temperature T_{ref}. The term $(\pi D_r^2 v\rho\, c/2)\left[T - T_{\text{ref}}\right]_{z+\Delta z}$ is the enthalpy of the liquid leaving the shell element. The length of the shell was Δz as depicted in Figure E.3.31.2. The term $\pi D_r \Delta z(T - T_{\text{env}})$ describes the enthalpy loss from the shell element to the environment with convection. The heating rate of the liquid in the shell element with microwaves was described as $\pi D_r^2 \Delta z \alpha\, e^{-\pi T}/4$, unsteady state thermal energy accumulation in the shell element was described as $(\pi D_r^2 \Delta z \alpha\, e^{-\pi T})(dT/dt)$.

Under steady state conditions the unsteady state thermal energy accumulation term becomes zero and the equation was rearranged as

$$\frac{dT}{dz} = K_1 \exp(-\beta T) - K_2(T - T_{\text{env}}), \tag{E.3.31.6}$$

where $K_1 = \alpha/v\rho c$ and $K_2 = U/D_r v\rho c$. Solutions of Equation E.3.31.6 as given in the MATLAB® code E.3.31 simulates the variation of the temperature profiles along the reactor.

Although temperature varies drastically with distance, the flow reactor may be considered as a combination of 1 cm long small segments, and the temperature of any of these segments may be considered constant. The fraction of biomass surviving each segment may be calculated as

$$\frac{x_i}{x_0} = \exp\left(-\frac{k_{di}}{v}\right), \tag{E.3.31.7}$$

where x_0 and x_i are the viable cell counts at the entrance and exit of the ith segment, respectively. Parameter k_{di} is the death rate constant calculated with Equation 3.5 at the average temperature of the ith segment T_i. Equation E.3.31.7 is solved in the MATLAB® code E.3.31, where parameter v

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MATLAB® CODE E.3.31

Command Window:

```
clear all
close all

% model of temperature profile development along the reactor
Beta = 0.00012;
v = [228 270 360 402];
K1 = (120./v);
K2 = 0.00518;
Tenv = 20;
Ti = 20;
for i = 1:length(v)
  [z T] = ode45(@(z,T) microwave(z,T,Beta,K1(i),K2,Tenv),0:1:200,Ti);
  T1(:,i) = T;
end
plot(z,T1(:,1),'-k',z,T1(:,2),'--k',z,T1(:,3),':k',z,T1(:,4),'-.k')
Ldata = [90 150 200];
Tdata1 = [56.3 73.8 85.4];
Tdata2 = [52.3 64.3 77.4];
Tdata3 = [41.9 56 63];
Tdata4 = [39.2 50 56.8];
hold all;
plot(Ldata,Tdata1,'*',Ldata,Tdata2,'*',Ldata,Tdata3,'*',Ldata,Tdata
4,'*')
xlabel('z (cm)')
ylabel('T (\circC)')
legend('v = 228 cm/min','v = 270 cm/min','v = 360 cm/min','v = 402 cm/
min',4,'Location','SouthEast')

% microbial death model
x0 = 100;
% enter the data (lnkd0 = A, E = Ea/R)
A = [35.1 34 31.5 28.9 ];
E = [11300 11000 10000 9800] ;
Lexp = [90 150 200 90 150 200 90 150 200 90 150 200];
xratioExp = [0.45 0.02 0.0 0.75 0.34 0.0 0.79 0.65 0.001 0.95 0.95
0.085];
figure
for k = 1: 4
for j = 1:200
  kd(j,k) = exp(A(k))*exp((-E(k))/(T1(j,k) + 273));
  x(j,k) = x0*exp(-kd(j,k)*60/v(k));
  xratio(j,k) = x(j,k)/x0;
  len(j) = j;
end
end
hold all;
plot(len', xratio(:,1),'--', len', xratio(:,2),'-', len',
xratio(:,3),':', len', xratio(:,4),'.-')
```

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```
plot(Lexp,xratioExp,'*')
ylabel('x/xo'); xlabel('L (cm)');
legend('v = 228 cm/min','v = 270 cm/min','v = 360 cm/min','v = 402 cm/
min',4,'Location','SouthWest')
```

M-File:

```
function dTdz = microwave(z,T,Beta,K1,K2,Tenv)
% model of temperature profile development along the reactor
  dTdz = (K1 * exp(-Beta*T)) - (K2 * (T-Tenv));
end
```

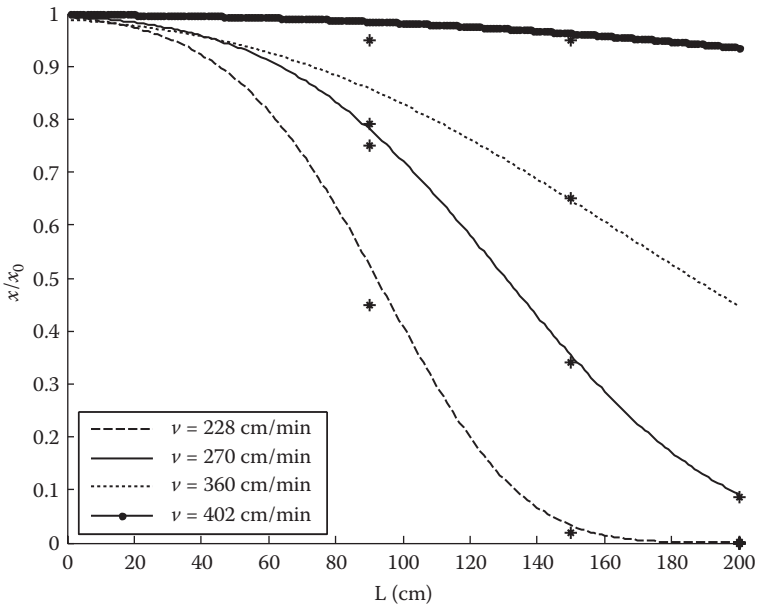


FIGURE E.3.31.3
Comparison of the model and the experimentally determined surviving microbial fractions along the flow reactor. (Adapted from Özilgen, S., and Özilgen, M., *Enzyme and Microbial Technology*, 13, 419–23, 1991.)

was the average velocity of the medium in the sterilization reactor. Parameter T_0 was the temperature of the medium before entering the microwave reactor, the ratio x_i/x_0 was the viable biomass fraction surviving the whole pasteurization process. The numerical values of x_i/x_0 were plotted against the reactor length in the microwave oven in Figure E.3.31.3.

Questions for Discussion and Problems

A. Metabolic Process Engineering and Microbial Kinetics

B.1. The following data were adapted from Cruz (2003), during the course of fermentation of the agave wort by a native yeast strain during a tequila production process:

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MATLAB® CODE

Command Lines:

```
clear all
close all

% input data
% variation of the biomass concentration with time:
tBiomassD = [0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34
36]; % h
BiomassD = [25 40 60 80 110 127 130 131 132 130 129 130 131
129 130 131 132 129 130]; % cells/mL

% variation of the ethanol concentration with time:
tEthanolD = [0 2 4 6 8 10 12 14 16 18 22 24 26 30 34]; % h
EthanolD = [7.2 7.23 7.25 7.27 7.29 7.40 7.45 7.52 7.58 7.6
7.61 7.61 7.65 7.6 7.6]; % g/L

% variation of the isoamyl + isobutyl alcohol concentration
with time:
tIsoamylIsobutylD = [0 2 4 6 8 10 12 14 16 18 26 28 30 34];
% h
IsoamylIsobutylD = [7.2 7.2 7.21 7.22 7.23 7.3 7.32 7.38 7.4
7.46 7.455 7.455 7.45 7.45]; % mg/L

% variation of the reducing sugar concentration with time:
tReducingSugarD = [0 2 4 6 10 14 16 18 20 22 24 26 28 30 34];
% h
ReducingSugarD = [8.3 8.2 8.075 8.05 7.8 7.65 7.63 7.45 7.44
7.35 7.34 7.32 7.31 7.3 7.3]; % g/L
```

Complete the MATLAB® code to develop biomass, ethanol, isoamyl plus isobutyl alcohol production, and reducing sugars consumption models. You will need to evaluate the constants of the model yourself and compare the models with the data.

B.2. The following models were used by Wang et al. (2004) while studying the kinetics growth of apple wine yeast *Saccharomyces cerevisiae* on fructose:

$$\text{Microbial growth: } \frac{dx}{dt} = \mu x\left(1 - \frac{x}{x_{\max}}\right), \tag{3.34}$$

$$\text{Ethanol production: } \frac{dP}{dt} = Y_{p/x}\frac{dx}{d(t-\Delta t)}. \tag{Q.3.B.2.1}$$

Where Δt was introduced to describe delay of ethanol production to cell growth

$$\text{Sugar consumption: } -\frac{dS}{dt} = \frac{1}{Y_{s/x}}\frac{dx}{dt} + mx, \tag{Q.3.B.2.2}$$

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where sugar is assumed to be consumed for biomass production and maintenance.

The initial values were $x_0 = 0.5$ g/L and $s_0 = 90$ g/L and the coefficients of the model were $\mu = 0.08$ g/L, $x_{max} = 7.23$ g/L, $Y_{p/x} = 5.79$ g/g, $\Delta t = 14.6$ h, $Y_{s/x} = 0.19$ g/g, and $m = 0.07$ h^{-1}. Write a MATLAB® code to simulate the process.

B. Microbial Death Kinetics

B.1. The surviving number of microorganisms were counted after processing a food for the following given times at 110°C and 121°C are

t (min) at 110°C	0	5	10	15	20
x (cfu/ml)	60,000	21,000	7400	2650	930

t (min) at 121°C	0	1	2	3	4
x (cfu/ml)	60,000	4100	290	19	2

a. Determine the death rate constant at 110°C and 121°C.
b. Convert these death rate constants into D values.
c. The death rate constant of the microorganism was calculated at different temperatures as

T (°C)	110	113	115	118	121	124
k_d (min^{-1})	0.208	0.397	0.743	1.44	2.62	5.01

Determine the activation energy and frequency factor of the Arrhenius expression for the death rate constant.

d. Calculate the z value from the activation energy at 110°C and 124°C ($T_{ref} = 121$°C). What is the average z value?

C. Rector Design

C.1. Solve the Example 5.30 with 3 and 4 CSTRs in series. Notice: $\tau = 600$ s when there are 3 CSTRs and $\tau = 450$ s when there are 4 CSTRs. Discuss your results by employing graphs when possible.

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4

Mathematical Modeling in Food Engineering Operations

4.1 Thermal Process Modeling

Thermal processing is among the first commercialized processing methods. It aims to kill the microorganisms, destroy the toxins, or inactivate the enzymes. Softening of the tissue is desired with some foods (i.e., beans, meat, etc.), but undesirable with the others (i.e., fruit preserves). Vitamins, flavor, or aromatic constituents may be lost with undesirable side reactions. Microorganisms are considered dead when they do not proliferate. With the sublethal heat treatment they may be injured and become more harmful, because they may escape detection on the selective media, while still being capable of repairing themselves and producing toxins (Hurst 1977).

Thermal process time required to reduce the initial microbial load x_0 to a safe final concentration x at a constant temperature T_{ref} is

$$F_{\text{required}} = D_{Tref} \log(x_0/x), \tag{4.1}$$

where $\log(x_0/x)$ is the number of the log cycles of microbial reduction required for a safe product and D_{Tref} is the heating time at T_{ref} for one log cycle of reduction. The parameter D_{Tref} may be used to compute D_T at any temperature T as

$$D_T = D_{Tref} 10^{(T-Tref)/z}. \tag{4.2}$$

Thermal processing received under variable temperature $T(t)$ may be calculated as

$$F_{\text{process}} = \int_0^t 10^{(T-Tref)/z_{\text{microorganisms}}} dt, \tag{4.3}$$

where t is the duration of the process. The definition of parameters D and z were given in Chapter 3 while discussing the microbial death kinetics. The can center is considered as the critical; that is, the latest sterilized point of the conduction heating foods. Therefore the right-hand side of Equation 4.3 is usually evaluated at the critical point of the food. Processing received by the food is regarded safe when

$$F_{\text{process}} \geq F_{\text{required}}. \tag{4.4}$$

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The *C* (cooking) value of a process is defined in terms of the kinetic parameters associated with the loss of nutrients or softening of the tissue in thermal processing.

$$C_{\text{process}} = \int_0^t 10^{(T-Tref)/z_{\text{nutrients}}}\, dt. \tag{4.5}$$

The *F* and *C* values are reported together in order to describe the effect of processing on the microbial load and nutritional value of the food.

Example 4.1: Calculations of Process Time and Nutrient Loss at a Constant Temperature

a. A food has a contaminant microorganism with $D = 75$ s at 100°C with $z = 10$°C. How long should this product be treated to get 10^7 cfu/ml of reduction at 100°C and 121°C?

   Solution: It is given in the problem statement that $D_{100} = 75$ s. We may choose $T_{Ref} = 100$°C and $D_{Tref} = 75$ s and use Equation 4.2 to calculate $D_{121} = D_{100}10^{(100-121)/10} = 0.60$ s. We can calculate F_{required} from $F_{\text{required}} = D_{Tref} \log(x_0/x)$ after substituting $x_0/x = 10^7$ and find $F_{\text{required}} = 525$ s at 100°C $F_{\text{required}} = 4.2$ s at 121°C.

b. The food has a major nutrient with $D = 90$ s at $T_{ref} = 121$°C and $z = 25$°C. What percentage of the nutrient will be lost at 100°C and 121°C?

   Solution: It is already given in the problem statement that $D = 90$ s at $T_{ref} = 121$°C and $z = 25$°C. We may calculate *D* value at 100°C by using Equation 4.2 as $D_{100} = D_{Tref}\, 10^{(Tref-100-)/z} = 623$ s. The *C* value of the process is $C_T \equiv D_T \log(c_0/c) = \int_0^t 10^{(T-Tref)/z} dt$, we may calculate from this equation that $c/c_0 = 89.8\%$ at 121°C and $c/c_0 = 14.4\%$ at 100°C.

Thermal processes are designed to obtain safe products. The nutrients that are sharing the same space with the microorganisms undergo degradation. The *z* values of the nutrients are the most important parameters determining the fraction of the nutrients that will survive these processes. MATLAB® code E.4.1 computes the fraction of the nutrients surviving the processes at 100 and 121°C as a function of their *z* values (Figure E.4.1).

MATLAB® CODE E.4.1

Command Window:

```
clear all
close all

% enter the data
T=[100 121]; % processing temperatures
z=[15:1:35]; % the range of the z values of the nutrients
ProcessTime=[525 4.6]; % process time at 100 and 121 oC,
respectively (s)
D=[623 90]; % D values for the degradation of the nutrient at 100
and 121 oC, respectively (s)
Tref=100; % reference temperature (oC)

for i=1:length(T)
   for j=1:length(z)
```

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```
      C(i,j)=((10^((T(i)-Tref)/z(j)))*ProcessTime(i)); % C value
with T(i) and z(j)
      cRatio(i,j)=1/exp(2.303*C(i,j)/D(i));
    end
end

% plot the fraction of the nutrients surviving the process as a
function of the z value
plot(z,cRatio(1,:),'-',z,cRatio(2,:),':'); hold on
grid on
legend('T=Tref=100 ^oC','T=121 ^oC',3,'Location','SouthEast')
xlabel('z (^o C)')
ylabel('fraction of the nutrients surviving the process')
```

When we run the code the Figure E.4.1. will appear on the screen.

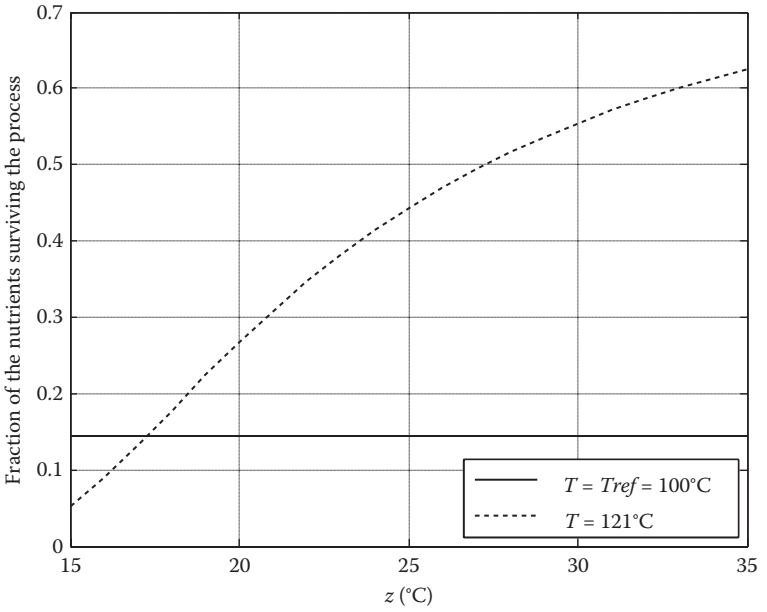


FIGURE E.4.1
Faction of the nutrients surviving the thermal process at 100 and 121°C as a function of the *z* value.

Example 4.2: Process Time Calculation With Variable Time Temperature Profile

A convection heating food was processed in still retort at 120°C. The critical point temperature was measured with 1.5 minutes intervals. In the heating cycle the average critical point temperature at each interval was

i	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**
T(°C)	46	56	74	92	102	109	113	115	116	117	118

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The critical point temperature remained almost constant at 118°C during the holding period, then the steam was turned off and the cooling period started. In the cooling cycle the critical point temperature was

j	**1**	**2**	**3**	**4**	**5**	**6**	**7**
T(°C)	111	66	45	35	30	28	27

The required processing time at 121°C is 6 minutes. The z value is 10.4°C. Determine the time to turn steam off for a safe process.

Solution: We may assume that the critical point temperature profiles remain the same in the heating and cooling periods under similar processing conditions. We may adjust the holding time to achieve the safe process. Equation 4.3 may be written to cover all the cycles as

$$F_{\text{process}} = \sum_{i=1}^{11} 10^{(T-T_{ref})/z}\Delta t_i + \sum_{n=1}^{N} 10^{(T-T_{ref})/z}\Delta t_n + \sum_{j=1}^{7} 10^{(T-T_{ref})/z}\Delta t_j,$$

where i, n, and j are the indices of the time increment in the heating, holding, and the cooling periods, respectively. MATLAB® code E.4.2 computes the time to turn the steam off as 23 minutes while computing the total processing time as 33 minutes.

MATLAB® CODE E.4.2

Command Window:

```
clear all
close all

% enter the data
Tref=121;
z=10.4; % C
Tholding=118; % C
Frequired=6; % min
DeltaTime=1.5; % min

Theating=[46 56 74 92 102 109 113 115 116 117 118]; % heating period
temperatures
Tcooling=[111 66 45 35 30 28 27]; % heating period temperatures
Nheating=length(Theating);
Ncooling=length(Tcooling);

% compute part of the Fprocess received in the heating period
IncrementH=(10.^(((Theating-Tref)/z)))*DeltaTime;
Fheating=sum(IncrementH);

% compute part of the Fprocess received in the cooling period
IncrementC=(10.^(((Tcooling-Tref)/z)))*DeltaTime;
```

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```
Fcooling=sum(IncrementC);

% compute part of the Fprocess received in each increment of the
holdinging period
Increment=(10.^(((Tholding-Tref)/z)))*DeltaTime;

% compute the number of the increments of the holdinging period
Nholding=(Frequired-(Fheating+Fcooling))/Increment;

% compute the time to turn steam off and the total processing time
tSteamOff=DeltaTime*(Nheating+Nholding);
tProcess=DeltaTime*(Nheating+Ncooling+Nholding);
fprintf('\ntime from steam on to off = %.2g minutes  \n', tSteamOff)
fprintf('\ntotal process time = %.2g minutes  \n', tProcess)
```

When we run the code the following lines will appear on the screen:

```
time from steam on to off = 23 minutes
total process time = 33 minutes
```

It was observed (Ball 1923) that in the heating cycle of a retorting process the difference between the retort (T_R) and the critical point (can center) temperatures $T(t)$ approaches zero logarithmically:

$$\frac{d\left[\log\left(T_R - T(t)\right)\right]}{dt} = -\frac{1}{f_h}, \tag{4.6}$$

where f_h is the time required for $[T_R - T(t)]$ to change one log cycle. A similar observation is generally made in the cooling cycle with $(T - T_{CW})$

$$\frac{d\left[\log\left(T(t) - T_{CW}\right)\right]}{dt} = -\frac{1}{f_c}, \tag{4.7}$$

where T_{CW} is the cooling water temperature and f_c is time required for $T(t) - T_{CW}$ to change one log cycle. Equations E.4.6 and E.4.7 may be solved by relating the critical point temperature to time elapsed from the beginning of each cycle:

$$t = f_h \log\left[j_h \frac{T_R - T_0}{T_R - T(t)} \right], \tag{4.8}$$

$$t = f_c \log\left[j_c \frac{T_h - T_{c0}}{T(t) - T_{CW}} \right], \tag{4.9}$$

where $T = T_0$ at $t = 0$ and $T = T_{C0}$ at $t_c = 0$ (the beginning of the cooling period); $T = T_h$ at the critical point at $t = t_h$ = the end of the heating period; j_h and j_c are correction factors to compensate for deviation of integrated forms of Equations 4.6 and 4.7 from the linear behavior in each cycle. Temperature profiles $T(t)$ may be evaluated at the can center by using Equations 4.8 and 4.9 to calculate the microbial reduction needed for safe processing.

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Although Ball's empirical model had simplifying assumptions and inaccuracies, it served the food industry satisfactorily for more than half a century (Merson, Singh, and Carroad 1978). Parameters f_h, j_h, f_c, and j_c may be determined theoretically for the processes where heat transfer occurs with perfect conduction or perfect convection, but in most real processes both convection and conduction may contribute to heat transfer and parameters with different values may appear.

When the food in the can is a perfectly mixed homogeneous liquid with uniform temperature and the retort is operating at a constant temperature T_R with no coming up time, the thermal energy balance around the can requires

$$UA(T_R - T) = mc\frac{dT}{dt}, \tag{4.10}$$

where A is the total heat transfer area, U is the total heat transfer coefficient, m is the total mass of the food, c is the average specific heat of the food, T is the food temperature, and t is time. The total heat transfer coefficient may be expressed in terms of its components

$$\frac{1}{U} = \frac{1}{h_o} + \frac{\Delta r}{k} + \frac{1}{h_i}, \tag{4.11}$$

where h_o and h_i are the outside and inside heat transfer coefficients, Δr is the thickness of the can, and k is the thermal conductivity of the can. When the food is at a constant temperature T_0 at time $t = 0$, Equation 4.10 may be solved as (Merson, Singh, and Carroad 1978)

$$t = \frac{2.303mc}{UA}\log\left(\frac{T_R - T_0}{T_R - T}\right). \tag{4.12}$$

Comparison of Equation 4.12 with Equation 4.8 implies that when pure convection is the prevailing mechanism of heat transfer (Merson, Singh, and Carroad 1978):

$$f_h = \frac{2.303mc}{UA}, \tag{4.13}$$

and

$$j_h = 1. \tag{4.14}$$

Heat transfer may be assumed to occur with perfect conduction when there is no mixing in the can. The governing transport equation for heat transfer is obtained after simplifying Equation 2.17 as

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial T}{\partial r}\right) + \frac{\partial^2 T}{\partial z^2} = \frac{1}{\alpha}\frac{\partial T}{\partial t}, \tag{4.15}$$

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where r and z are distances along the radial and the longitudinal directions, respectively, and parameter α is the thermal diffusivity of the food. Equation 4.15 may be solved with the following initial and the boundary conditions:

$$T(r,z,0) = T_0, \tag{4.15a}$$

$$T(R,z,t) = T_R, \tag{4.15b}$$

$$T(r,\pm L,t) = T_R, \tag{4.15c}$$

$$\frac{dT}{dr} = 0 \text{ at } r = 0, \tag{4.15d}$$

$$\frac{dT}{dz} = 0 \text{ at } z = 0, \tag{4.15e}$$

where R and $2L$ are the radius and the height of the can, respectively. Equation 4.15a implies that the food was initially at a constant temperature T_0, Equations 4.15b and 4.15c show that the food surfaces were at the retort temperature throughout processing. Equations 4.15d and 4.15e indicate the symmetrical temperature profiles around the centerline and the horizontal plane between the lower and the upper halves of the can. A new dependent variable may be defined to apply the method of the separation of variables:

$$Y_{\text{can}} = \frac{T_R - T}{T_R - T_0} R(r,t)Z(z,t). \tag{4.16}$$

Equation 4.16 may be arranged as

$$Z\left(\frac{\partial^2 R}{\partial r^2} + \frac{1}{r}\frac{\partial R}{\partial r} - \frac{1}{\alpha}\frac{\partial R}{\partial t}\right) + R\left(\frac{\partial^2 Z}{\partial z^2} - \frac{1}{\alpha}\frac{\partial Z}{\partial t}\right) = 0. \tag{4.17}$$

Equation 4.17 is satisfied if

$$\frac{\partial^2 R}{\partial r^2} + \frac{1}{r}\frac{\partial R}{\partial r} - \frac{1}{\alpha}\frac{\partial R}{\partial t} = 0 \tag{4.18}$$

and

$$\frac{\partial^2 Z}{\partial z^2} - \frac{1}{\alpha}\frac{\partial Z}{\partial t} = 0. \tag{4.19}$$

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Equations 4.18 and 4.19 are actually thermal energy balances for an infinitely long cylinder and an infinitely long slab, respectively, with

$$R(r,t) = Y_{\text{cylinder}} = \left(\frac{T_R - T}{T_R - T_0}\right)_{\text{cylinder}} \text{ and } Z(z,t) = Y_{\text{slab}} = \left(\frac{T_R - T}{T_R - T_0}\right)_{\text{slab}}.$$

The initial and the boundary conditions for Equation 4.18 are

$$R(r,0) = 1, \tag{4.18a}$$

$$R(R,t) = 0, \tag{4.18b}$$

$$\frac{dR}{dr} = 0 \text{ at } r = 0. \tag{4.18c}$$

The initial and boundary conditions for Equation 4.19 are

$$Z(z,0) = 1, \tag{4.19a}$$

$$Z(L,t) = 0, \tag{4.19b}$$

$$\frac{dZ}{dz} = 0 \text{ at } z = 0. \tag{4.19c}$$

Equations 4.18a and 4.19a imply that the cylinder and the slab were initially at a constant temperature T_0, Equation 4.18b and 4.19b show that the cylinder and the slab surfaces were at the retort temperature T_R throughout processing. Equations 4.18c and 4.19c indicate the symmetric temperature profiles around the centerline of the cylinder and the horizontal plane between the lower and the upper halves of the slab. Solutions to the cylinder and the slab equations are

$$Y_{\text{cylinder}} = 2\sum_{n=1}^{\infty} \frac{J_0\left(B_n \frac{r}{R}\right)}{J_1(B_n) B_n} \exp\left(B_n (k/\rho c)(t/R^2)\right), \tag{4.20}$$

where J_0 and J_1 are zero and first-order Bessel functions of type one, B_n is the nth Eigen value of $J_0(B_n)$, ρ and c are the average density and heat capacity of the food.

$$Y_{\text{slab}} = \sum_{m=1}^{\infty} \left[2\frac{(-1)^{m+1}}{\beta_m}\right] \text{Cos}\left[\beta_m \frac{2z}{L}\right] \exp[-\beta_m^2 (k/\rho c)(t/L^2)], \tag{4.21}$$

where $\beta_m = (2m - 1)\pi/2$. Values of the Bessel functions $J_0(x)$, $J_1(x)$, and $J_1(B_n)$ for the Eigen values B_n of $J_0(B_n) = 0$ are given in Tables 2.10 and 2.14.

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Equation 4.16 requires (Merson, Singh, and Carroad 1978)

$$Y_{\text{can}} = \sum_{m=1}^{\infty}\sum_{n=1}^{\infty}\left[2\frac{(-1)^{m+1}}{\beta_m}\right]\text{Cos}\left[\beta_m\frac{z}{L}\right]\frac{2J_0\left(B_n\frac{r}{R}\right)}{B_nJ_1(B_n)}\exp\left[-\left(\frac{\beta_m^2}{L^2}+\frac{B_n^2}{R^2}\right)\left(\frac{k}{\rho c}\right)t\right] \tag{4.22}$$

Equation 4.22 describes the unsteady state temperature variations within the can as a function of the radial location r and the longitudinal location z. When the processing times are long, the solution of Equation 4.22 may be approximated with the first term of the series solution; that is, $m = 1$, $\beta_1 = \pi/2$, $n = 1$, $B_1 = 2.4048$, $J_1(B_1) = 0.5191$. Further simplifications may be done when the long time solution is sought at the can center; that is, $z = 0$, $\text{Cos}(0) = 1$, $r = 0$, $J_0(0) = 1$ and Equation 4.22 may be rewritten as (Merson, Singh, and Carroad 1978)

$$Y_{\text{can center}} = \frac{T_R - T}{T_R - T_0} = 2.04\exp\left\{-\left(\frac{\pi^2}{4L^2}+\frac{B_1^2}{R^2}\right)\left(\frac{k}{\rho c}\right)t\right\}. \tag{4.23}$$

Equation 4.23 may be rearranged as

$$t = \frac{2.303}{\left(\frac{\pi^2}{4L^2}+\frac{B_1^2}{R^2}\right)\left(\frac{k}{\rho c}\right)}\log\left(2.04\frac{T_R - T_0}{T_R - T}\right). \tag{4.24}$$

The comparison of Equation 4.24 with Equation 4.9 implies that, when pure conduction is the prevailing mechanism of the heat transfer (Merson, Singh, and Carroad 1978)

$$f_h = \frac{2.303}{\left(\frac{\pi^2}{4L^2}+\frac{B_1^2}{R^2}\right)\left(\frac{k}{\rho c}\right)} \tag{4.25}$$

and

$$j_h = 2.04. \tag{4.26}$$

The method we employed here to solve the partial differential equation is also referred to as the *Newman's method* (Newman 1936).

Equations 4.13 and 4.25 show that the f_h values are affected by the can size. The mass of the food in the can is $m = \rho\pi R^2 2L$, the total heat transfer area of a cylindrical can (radius = R, height = $2L$) is $A = 2\pi R^2 L(2/R^2 + 1/L)$. It may be assumed that the total heat transfer coefficient U may be regarded independent of the can size. After substituting the equations for m and A into Equation 4.13, the ratio of the f_h values may be expressed as a function of the can size as

$$\frac{f_{h2}}{f_{h1}} = \frac{R_2L_2}{R_2 + 2L_2}\frac{R_1 + 2L_1}{R_1L_1}. \tag{4.27}$$

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A similar conversion factor may be obtained for the conduction heating foods after substituting $B_1 = 2.405$ in Equation 4.25 as

$$\frac{f_{h2}}{f_{h1}} = \left(\frac{5.78}{R_1^2} + \frac{\pi^2}{4L_1^2}\right) \Big/ \left(\frac{5.78}{R_2^2} + \frac{\pi^2}{4L_2^2}\right). \tag{4.28}$$

Example 4.3: Variation of the Ball's Formula Method Parameters With Can Size

A convection heating product ($c_p = 3.8$ kJ/kg K, $\rho_p = 960$ kg/m^3) is heated in a 307 × 306 size can of 0.03 cm thickness. The can wall has $k = 69$ W/mK with $h_{inside} = 350$ W/m^{2}K, $h_{outside} = 450$ W/m^{2}K. Calculate the f_h and j_h values for this process.

Solution: The first and the second numbers in the can size indicate the height and the diameter, respectively. Where the first digits are an integer number of inches, the second and the third digits are the additional 1/16 folds of one inch. We may calculate the can height as $2L = (3 + 7/16)(2.54) = 8.7$ cm, and the can radius as $R = (3 + 6/16)(2.54)(1/2) = 4.3$ cm, where 2.54 is a constant to convert the numbers in cm from inches. The volume of the can is $V = \pi R^2 2L = 5.05 \times 10^{-4}$ m^3, mass of the food in the can is $m = \rho V = 0.485$ kg and the heat transfer area of the can is $A = 2\pi R^2 L(2/R + 1/L) = 3.51 \times 10^{-2}$m^2. The total heat transfer coefficient is

$$\frac{1}{U} = \frac{1}{h_o} + \frac{\Delta r}{k} + \frac{1}{h_i}. \tag{E.4.3.1}$$

After substituting the numbers in Equation E.4.3.1 we will obtain $U = 197$ W/m^{2}K. The f_h and j values for a convection heated food are

$$f_h = \frac{2.303mc}{UA} \tag{4.13}$$

and

$$j_h = 1. \tag{4.14}$$

After substituting the numbers in Equation 4.13, we will calculate $f_h = 10.2$ minutes.

Example 4.4: Heating Time Computation With the Ball's Formula Method

A conduction heated product will be processed in 211 × 212 size cans. Temperature profiles $T(t)$ may be simulated at the can center with Equations 4.8 and 4.9 after using $f_h = f_c = 60$ minutes, $j_h = j_c = 2.00$. Operating conditions are $T_R = 121$°C, $t_{CUT} = 10$ minutes, $T_0 = 70$°C, and $T_{CW} = 21$°C. The $F_{required}$ for the process (defined in Equation 4.1) is 10 minutes at 121°C with $z = 13.3$°C. The MATLAB® code E.4.4 computes the time from steam on to steam off and determines the percentage of the nutrient loss at the can center at the end of the process.

The food has a heat sensitive nutrient with $D = 180$ minutes at $T_{ref} = 121$°C, $z = 24.5$°C. The MATLAB® code E.4.4 prints out the amounts of nutrients surviving the process as 72%.

Note: Retort coming-up time t_{CUT} is the time required to reach T_R after turning the steam on. It is advised to compute the heating period with a constant T_R, then compute the real heating time as $t_{\text{with CUT time}} = t_{\text{with constant TR}} + 0.58 \times t_{CUT}$.

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MATLAB® CODE E.4.4

Command Window:

```
clear all
close all
format short g

% enter the data
Freq=10; % min
Tref=121; % C
Tr=121; % C
Tcw=21; % C
Tg=116; % C
z=24.5; % C
Dref=180;
tcut=10; % min
fh=60; % min
jh=2;
To=70; % min

% process calculation
U=Freq*10^((Tref-Tr)/z)
theating=fh*(log10(jh*(Tr-To))-log10(Tr-Tg))+0.58*tcut
U2=fh/2.29
cprocess=U2(10^((Tref-Tr)/10))
nutrientpercent=100*10^(-cprocess/Dref);
fprintf('%.2g percent of the nutrients are surviving the
process',nutrientpercent)
```

When we run the code the following lines will appear on the screen:

```
U =
    10

theating =
       84.378

U2 =
       26.201

cprocess =
       26.201

72 percent of the nutrients are surviving the process
```

Example 4.5: Wehrle–Merson Model to Predict Critical Point Temperatures of Conduction Heated Foods at Short Heating Times

a. Temperature distribution in an infinite slab may be expressed as (Carslaw and Jaeger 1959):

$$\frac{T-T_0}{T_R-T_0}=\left[\sum_{n=0}^{\infty}(-1)^n erfc\left\{\frac{(2n+1)L-z}{2\sqrt{\alpha t}}\right\}\right]+\sum_{n=0}^{\infty}(-1)^n erfc\left\{\frac{(2n+1)L+z}{2\sqrt{\alpha t}}\right\}, \quad \text{(E.4.5.1)}$$

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where z is the distance from the midplane of the slab, α is thermal diffusivity of the food, and $2L$ is the thickness of the slab. A short time solution for the axis of an infinite cylinder may be expressed as (Carslaw and Jaeger 1959)

$$\frac{T-T_0}{T_R-T_0}=\frac{R}{\sqrt{\pi\alpha t}}\exp\left\{-\frac{R^2}{8\alpha t}\right\}\left[K_{1/4}\left(\frac{R^2}{8\alpha t}\right)\right], \tag{E.4.5.2}$$

where $K_{1/4}$ is the modified Bessel function of the second kind of order 1/4. We will make a one-term approximation of the first expression, then combine the two expressions to obtain an expression for variation of the temperature at the critical point of the can of a conduction heated food. With $n = 0$ and $z = 0$, Equation E.4.5.1 reduces to the following form:

$$\frac{T-T_0}{T_R-T_0}=erfc\left\{\frac{L}{2\sqrt{\alpha t}}\right\}. \tag{E.4.5.3}$$

After following the same procedure as in the solution of Equation 4.15, we can state that

$$\left(\frac{T_R-T}{T_R-T_0}\right)_{can}=\left(\frac{T_R-T}{T_R-T_0}\right)_{slab}\left(\frac{T_R-T}{T_R-T_0}\right)_{cylinder}. \tag{E.4.5.4}$$

After substituting Equations E.4.5.2 and E.4.5.3 in Equation E.4.5.4 we will obtain

$$\left(\frac{T_R-T}{T_R-T_0}\right)_{can}=\left(1-erfc\left\{\frac{L}{2\sqrt{\alpha t}}\right\}\right)\left(1-\frac{R}{\sqrt{\pi\alpha t}}\exp\left\{-\frac{R^2}{8\alpha t}\right\}\left[K_{1/4}\left(\frac{R^2}{8\alpha t}\right)\right]\right). \tag{E.4.5.5}$$

Equation E.4.5.5 was originally used to simulate the can center temperature data (Wehrle 1980) during heating of tomato paste.

Equation 4.24 will be rearranged to obtain

$$\frac{T_R-T}{T_R-T_0}=2.04\exp\left\{-\left(\frac{\pi^2}{4L^2}+\frac{B_1^2}{R^2}\right)\left(\frac{k}{\rho c}\right)t\right\}. \tag{E.4.5.6}$$

In a study when $T_R = 87.8°C$, $T_0 = 7.2°C$, $f_h = 42.3$ minutes for processing in 307×296 size can where can height is $2L = (2 + 6/16)(2.54) = 6.03$ cm and can radius is $R = (3 + 7/16)(2.54)(1/2) = 4.36$ cm. We may calculate the thermal diffusivity $\alpha = k/\rho c$ from f_h by using Equation 4.25 as

$$f_h=\frac{2.303}{\left(\frac{\pi^2}{4L^2}+\frac{B_1^2}{R^2}\right)\alpha}=\frac{2.303}{\left(\frac{3.14^2}{6.03^2}+\frac{2.41^2}{4.36^2}\right)(\alpha)}=42.3.$$

After substituting the numbers we will get $\alpha = 0.094$ cm^2/min. After substituting the constants, Equation E.4.5.6 will be rewritten as

$$\frac{T_R-T}{T_R-T_0}=2.04\exp\left\{-\left(\frac{3.14^2}{6.03^2}+\frac{2.41^2}{4.36^2}\right)(0.094)t\right\}=2.02\exp\{-0.054t\}. \tag{E.4.5.7}$$

MATLAB® code E.4.5 simulates the variation of the can center temperature with time by using Equations E.4.5.5 and E.4.5.7 as depicted in Figure E.4.5.

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MATLAB® CODE E.4.5

Command Window:

```
clear all
close all
clc;

L = 3.015; % cm
R = 4.36; % cm
a = 0.0938; % alpha
TR = 87.8;
T0 = 7.2;
B1 = 2.41;

times= [0 7 12 15 18 22 27 30 38 47 57 64 73]';
for i=1:length(times)
    R_over_sqrt_etc(i) = (R/(sqrt(pi*a*times(i))));
    if isinf(R_over_sqrt_etc(i))==1 ; R_over_sqrt_etc(i)=0; end;
    expon(i) = exp((-R^2)/(8*a*times(i)));
    K14_besselfunction(i) = besselk(0.25,(R^2)/(8*a*times(i)));
    if isnan(K14_besselfunction(i))==1; K14_besselfunction(i)=0;
end;
    error_func(i) = erfc(L/(2*sqrt(a*times(i))));
    Tcan(i) = (1-2*error_func(i)) * (1-(R_over_sqrt_etc(i)*expon(i)
* K14_besselfunction(i)));
    T(i) = TR - (Tcan(i) * (TR-T0));
    %% Equation 4.8.7
    Tcan2(i) = 2.04 * exp(-((pi^2/(4*L^2))+(B1^2/
R^2))*0.094*times(i));
    T2(i) = TR - (Tcan2(i) * (TR-T0));
end
fprintf(1,'Equation 4.8.5\n----------------------------------------
------------------------------------------------------------\n')
for i=1:length(times)
fprintf(1,'t= %2.0f\tR/sqrt() = %4.3f\t exp()= %4.3f\t K14()= %5.4f\
terfc()= %4.3f\t Tcan= %4.3f\tT=
%4.1f\n',times(i),R_over_sqrt_etc(i),expon(i),K14_
besselfunction(i),error_func(i),Tcan(i),T(i))
end
fprintf(1,'\nEquation 4.8.7\n----------------------------------------
------------------------------------------------------------\n')
for i=1:length(times)
fprintf(1,'t= %2.0f\tTcan= %4.3f\tT=
%4.1f\n',times(i),Tcan2(i),T2(i))
end

y = [7.2 12.8 17.8 27.2 38.9 47.8 54.4 61.1 70 77.8 80 82.2 83.9];
plot(times,T,'-k',times,T2,'--k',times,y,'*k')
legend('Eq 4.8.5','Eq 4.8.7','Experimental
Data',3,'Location','SouthEast')
xlabel('Time (min)')
ylabel('Temperature ( \circ C)')
title('Comparison of E.4.8.5 and E.4.8.7 With The Experimental Data')
```

When we run the code Figure E.4.5 will appear on the screen

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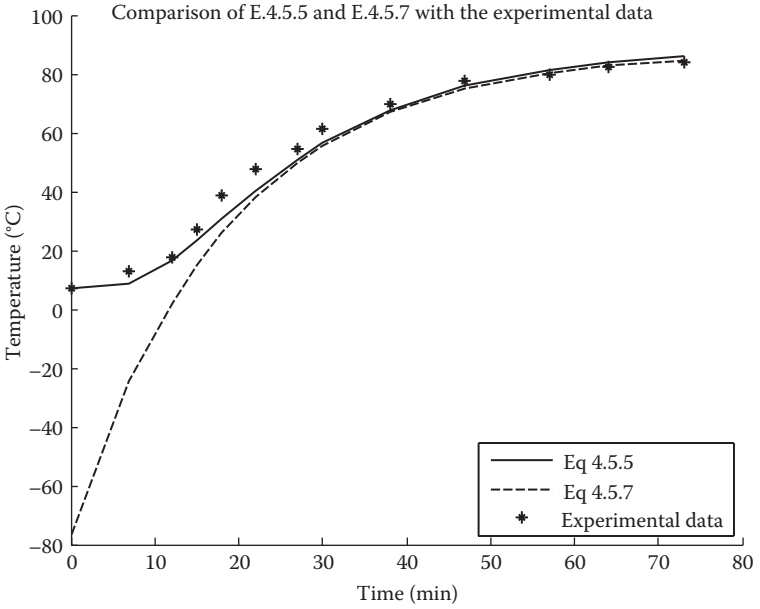


FIGURE E.4.5
Comparison of Equations E.4.5.5 and E.4.5.7. (From Ward, D. R., Pierson, M. D., and Minnick, M. S., *Journal of Food Science*, 49, 1003–4, 1017, 1984.)

Example 4.6: Lethality-Fourier Number Method for Thermal Process Time Computation With Conduction Heated Foods

During heat treatment of conduction heated food, the death rate of the microorganisms and the temperature effects on the death rate constant are modeled as

$$\frac{dx}{dt} = -kx, \tag{3.31d}$$

$$k = k_0 \exp\left\{-\frac{E_a}{RT}\right\}. \tag{3.5}$$

Equations 3.31d and 3.5 were combined and arranged as (Lenz and Lund 1977)

$$\mathcal{L} = -\frac{\alpha \ln\left(x/x_0\right)}{k_{ref} R_{can}^2} = \int_0^{\tau} \exp\left(-\frac{E_a}{RT}\left(\frac{1}{T} - \frac{1}{T_{ref}}\right)\right) d\tau. \tag{E.4.6.1}$$

Where $\mathcal{L}$ is referred to as the Lethality number, x_0 is the initial number of the microorganisms, x is the number of the microorganisms surviving at $\tau = \alpha t / R_{can}^2$ (τ is also named as the Fourier number). The parameter k_{ref} is the death rate constant at T_{ref}. Temperatures T_{ref} and are in K.

Temperature profiles in the can during the heating period may be described with the unsteady state heat conduction equation for a finite cylinder:

$$\frac{T(\tau,\zeta,\eta) - T_R}{T_0 - T_R} = \frac{4}{I} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{(-1)^{m+1}}{B_n J_1(B_n) \beta_m} J_0(B_n \zeta) \cos(\beta_m \ell \eta) \exp\left[-\left(\beta_m^2 + B_n^2\right) \tau_H\right], \tag{E.4.6.2}$$

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where R_{can} and L are the radius and the half of the height of the can, respectively, $\tau_H = \alpha t/R_{can}^2$ is the heating period Fourier number, $\alpha = k/\rho c$ is thermal diffusivity, and β_k are the roots of $J_0(\beta) = 0$. Derivation of Equation E.4.6.2 is the same as that of the mass transfer equation given in Example 2.12.

A similar expression may be employed for modeling the cooling period temperatures:

$$\frac{T(\tau,\zeta,\eta)-T_{cw}}{T_0-T_{cw}} = \frac{4}{\ell}\sum_{n=1}^{\infty}\sum_{m=1}^{\infty}\frac{(-1)^{m+1}}{B_n J_1(B_n)\beta_m} J_0(B_n\zeta)\cos(\beta_m \ell\ \eta)\exp\left[-(\beta_m^2 + B_n^2)\ \tau_w\right], \qquad \text{(E.4.6.3)}$$

where τ_w is the cooling period Fourier number. Variation of the lethality number with the Fourier number (Figure E.4.6.1) and variation of the surviving fraction of microorganisms x/x_0 with time (Figure E.4.6.2) are computed by MATLAB® code E.4.6 after solving Equation E.4.6.1 simultaneously with Equation E.4.6.2 or Equation E.4.6.3.

MATLAB® CODE E.4.6

Command Window:

```
clear all
close all

% Determine the temperature profile within the can

Rcan=3.4e-2; % m
L=3.8e-2; % m
TR=121.7; % oC
T0=20; % oC
Tcw=15.5; % oC

% you may compute the temperatures at any point of the can by
choosing an appropriate j and k
tauLimit=0.4;
tauIncrement=tauLimit/10;
zIncrement=L/10;
rIncrement=Rcan/10;
j=4;
k=4;
z=zIncrement*j; % distance from the can center in longetidual
direction (m)
r=rIncrement*k; % distance from the can center in axial
direction (m)

% HEATING PERIOD MODEL
[tauH TH]=ConductionHeating(Rcan, L,r, z, T0, TR, tauIncrement);

% COOLING PERIOD MODEL
T0=TR;
[tauC TC]=ConductionCooling(Rcan,L,r,z,T0,Tcw,tauIncrement);

% COMPUTE THE LETHALITY NUMBERS
K0=2.9e36; % 1/min
```

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```
Ea=2.7e5; % J/mol
Tref=121.1; % oC
kref=4.6; % 1/min
R=8.314; % J/mole K
alpha=9.68e-6; % m2/mkin

A=length(TH);
B=length(TC);
LN1=0;
for i=1:1:A;
tauH(i)=tauIncrement*i;
LethalityIncrementH(i)= (exp(-(Ea/R)*((Tref-TH(i))/((Tref+273)*(TH
(i)+273)))))*tauIncrement;
end

for k=1:1:B;
tauC(k)=tauIncrement*k;
LethalityIncrementC(k)= (exp(-(Ea/R)*((Tref-TC(k))/((Tref+273)*(TC
(k)+273)))))*tauIncrement;
end

C=A+B;
D=tauH(i);
E=0;
for j=1:1:C;
if j<=A
tau(j)=tauH(j);
E=E+LethalityIncrementH(j);
Lethalithy(j)=E;
lnSurvivingFraction(j)=-Lethalithy(j)*kref*(Rcan^2)/alpha;
end
if j>A
k=j-A;
tau(j)=D+tauC(k);
E=E+LethalityIncrementC(k);
Lethalithy(j)=E;
lnSurvivingFraction(j)=-Lethalithy(j)*kref*(Rcan^2)/alpha;
end
% compute processing times (min)
time(j)= tau(j)*(Rcan^2)/alpha;
end

% plot the lethality numbers versus the Fourier numbers
semilogy(tau,Lethalithy,'--')
xlabel('Fourier Number')
ylabel('Lethality Number')

figure
plot(time, lnSurvivingFraction,'--')
ylabel('ln(microbial reduction ratio), ln(x/x0)')
xlabel('time (min)')
```

M-file1:

```
function [tauHeating TH]=ConductionHeating(Rcan,L,r,z,T0,TR,tauIncre
ment)
```

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```
% this function presumes that the finite cylinder has a uniform
initial
% temperature T0.
% Rcan= radius of the cylinder
% L= half of the height of the cylinder

% Introduce the data
Bn=[2.405 5.520 8.654 11.792 14.93 18.07 21.212 24.353 27.494];

% tabulate the heating period temperatures:
fprintf('\n heating period temperatures \n\n')
fprintf(' r (cm)          z (cm)     tauH      T (C)\n')
fprintf('---------     ---------  --------    --------\n')

% heating period model
for i=1:1:10; % tauC(i)
tauH= tauIncrement*i;
sum2=0;
for m=1:1:9;
beta(m)=(2*m-1)*pi*Rcan/(4*L);
sum1=0;
for n=1:1:9;
s(m,n)=(((1)^(m+1))/(Bn(n)*besselj(1,Bn(n))*(beta(m))))*besselj(0,Bn
(n)*(r/Rcan)) *(cos(((beta(m))*(Rcan/L)*(z/L))))*(exp(-
tauH*(((Bn(n))^2)+((beta(m))^2))));
sum1=sum1+s(m,n);
end
sum2=sum2+sum1;
end
Theating=TR+(T0-TR)*sum2;
fprintf('%-10g %7g  %5g     %5g \n',r,z,tauH,Theating)
TH(i)=Theating;
tauHeating(i)=tauH;
end
```

M-file2:

```
function [tauCooling TC]=ConductionCooling(Rcan,L,r,z,T0,Tcw,tauIncr
ement)

% this function presumes that the finite cylinder has a uniform
initial
% temperature T0.
% Rcan= radius of the cylinder
% L= half of the height of the cylinder

% Introduce the data
Bn=[2.405 5.520 8.654 11.792 14.93 18.07 21.212 24.353 27.494];

% tabulate the cooling period temperatures:
fprintf('\n cooling period temperatures \n\n')
fprintf(' r (cm)          z (cm)    tauC       T (C)\n')
fprintf('---------     ---------  --------    --------\n')

% cooling period model
for i=1:1:10; % tauC(i)
tauC= tauIncrement*i;
```

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```
sum2=0;
for m=1:1:9;
beta(m)=(2*m-1)*pi*Rcan/(4*L);
sum1=0;
for n=1:1:9;
s(m,n)=(((1)^(m+1))/(Bn(n)*besselj(1,Bn(n))*(beta(m))))*besselj(0,Bn
(n)*(r/Rcan)) *(cos(((beta(m))*(Rcan/L)*(z/L))))*(exp(-tauC*
(((Bn(n))^2)+((beta(m))^2))));
sum1=sum1+s(m,n);
end
sum2=sum2+sum1;
end
Tcooling=Tcw+(T0-Tcw)*sum2;
fprintf('%-10g %7g  %5g     %5g \n',r,z,tauC,Tcooling)
TC(i)=Tcooling;
tauCooling(i)=tauC;
end
```

When we run the code the following lines and Figures E.4.6.1 and E.4.6.2 will appear on the screen:

```
heating period temperatures

r (cm)          z (cm)       tauH         T (C)
---------      --------    --------     --------
0.0136          0.0152       0.04        42.7286
0.0136          0.0152       0.08        58.8623
0.0136          0.0152       0.12        73.6232
0.0136          0.0152       0.16        85.0551
0.0136          0.0152       0.2         93.7261
0.0136          0.0152       0.24        100.293
0.0136          0.0152       0.28        105.279
0.0136          0.0152       0.32        109.078
0.0136          0.0152       0.36        111.98
0.0136          0.0152       0.4         114.204

cooling period temperatures

r (cm)          z (cm)       tauC         T (C)
---------      --------    --------     ---------
0.0136          0.0152       0.04        97.9657
0.0136          0.0152       0.08        81.1181
0.0136          0.0152       0.12        65.7041
0.0136          0.0152       0.16        53.7663
0.0136          0.0152       0.2         44.7117
0.0136          0.0152       0.24        37.8541
0.0136          0.0152       0.28        32.6471
0.0136          0.0152       0.32        28.6806
0.0136          0.0152       0.36        25.6498
0.0136          0.0152       0.4         23.3277
```

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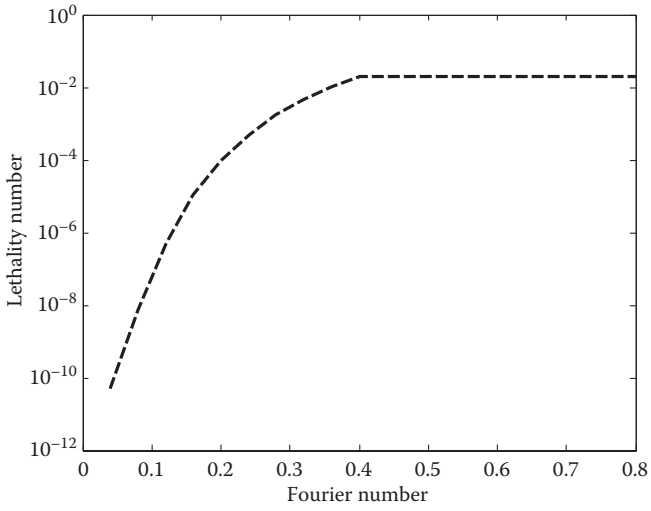


FIGURE E.4.6.1
Variation of the Lehality number with the Fourier number in combined heating and cooling cycles. (Model parameters were adapted from Lenz, M. K., and Lund, B., *Journal of Food Science,* 42, 989–96, 1001, 1977.)

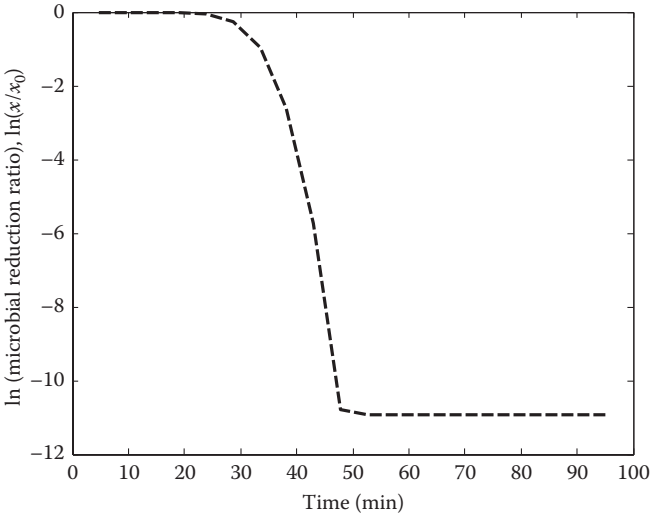


FIGURE E.4.6.2
Variation of the ln (surviving fraction) of the microorganisms with time in combined heating and cooling cycles. It should be noticed that x/x_0 becomes 1.67×10^{-5} after about 50 minutes. (Model parameters were adapted from Lenz, M. K., and Lund, B., *Journal of Food Science,* 42, 989–96, 1001, 1977.)

Example 4.7: A Transfer Function Approach to Predict Transient Internal Temperatures During Sterilization

The transfer function approach to predict transient internal temperatures during sterilization was originally developed by Chiheb et al. (1994). A noninteracting physical system can be represented by several first-order processes connected in series. The term noninteracting implies that the individual processes described by each box do not interfere with the others.

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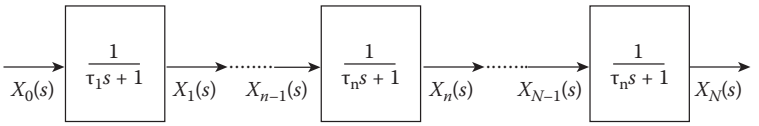


FIGURE E.4.7.1
Representation of a canned food during sterilization as a linear system. Transfer functions for the individual processes are given in the related box, such as $X_1(s)/X_o(s) = 1/(\tau_1 s + 1)$.

The transfer function for the entire system described in Figure E.4.7.1 is (Coughanowr and LeBlanc 2008)

$$\frac{X_N(s)}{X_o(s)} = \frac{1}{\prod_{i=1}^{N}(1+\tau_i s)}. \tag{E.4.7.1}$$

There is generally a time delay t_d between the input and the output, which may be incorporated into Equation E.4.7.1 as

$$\frac{X_N(s)}{X_o(s)} = \frac{\exp(t_d s)}{\prod_{i=1}^{N}(1+\tau_i s)}, \tag{E.4.7.2}$$

where N is the number of the noninteracting linear stages involved into the process and $\tau_1 > \tau_2 > \tau_3 > \ldots > \tau_N$ are the time constants. Equation E.4.7.2 will be used to describe the relation between the dimensionless can center temperature $X_o(t) = [T_R(t) - T_R] / [T_0 - T_R]$ and the dimensionless retort temperature $X_N(t) = [T(t) - T_0] / [T_R - T_0]$ where $T(t)$ is the internal temperature, and $T_R(t)$ is the unsteady state retort temperature before attaining the final steady state retort temperature T_R. At the beginning of the heating phase, the temperature of the food is T_0. Time delay t_d represents the time needed for an input signal to produce a variation at the output after its propagation within the system. Time constants may be calculated from the roots of the denominator $\prod_{i=1}^{N}(1+\tau_i s) = 0$. Equation E.4.7.2 may be used to describe the relation between the can center temperature $T(t)$ and the retort temperature T_R as

$$\frac{T(t)-T_R}{T_0-T_R} = \sum_{j=1}^{N} j_i \exp\left(-\frac{t}{\tau_i}\right) \text{ when } t > t_d, \tag{E.4.7.3}$$

where

$$j_i = \frac{\left[(\tau_i)^{N-1}\exp(t_d/\tau_i)\right]}{\prod_{k=1\ k\neq i}^{N}\tau_i - \tau_k}. \tag{E.4.7.4}$$

When the retort temperature attains T_R with some delay we will have

$$\frac{T(t)-T_R}{T_0-T_R} = 1 - \frac{1}{t_{CUT}}\left[(t-t_d) - \sum_{i=1}^{N}\tau_i + \sum_{i=1}^{N} j_i\tau_i \exp\left(-\frac{t}{\tau_i}\right)\right] \text{ when } t_d < t < t_{CUT}, \tag{E.4.7.5}$$

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$$\frac{T(t)-T_R}{T_0-T_R}=\sum_{i=1}^{N}\frac{j_i\tau_i\left[\exp\left(t_{CUT}/\tau_i\right)-1\right]}{t_{CUT}}\exp\left(-\frac{t}{\tau_i}\right)\text{ when } t_d<t_{CUT}<t. \tag{E.4.7.6}$$

Changes on the can center temperature influences the critical point with time delay, therefore the critical point temperature may keep increasing for a while after turning the steam off and the cooling water on. To account for this phenomenon, the can center temperature may be expressed as

$$T(t)=T_h-\left(T_h-T_0\right)\frac{T-T_h}{T_0-T_h}\quad\text{when } t\le t_g, \tag{E.4.7.7}$$

and

$$T(t)=T_c-\left(T_h-T_0\right)\frac{T-T_h}{T_0-T_h}-\left(T_c-T_h\right)\frac{T-T_c}{T_h-T_c}\left(t-t_g\right)\text{ when } t>t_g, \tag{E.4.7.8}$$

where t_g is the time length of the heating period. Subscripts *c* and *h* describes the cooling and the heating periods, respectively. MATLAB® code E.4.7 compares the model with the data (Figure E.4.7.2).

MATLAB® CODE E.4.7

Command Window:

```
clear all
close all

% Introduce the retort time-temperature data
tre=[0 8 10 20 30 40 50 60 70 80 90 100 120 140 150];
Tre=[20 108 110 110 110 110 110 110 110 20 17 15 15 15 15];
Tcenter=[18 18 20 32 50 70 80 95 100 105 107 73 39 21 18];
timeCooling=[70 80 90 100 120 140 150];
TcenterCooling=[100 105 107 73 39 21 18];
hold on, plot(tre,Tre, '--')
hold on, plot(tre,Tcenter, '*')

% Introduce the model parameters
J1=1.87;
J2=-0.917;
td=4.2;
tao1=24;
tao2=8.84;
T0=20;
T0c=100;
Tr=110;
tcut=8;
Th=110;
Tc=10;
Trc=8;
tg=73;

t1=[0:4];
A=[1 1 1 1 1];
```

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```
t2=[4:8];
B=1-(1./tcut).*((t2-td)-(tao1+tao2)+(J1.*tao1.*exp(-t2./
tao1))+(J2.*tao2.*exp(-t2./tao2)));

t3=[8:73];
C=(((J1*tao1*(exp(tcut/tao1)-1)/tcut))*exp(-t3./
tao1))+(((J2*tao2*(exp(tcut/tao2)-1)/tcut))*exp(-t3./tao2));

% Introduce the cooling period times. Beginning of the cooling
period was determined with trial and error procedure in order to
have a continuous can center temperature profile.
t4=[73:150];

% evaluate the cooling period model coefficients
[COEFF,resid,J]=nlinfit(timeCooling, TcenterCooling,'CoolingPeriod',
[0.1 35 0.917 20]);
D=((COEFF(1)*tao1*(exp(tcut/COEFF(2))-1))/tcut).*exp(-t4./COEFF(2))+
((COEFF(3)*COEFF(4)*(exp(tcut/COEFF(4))-1))/tcut).*exp(-t4./
COEFF(4));

% compute the  model can center temperatures
T1=(A*(T0-Tr))+Tr;
T2=(B.*(T0-Tr))+Tr;
T3=(C.*(T0-Tr))+Tr;
T4=(D.*(T0c-Trc))+Trc;
Theat1=Th-(Th-T0).*(T1-Th)./(T0-Th);
Theat2=Th-(Th-T0).*(T2-Th)./(T0-Th);
Theat3=Th-(Th-T0).*(T3-Th)./(T0-Th);
Tcool=Tc+(Th-T0).*(T4-Th)./(T0-Th)-(Tc-Th).*(T4-Tc)./
(Th-Tc).*(t4-tg);

% plot the model
hold on, plot(t1,Theat1,':')
hold on, plot(t2,Theat2,':')
hold on, plot(t3,Theat3,':')
hold on, plot(t4,Tcool,':')
xlabel('Time (min)')
ylabel('Temperature (^oC)')
legend('Tretort','Tcan center','Tmodel','Location','NorthEast');
```

M-file:

```
function Tcool=CoolingPeriod(coeff, TimeCooling)

% introduce  the constants and coefficients and the independent
variable
T0=20;
tcut=8;
Th=110;
Tc=10;
Trc=8;
T0c=95;
tcut=8;
tao1=24;
tg=73;
J21=coeff(1);
```

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```
tao21=coeff(2);
J22=coeff(3);
tao22=coeff(4);
T0c=100;

%  model:
Tcool=Tc+(Th-T0).*((((((J21*tao1*(exp(tcut/tao21)-1))/tcut).*exp(-
TimeCooling./tao21)+((J22*tao22*(exp(tcut/tao22)-1))/tcut).*exp(-
TimeCooling./tao22)).*(T0c-Trc))+Trc)-Th)./(T0-Th)-(Tc-Th).*((
((((J21*tao1*(exp(tcut/tao21)-1))/tcut).*exp(-TimeCooling./
tao21)+((J22*tao22*(exp(tcut/tao22)-1))/tcut).*exp(-TimeCooling./
tao22)).*(T0c-Trc))+Trc)-Tc)./(Th-Tc).*(TimeCooling-tg);
```

When we run the code Figure E.4.7.2. will appear on the screen.

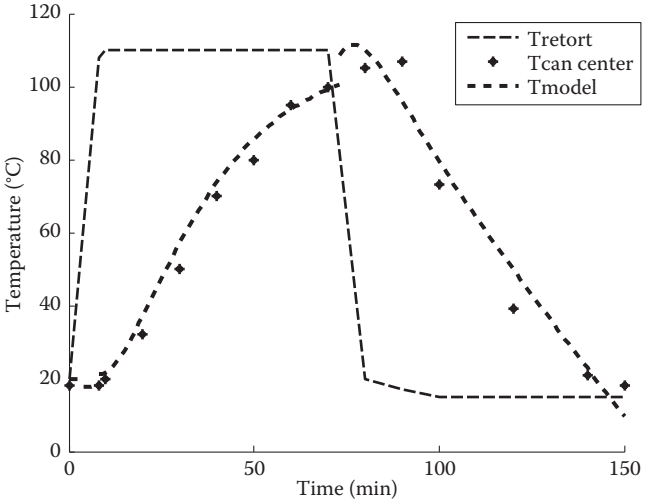


FIGURE E.4.7.2
Comparison of the model with the data. (Adapted from Chiheb, A., Debray, E., Le Jean, G., and Piar, G., *Journal of Food Science,* 59, 441–46, 1994.) Heating time model constants were obtained from the literature (From Chiheb, A., Debray, E., Le Jean, G., and Piar, G., *Journal of Food Science,* 59, 441–46, 1994); cooling period model coefficients were obtained by the MATLAB® code by using function nlinfit.

In *continuous processing* time-temperature, history of the individual liquid pockets is needed in order to calculate the sterilization given to them. When the flow model of the fluid is available, time spent by each pocket in the sterilization equipment may be determined by the help of the flow model. When such a model is not available, the residence time distribution of the liquid pockets is needed. Time spent by a liquid pocket in the process vessel is called the residence time. Process analysis may be simplified by considering the constant temperature holding tube only. The average exit concentration of the microorganisms, $\bar{x}$, from the holding tube may be calculated as

$$\bar{x} = \int_0^\infty x_0 \exp(-kt)\, E(t) dt, \tag{4.29}$$

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where x_0 is the potential average microbial load of the pockets at the entrance, k is the death rate constant and $E(t)$ is the residence time distribution function. Equation 4.29 considers the pockets with residence times between 0 and ∞. The residence time distribution function $E(t)$ may have values between 0 and 1. When there are no liquid pockets with a specific residence time t_s the residence time distribution function corresponding to t_s will be assigned $E(t_s) = 0$. The residence time distribution function $E(t)$ is different for each process vessel and changes with the flow conditions. It needs to be determined experimentally.

Example 4.8: Thermal process calculation by using the residence time distribution in a holding tube

In a HTST process liquid food enters into the heating section at 4°C and leaves at 72°C. The holding temperature is constant at 72°C. The food leaves the cooling section at 12°C. Residence time of the food is very small in the heating and the cooling sections, therefore sterilization calculations may be based on the holding section only. When a tracer was injected into milk at the inlet of the holding tube, the tracer concentrations, $c_t(t)$, were recorded at the exit as

***t*(s)**	**< 26**	**28**	**30**	**32**	**34**	**36**	**38**	**40**	**42**	**44**	**> 46**
$c_t(t)$ (g/l)	0	2	6	9	15	14	9	5	1	1	0

a. Calculate the ratio of the viable microorganism concentration at the exit of the holding tube to the initial microbial load when $D = 0.2$ min at $T_{ref} = 72$°C and $z = 6.7$°C. What is $F_{process}$?
b. What percentage of an enzyme with $D = 5$ min at $T_{ref} = 72$°C and $z = 33$°C will survive the process?

Solution: The residence time distribution function is: $E(t_i) = c(t_i)/A$, where A is the area under the $c_t(t)$ versus the time curve and may be calculated with the Simpson's method:

$$A = \frac{\Delta t}{3}\left(c_{t1} + 4c_{t2} + 2c_{t3} + 4c_{t4} + 2c_{t5} + 4c_{t6} + 2c_{t7} + 4c_{t8} + 2c_{t9} + 4c_{t10} + c_{t11}\right) = 122.$$

It should be noticed that $\int_0^\infty E(t)dt = 1$. Equation 4.29 may be rewritten as

$$\frac{\overline{x}}{x_0} = \int_0^\infty \exp\left(-\frac{2.303t}{D}\right)E(t)dt.$$

The integral may be calculated with the Simpson's method as

$$\frac{\overline{x}}{x_0} = \frac{\Delta t}{3}\left[\exp\left(-\frac{2.303t_1}{D}\right)E(t_1) + 4\exp\left(-\frac{2.303t_2}{D}\right)E(t_2) + 2\exp\left(-\frac{2.303t_3}{D}\right)E(t_3) + \ldots.\right.$$
$$\left. + 4\exp\left(-\frac{2.303t_{10}}{D}\right)E(t_{10}) + \exp\left(-\frac{2.303t_{11}}{D}\right)E(t_{11})\right].$$

MATLAB® code E.4.8 employs the model to compute $F_{process} = 0.57$ minutes and predicts that 76% of the initial enzyme activity will survive the process.

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MATLAB® CODE E.4.8

Command Window:

```
clear all
close all
format short g

% introduce the data
% a(:,1) = t (s)
% a(:,2)=c(t)
a(:,1) = [26 28 30 32 34 36 38 40 42 44 46];
a(:,2) = [0 2 6 9 15 14 9 5 1 1 0];
Da = 0.2*60; Db = 5*60; Tref = 72; z = 6.7;

% part a

for i=1:(length(a(:,1)));
    if (2*i)<length(a(:,1));
        S4(i) = 4*a((2*i),2);
    end
    if (2*i+1)<length(a(:,1));
        S2(i) = 2*a((2*i+1),2);
    end
end

A = (2/3)*(a(1,2) + sum(S4) + sum(S2) + a((length(a(:,1))),2));

for i = 1:length(a(:,1));
    a(i,3) = exp(-2.303*a(i,1)/Da);
    a(i,4) = a(i,2)/A;
end
 % tabulate the data:
fprintf('\nAge and fraction of the liquid pockets\n\n')
fprintf('   t(s)             Fraction\n')
fprintf('-----------       -----------\n')
for i=1:11
fprintf('%-15g %7g\n',a(i,1), a(i,4))
end

for i=1:(length(a(:,1)));
    if (2*i)<length(a(:,1));
        x4(i) = a((2*i),3)*a((2*i),4)*4;
    end
    if (2*i+1)<length(a(:,1));
        x2(i) = a((2*i),3)*a((2*i),4)*2;
    end
end

x = (2/(3))*(a(1,3)*a(1,4) + sum(x4) + sum(x2) + a((length(a(:,1))),
3)*a((length(a(:,1))),4));

Fprocess = (Da/60)*log10(1/x);
fprintf('\na)');
fprintf(' Fprocess is %.2g minutes',Fprocess);
```

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```
% part b

for i = 1:length(a(:,1));
    a(i,3) = exp(-2.303*a(i,1)/Db);
end

for i=1:(length(a(:,1)));
    if (2*i)<length(a(:,1));
        x4(i) = a((2*i),3)*a((2*i),4)*4;
    end
    if (2*i+1)<length(a(:,1));
        x2(i) = a((2*i),3)*a((2*i),4)*2;
    end
end
C = (2/(3))*(a(1,3)*a(1,4) + sum(x4) + sum(x2) + a((length(a(:,1))),
3)*a((length(a(:,1))),4));

Percent = C*100;

fprintf ('\nb)');
fprintf('It is predicted that %.2g %% of the enzyme activity will
survive the process',Percent)
```

The following lines will appear on the screen after running the code:

```
   t(s)              Fraction
-----------         -----------
26                   0
28                   0.016129
30                   0.0483871
32                   0.0725806
34                   0.120968
36                   0.112903
38                   0.0725806
40                   0.0403226
42                   0.00806452
44                   0.00806452
46                   0

a) Fprocess is 0.57 minutes
b)It is predicted that 76 % of the enzyme activity will survive the
process>>
```

The nonidealities associated with a real flow reactor may be described by superimposing axial dispersion on plug flow behavior. In such reactors sterilization in the heating and cooling sections of the sterilizer are usually neglected and process analysis are simplified by considering the constant temperature holding tube only. Plug flow in a tube is characterized with the flat velocity profile. Axial dispersion describes the additional random motion of the liquid pockets due to the molecular or turbulent diffusion. The intensity of axial dispersion may be described with the axial dispersion coefficient (D_z) or the Peclet number ($Pe = vL/D_z$), where v and L are the average velocity of the fluid and the length of the flow vessel, respectively. The limiting case with $Pe \to 0$ (or $D_z \to \infty$) describes

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the totally mixed flow, like flow in a CSTR, and Pe $\to \infty$ (or $D_z \to 0$) describes the plug flow with no mixing. In the holding tube equation of continuity describing the death of the spores is

$$\frac{\partial x}{\partial t} + \frac{\partial N_m}{\partial z} = R_d, \tag{4.30}$$

where N_m and R_d are the net flux in the flow direction and the death rate of the microorganisms, respectively. The net flux, including the axial dispersion is

$$N_m = -D_z \frac{dx}{dz} + vx. \tag{4.31}$$

Under steady state conditions after substituting $R_d = -kx$ and Equation 4.31 for N_m Equation 4.30 becomes

$$-D_z \frac{\partial^2 x}{\partial z^2} + v\frac{\partial x}{\partial z} = -kx. \tag{4.32}$$

The boundary conditions for Equation 4.32 are

$$\text{at } z = 0^+ \quad vx_0 = \left[vx - D_z \frac{dx}{dz} \right]_{z=0+} \tag{4.32a}$$

and

$$\text{at } z = L \qquad \left[\frac{dx}{dz} \right]_{z=L} = 0. \tag{4.32b}$$

We may substitute $Z(z) = e^{rz}$, $dx/dz = z' = re^{rz}$ and $d^2x/dz^2 = z''r^2e^{rz}$, therefore Equation 4.32 becomes $-Dzz'' + vz' + z = 0$ or

$$-Dzr^2 + vr + 1 = 0, \tag{4.32c}$$

with $r_{1,2} = v \pm \sqrt{v^2 + 4kDz}/2Dz$. The solution to Equation 4.13c is

$$x(z) = C_1e^{r1z} + C_2e^{r2z}, \tag{4.32d}$$

therefore $dx/dz = C_1r_1e^{r1z} + C_2r_2e^{r2z}$.

Boundary condition 4.13b requires $dx/dz = C_1r_1e^{r1z} + C_2r_2e^{r2z} = 0$ at $z = L$, therefore $C_1r_1e^{r1z} = C_2r_2e^{r2z}$ or $C_1r_1/C_2r_2 = e^{L(r1-r2)}$. Boundary condition 4.13a requires $vx_0 = (vx - Dz(C_1r_1 + C_2r_2))$ at $z = 0$, therefore we may evaluate the constants C_1 and r_2 as

$$C_1 = \frac{vx - vx_0}{Dzr_1\left(1 + 1/\left(\exp\left(2Lr_2\right) - 1\right)\right)} \quad \text{and} \quad C_2 = \frac{vx - vx_0}{Dzr_1\left(1 + 1/\left(\exp\left(2Lr_2\right) - 1\right)\right)} \frac{r_1/r_2}{\exp\left(L\left(r_1 - r_2\right)\right)}.$$

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After substituting the constants C_1 and C_2 in Equation 4.32d we will have

$$x(z) = \frac{vx - vx_0}{Dzr_1\left(1 + 1/\left(\exp(2Lr_2) - 1\right)\right)}\exp(r_1 z) + \frac{vx - vx_0}{Dzr_1\left(1 + 1/\left(\exp(2Lr_2) - 1\right)\right)}\frac{r_1/r_2}{\exp\left(L(r_1 - r_2)\right)}\exp(r_2 z). \tag{4.32e}$$

After rearranging, Equation 4.32e will become

$$\frac{x(L)}{x_0} = \frac{4y\ \exp(\mathrm{Pe}/2)}{(1+y)^2\exp\left(\mathrm{Pe}\ y/2\right) - (1-y)^2\exp\left(\mathrm{Pe}\ y/2\right)}, \tag{4.33}$$

where Pe = vL/D_z, Da = kL/v, and $y = \sqrt{1 + 4\mathrm{Da}/\mathrm{Pe}}$ (Aiba, Humphrey, and Millis 1973). We will employ MATLAB® code 4.1 to produce Figure 4.1 to relate $x(L)/x_0$ to Pe and Da.

MATLAB® CODE 4.1

Command Window:

```
clear all
close all

% introduce the Pe and Da numbers
Da = [20 30 40 50 60 70 80 90 100 110 120 130 140];
Pe = [10 20 30 40 50 70 100 200 400 1000];

% calcule x(L)/x0
for i = 1:10
    y = (1 + (4*Da/Pe(i))).^0.5; xratio(i,1:13) =
(4*y*exp(Pe(i)/2))./(((1 + y).^2).*exp((Pe(i)./2).*y)-((1-
y).^2).*exp(-Pe(i)./2.*y));
end

% prepare a semilog plot
semilogy(Da,xratio(1,:), '-x')
hold on,semilogy(Da,xratio(2,:), ': x')
hold on, semilogy (Da,xratio(3,:), '-.x')
hold on, semilogy(Da,xratio(4,:), '-o')
hold on, semilogy(Da,xratio(5,:), ':o')
hold on, semilogy(Da,xratio(6,:), '-.o')
hold on, semilogy(Da,xratio(7,:),'-d')
hold on, semilogy(Da,xratio(8,:),':d')
hold on, semilogy(Da,xratio(9,:),'-.d')
hold on, semilogy(Da,xratio(10,:),'- + ')

% insert label
xlabel('Da = kL/v')
ylabel('x(L)/xo')
```

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```
%  insert legend and define its location
legend('Pe = 10','Pe = 20','Pe = 30', 'Pe = 40', 'Pe = 50', 'Pe =
70', 'Pe = 100', 'Pe = 200', 'Pe = 400', 'Pe = 1000' ,'Location',
'SouthWest');
```

When we run the code the Figure 4.1 will appear on the screen.

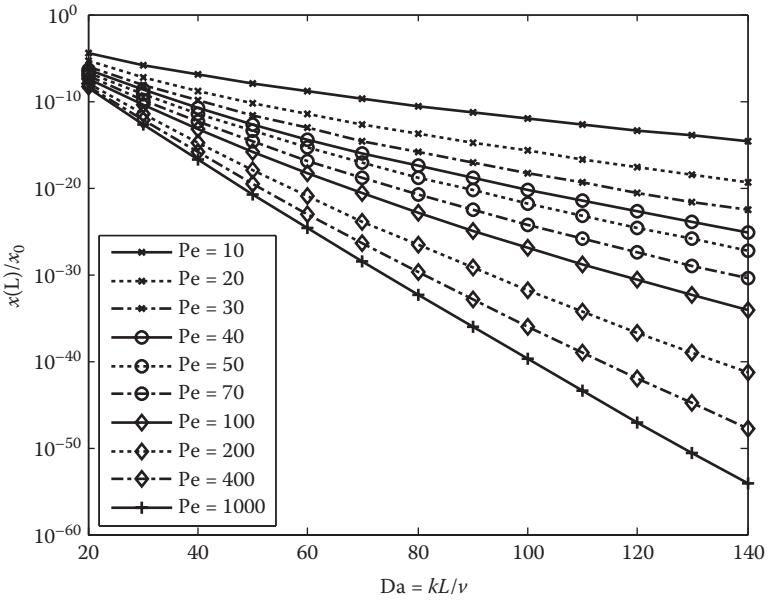


FIGURE 4.1
Effect of axial dispersion on the destruction of the microorganisms at a constant temperature in the holding tube of a continuous pasteurizer.

Example 4.9: Use of the Axially Dispersed Plug Flow Model in Continuous Thermal Process Calculations

The 150 m^3/day of liquid food with a potential microbial load of 10^4 cfu/ml will be sterilized at 72°C in a continuous sterilizer. There are 50 parallel tubes of 1 cm diameter in the holding section. MATLAB® code E.4.9 produces Figure E.4.9, which relates the fraction of the surviving microorganisms $x(L)/x_0$ to Pe at $D = 17$.

Example 4.10: Continuous Processing of Liquid Foods Containing Particles

In the holding tube of the aseptic processing equipment, when the heat transfer from liquid to the particles may be neglected, the temperature of the liquid (T_L) approaches the ambient temperature (T_a) exponentially:

$$\frac{T_L - T_a}{T_{L0} - T_a} = \exp\left\{-\frac{U_{\text{tube}} A_{\text{tube}}}{\rho_L c_L V_{\text{tube}}}\right\}, \tag{E.4.10.1}$$

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MATLAB® CODE E.4.9

Command Window:

```
clear all
close all

r=0.01; %m
A=pi*r.^2;%m2
D=0.02; %min
v=3/(A*24*60); % flow rate m/min for 50 tubes
k=2.303/D; %min-1
L=1; %Assume that lenght is 1m
Da=k/v;
Pe=[10 20 40 100 150 200 400 600 700 800 900 1000];

for i=1:12
    y=(1+(4*Da./Pe(i))).^0.5;
    xratio(i,1)=(4*y*exp(Pe(i)/2))./(((1+y).^2).*exp((Pe(i)./2).*y)-
((1-y).^2).*exp(-Pe(i)./2.*y));
end

% plot the results
semilogy(Pe,xratio,'-*')

% insert label
xlabel('Pe')
ylabel('x(L)/xo')
```

When we run the code the Figure E.4.9 will appear on the screen.

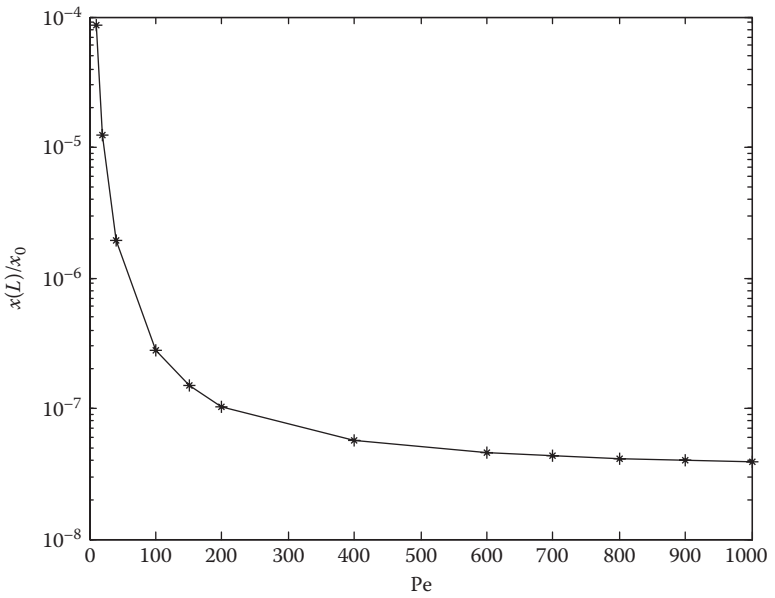


FIGURE E.4.9
Variation of the $x(L)/x_0$ ratio with Pe number at Da = 17.

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where T_{L0} is the initial temperature of the liquid at the entrance of the tube; A_{tube}, U_{tube}, and V_{tube} are the heat transfer area, total heat transfer coefficient and the volume of the tube, respectively. Parameter ρ_L is the density and c_L is the specific heat of the liquid. Governing the equation of heat transfer into the particle with conduction is obtained after simplification of Equations 2.16 through 2.18 (Yang, Nunes, and Swartzel 1992)

$$\rho_p C_p \frac{\partial T}{\partial t} = k_p \frac{\partial^2 T}{\partial r^2} + k_p \frac{\beta - 1}{\rho} \frac{\partial T}{\partial r}, \tag{E.4.10.2}$$

where β is a geometric factor ($\beta = 1$ for infinite slab, $\beta = 2$ for infinite cylinder, $\beta = 3$ for sphere), r is the distance in the heat transfer direction; k_p, ρ_p, and c_p are thermal conductivity, density, and specific heat of the particles, respectively. The initial and the boundary conditions for Equation E.4.10.2 are

$$T = T_{p0} \text{ at } 0 < r < r_p \text{ when } t = 0, \tag{E.4.10.2a}$$

$$\frac{dT}{dr} = 0 \text{ at } r = 0 \text{ when } t > 0, \tag{E.4.10.2b}$$

$$-k_p \frac{dT}{dr} = h_{Lp}\left[T_L(t) - T\right] \text{ at } r = r_p \text{ when } t \geq 0, \tag{E.4.10.2c}$$

where r_p is the radius of the particle, h_{Lp} is the convective heat transfer coefficient from liquid to particle. With a spherical particle ($\beta = 3$) after applying the L'Hopital rule at $r = 0$ on the second term Equation E.4.10.2 gives

$$\rho_p C_p \frac{\partial T}{\partial t} = 3k_p \frac{\partial^2 T}{\partial r^2} \text{ at } r = 0 \text{ when } t > 0. \tag{E.4.10.3}$$

Equation E.4.10.3 is the only equation to be solved to evaluate the time temperature history at the critical point of the particle. F values may be calculated at the particle center after using the time-temperature data with

$$F_i = \int_0^t 10^{(T - T_{ref})/z} dt. \tag{E.4.10.4}$$

The average $F_{process}$ of the food is

$$F_{process} = \int_0^\infty F_i(t) E(t) dt. \tag{E.4.10.5}$$

MATLAB® code E.4.10 computes the time–temperature profile of the fluid and the particles (at the surface and the center) and the F values of particle (on the surface and center). The results are presented in Figure E.4.10.

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MATLAB® CODE E.4.10

Command Window:

```
clear all
close all
format compact

% define E(t) as a gaussian distribution function
deltaE=0.5; % notice that sum(E)=1.0
mu=200; % population mean residence time in the holding tube
sigma=10; % variance of the holding times in the holding tube

% compute the minimum and the maximum residence times
RTmin=mu-3*sigma; % the minimum residence time
RTmax=mu+3*sigma; % the maximum residence time
RTincrement=(RTmax-RTmin)/61
RT=[RTmin:RTincrement:RTmax]

% compute the expected fraction of the  residence times
for j=1:1:length(RT)
E(j)=(1/(sigma*sqrt(2*pi)))*exp(-(1/2).*((RT(j)-mu)/sigma)^2);
end
 % check the sum of the fractions of the redidence times (notice
sum(E) must be 1)
Esum=sum(E)

n = 22; % n=1 and n=22 refers to fluid,  n=2 and n=21 refers to
surface,  n=12 refers to center

dr = 0.001; % m
dt = 1; % s

% the following constants are adapted from Yang et al (1992)
kp = 0.556; % W/m2 C
Cpp = 3.27e3; % specific heat of the particles (J/kg C)
Pp = 1040; % particle density (kg/m3)
Ta = 27; % C (air temperature)
Tfi = 135; % initial temperature of the fluid in the holding tube
(C)
Uhd = 10; % Heat transfer coefficient (W/m2 C)
D = 0.0508; % diameter of the holding tube (m)
Pf = 930.8; % fluid density (kg/m3)
Cpf = 4.266e3; % specific heat of the fluid (J/kg C)
Tref = 121.1; % reference temperature (C)
z = 10;

% finite difference solution
T(:,1) = ones(1,(n+1)) * 100;
T(1,1) = Tfi; T((n+1),1) = T(1,1);
time(1) = 0;

for t = 1:mu
    T(1,(t+1)) = Ta - (Ta - Tfi) * exp(- Uhd * 4 * t / (Pf * Cpf *
D));
```

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```
    T((n+1),(t+1)) = T(1,(t+1));
    for i = 2:n
        T(i,(t+1)) = ((3 * kp / (Pp * Cpp)) * dt / (dr^2)) *
(T((i+1),t) - 2*(T(i,t)) + T((i-1),t)) + T(i,t);
        F(i,(t+1)) = 10^((T(i,(t+1)) - Tref) / z) * (t / 60); %
minutes
    end
    % redefine time in seconds for plotting
    time(t+1) = t;
end

% plot the model
 plot(time, T(1,:), '-.'); hold on % T fluid
[AX,H1,H2] = plotyy(time, T(2,:), time, F(2,:)); hold on % T
particle surface and F surface
[AX,H3,H4] = plotyy(time, T(12,:), time, F(12,:)); hold on % T
particle center and F particle center
set(H1,'LineStyle','- -')
set(H2,'LineStyle','-')
set(H3,'LineStyle',':')
set(H4,'LineStyle','-.')
xlabel('Time (s)')
ylabel('Temperature \circ C')
set(get(AX(2),'ylabel'), 'string', 'F (min)')
ylim(AX(2), [0 40])
ylim(AX(1), [80 140])
legend('T fluid','T particle surface','T particle
center','Location','West')
legend(H2,'F particle surface','F particle
center','Location','East')
legend(H4,'F particle center','Location','SouthEast')

% compute the minimum and the maximum processing received by the
paricle on the surface and at the center

for t = 1:RTmin
    T(1,(t+1)) = Ta - (Ta - Tfi) * exp(- Uhd * 4 * t / (Pf * Cpf *
D));
    T((n+1),(t+1)) = T(1,(t+1));
    for i = 2:n
        T(i,(t+1)) = ((3 * kp / (Pp * Cpp)) * dt / (dr^2)) *
(T((i+1),t) - 2*(T(i,t)) + T((i-1),t)) + T(i,t);
        F(i,(t+1)) = 10^((T(i,(t+1)) - Tref) / z) * (t / 60); %
minutes
    end
end

fprintf('\nminimum processing received by the particle surface is
%.2g min',F(2,RTmin))
fprintf('\nminimum processing received by the particle center is
%.2g min \n',F(12,RTmin))

for t = 1:RTmax
    T(1,(t+1)) = Ta - (Ta - Tfi) * exp(- Uhd * 4 * t / (Pf * Cpf *
D));
    T((n+1),(t+1)) = T(1,(t+1));
```

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```
    for i = 2:n
        T(i,(t+1)) = ((3 * kp / (Pp * Cpp)) * dt / (dr^2)) *
(T((i+1),t) - 2*(T(i,t)) + T((i-1),t)) + T(i,t);
        F(i,(t+1)) = 10^((T(i,(t+1)) - Tref) / z) * (t / 60); %
minutes
    end
end

fprintf('\nmaximum processing received by the particle surface is
%.2g min',F(2,RTmax))
fprintf('\nmaximum processing received by the particle center is
%.2g min \n',F(12,RTmax))

% compute the average processing received by the paricle on the
surface and at the center
for j=1:1:length(RT)
E(j)=(1/(sigma*sqrt(2*pi)))*exp(-(1/2).*((RT(j)-mu)/sigma)^2);

for t = 1:RT(j)
    T(1,(t+1)) = Ta - (Ta - Tfi) * exp(- Uhd * 4 * t / (Pf * Cpf *
D));
    T((n+1),(t+1)) = T(1,(t+1));
    for i = 2:n
        T(i,(t+1)) = ((3 * kp / (Pp * Cpp)) * dt / (dr^2)) *
(T((i+1),t) - 2*(T(i,t)) + T((i-1),t)) + T(i,t);
        F(i,(t+1)) = 10^((T(i,(t+1)) - Tref) / z) * (t / 60); %
minutes
    end
end
FincrementSurface(j)=F(2,(t+1));
FincrementCenter(j)=F(12,(t+1));

end

FsurfaceAverage=sum(FincrementSurface.*E);
FcenterAverage=sum(FincrementCenter.*E);

fprintf('\naverage processing received by the particle surface is
%.2g min',FsurfaceAverage)
fprintf('\naverage processing received by the particle center is
%.2g min \n',FcenterAverage)
```

When we run the code the following lines and Figure E.4.10 will appear on the screen:

```
Esum =
    1.0143

minimum processing received by the particle surface is 25 min
minimum processing received by the particle center is 7.5 min

maximum processing received by the particle surface is 29 min
maximum processing received by the particle center is 19 min

average processing received by the particle surface is 28 min
average processing received by the particle center is 13 min
```

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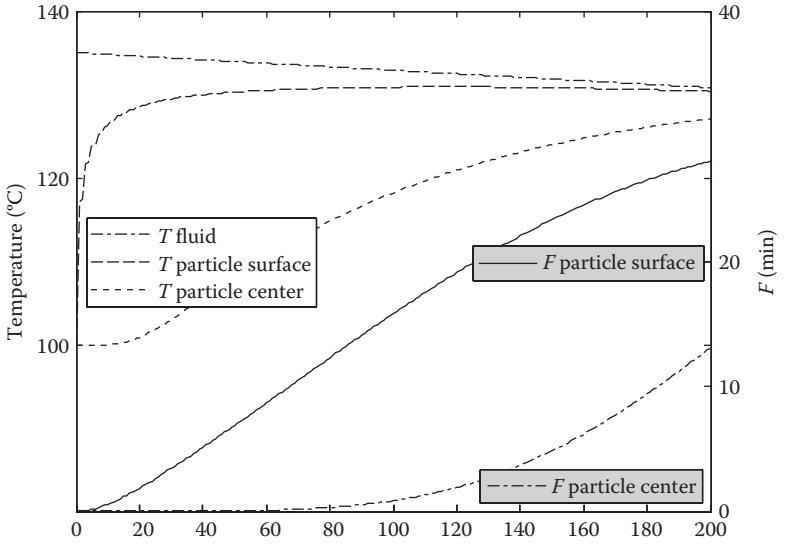


FIGURE E.4.10
Variation of the temperature and processing received at different locations with time, when there is no residence time distribution (residence time = population mean residence time).

4.2 Moving Boundary and Other Transport Phenomena Models for Processes Involving Phase Change

In a freezing process, liquid water is converted into a solid, or ice. In a thawing process solid water, or ice, is converted into liquid. In both drying and frying processes liquid water entrapped in the food is converted into vapor, then transported into the other phases (e.g., air or oil). In all of these processes an interface is established first, than it usually moves from the surface toward the depths. Mathematical models involving such a moving interface are usually referred to as the moving boundary problems.

In moving boundary problems thermal energy balance may be written as (Smith and Farid 2004)

$$\frac{\partial T}{\partial t} = \frac{\alpha}{z^n}\frac{\partial}{\partial z}\left[z^n \frac{\partial T}{\partial z}\right], \tag{4.34}$$

where for rectangular coordinates $n = 0$, for cylindrical coordinates $n = 1$ and $y = r$, and for spherical coordinates $n = 2$ and $y = r$. The movement of the interface is governed by the following boundary conditions (Smith and Farid 2004)

$$\rho\omega_0 \Delta H_{\text{phase change}} \frac{dz_{\text{interface}}}{dt} = k_{\text{crust}}\left(\frac{\partial T_{\text{crust}}}{\partial z}\right)_{z_{\text{crust}}} - k_{\text{core}}\left(\frac{\partial T_{\text{core}}}{\partial z}\right)_{z_{\text{crust}}}, \tag{4.35}$$

where ρ and ω_0 are the initial density and moisture content of the food, respectively; k_{crust} is the thermal conductivity of the crust, k_{core} is the thermal conductivity of the core, and z_{crust}

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is the position of the interface from the surface. Parts of the food, where water remains in its initial phase is referred to as the core and the places where it is in a different phase is referred to as the crust. The interface temperature of the core and the crust may be assumed to be equal. Thermal energy balance on the external surface of the food requires

$$-k_{\text{crust}}\frac{dT}{dz} = h\left(T_{\text{surface}} - T_{\text{fluid}}\right). \tag{4.36}$$

Where T_{surface} is temperature of the food on its external surface, T_{fluid} is the temperature of the external medium (e.g., temperature of the coolant in a freezing process, or temperature of the oil in a frying process, etc.), and h is the convective heat transfer coefficient. Equations 4.34 through 4.36 lead to the following expression for an infinite slab or infinite cylinder:

$$z_{\text{crust}}^2 + \frac{2k}{h}z_{\text{crust}} - 2\beta k_{\text{crust}}t = 0, \tag{4.37}$$

or to the following equation for a sphere:

$$t = \frac{1}{2k\beta}\left(r_{\text{sphere}}^2 - r_{\text{interface}}^2\right) + \frac{1}{3\beta}\left(\frac{1}{r_{\text{sphere}}^2 h} - \frac{1}{r_{\text{sphere}}k_{\text{crust}}}\right)\left(r_{\text{sphere}}^3 - r_{\text{interface}}^3\right), \tag{4.38}$$

where $r_{\text{interface}}$ is the distance of the interface from the center of the sphere, r_{sphere} is the radius of the sphere, and $\beta = (T_{\text{fluid}} - T_{\text{phase change}})/\rho\Delta H_{\text{phase chance}}\omega_0$. The drying, frying, or freezing process is usually considered finished when the interface disappears (reaches to the thermal center), implying that $z_{\text{crust}} = L$ or $r_{\text{interface}} = 0$.

Equation 4.37 may be solved to estimate the location of the crust as

$$z_{\text{crust}} = -\frac{k_{\text{crust}}}{h} \pm \sqrt{\left(\frac{k_{\text{crust}}}{h}\right)^2 + 2\beta k_{\text{crust}}t}, \tag{4.39}$$

where $\beta = (T_{\text{fluid}} - T_{\text{phase change}})/\rho\Delta H_{\text{phase chance}}\omega_0$. Equation 4.39 may be rearranged and used to estimate the average moisture content of the food during the crust formation as

$$w = \frac{1 - (z_{\text{crust}}/L)\varepsilon_0}{1 - \varepsilon_0}. \tag{4.40}$$

Example 4.11: A Model for the Prediction of the Crust Thickness, Remaining Moisture Fraction, and Temperature Variations in a Potato Slab During the Frying Process

The Smith and Farid (2004) model relates the moving interface to moisture movement. The model assumes the food to consist of three regions: the dried crust, the partially dried region, and the completely wet region. The dried crust contains only bound moisture, the partially dried region is the diffusion region, and the completely wet region is assumed to be at the initial moisture content of the food. The extent of the diffusive region depends on the ratio of the rates of moisture and heat transport.

The model assumes that the diffusive region, where evaporation occurs, expands during the drying or frying processes. The diffusion region has the maximum moisture content at the interface with the core and the minimum moisture content (bound moisture) at the interface with the

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dry crust. Water may diffuse through the partially dried crust by a capillary or diffusion driven mechanism. MATLAB® codes E.4.11.a and E.4.11.b compute the crust thickness (Figure E.4.11.1) and the average moisture content (Figure E.4.11.2) of a food by using Equations 4.39 and 4.40 in an immersion frying process.

Equation E.4.11.1 may be rewritten as

$$\rho c_p \frac{\partial T}{\partial t} = \frac{\partial}{\partial r}\left(k \frac{\partial T}{\partial r}\right). \tag{E.4.11.1}$$

During frying, the energy balance around the food may be stated with the IC (initial condition) and BC as

$$\text{BC1a } k\left[\frac{dT}{dr}\right]_{r=R} = h\left(T_{\text{oil}} - T_s\right) \quad \text{convective BC,} \tag{E.4.11.2}$$

MATLAB® CODE E.4.11.a

Command Window:

```
clear all
close all
format compact

% enter the data
hData=[0 0.5 0.9 1 1.9 2.9 3.7]; % crust thickness (mm)
tData=[0 50 120 210 430 970 1460]; % time when crust size was
determined (s)

% plot the data
plot (tData,hData,'*'); hold on;
xlabel ('t (s), Time');
ylabel ('Crust Thickness (mm)')

% constants (adapted from Southern et al, 2000)
Tfluid=180; % oC (oil temperature)
Tphase_change=100; % oC (evaporation temperature)
rho=1132; % kg/m3 (density of the core)
deltaH=2256900; % latent heat of evaporation (J/kg)
w=0.83; % fraction of the initial free moisture of the food

beta=(Tfluid-Tphase_change)/(rho*deltaH*w);

kcrust=0.14; % thermal conductivity of the phase change material
(J/s m K)
h=500; % surface heat transfer coefficient (J/s m2 K)

zCrust=-(kcrust/h)+sqrt(((kcrust/h)^2)+2*beta*kcrust.*tData);
plot (tData,zCrust*1000,'-'); hold on;
legend('data','model','Location','SouthEast')
```

When we run the code Figure E.4.11.2 will appear on the screen.

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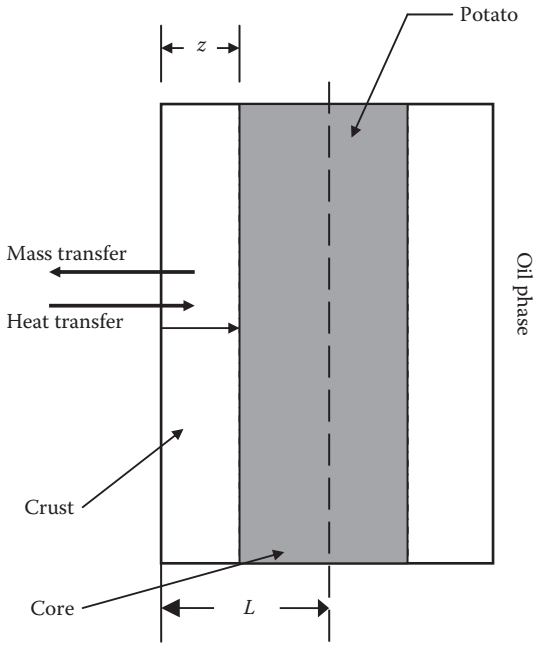


FIGURE E.4.11.1
Schematic description of the core and crust sections in a frying operation.

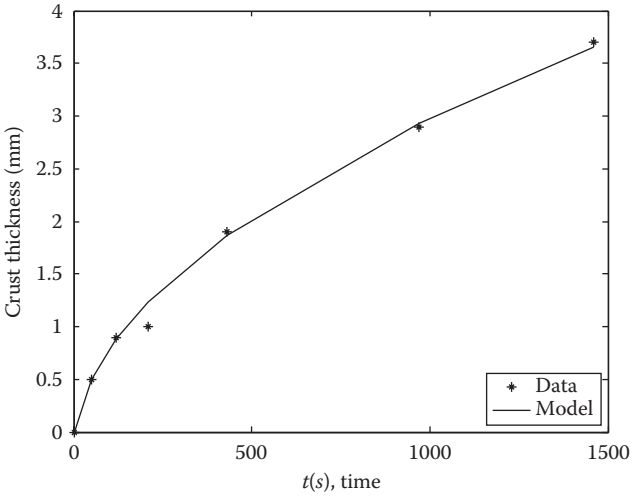


FIGURE E.4.11.2
Variation of the crust thickness of an infinite potato slab with time during immersion frying (slab thickness = 25.4 mm, oil temperature 180°C). (Data and model constants adapted from Farid, M., and Kizilel, R., *Chemical Engineering and Processing*, 48, 217–23, 2009; Southern, C. R., Chen, X. D., Farid, M., Howard, B., and Eyres, L., *Transactions of IChemE* 78, Part C, 119–25, 2000, respectively.)

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MATLAB® CODE E.4.11.b

Command Window:

```
clear all
close all
format compact

% enter the data
tData=[75 125 250 500 1000]; % times when the data is recorded (s)

mData=[2.3 2.2 2.0 1.8 1.5]; % moisture contents (kg water/kg dry
solids)
plot(tData, mData, 'd'); hold on

% modeling
t=[0:5:1000];
Toil=180; % in celcius, ambiant temperature
Tcrust=100; % critical temperature
epsylon0=0.6; % initial free moisture content (kg water/kg total)
rho=1132; % density of the core (kg/m^3)
deltaH=2256900; % latent heat of evaporation
kCrust=0.95; % thermal conductivity of crust (J/s m K)
h=500; % hboiling (J/s m K)
L=0.0127; % half thickness of the potato chips (m)

% by assuming the material is pure
beta=(Toil-Tcrust)/(rho*deltaH*epsylon0);
for i=1:length(t)
zCrust(i)=(-kCrust/h)+sqrt(((kCrust/h)^2)+2*beta*kCrust*t(i));
w(i)=(1-(zCrust(i)/L)*epsylon0)/(1-epsylon0);
end
plot(t,w); hold on,
xlabel('time (s)')
ylabel('moisture content (kg water/kg dry solids)')
ylim([0 5]);
xlim([0 1000]);
legend('data','model','Location','SouthEast')
```

When we run the code Figure E.4.11.3 will appear on the screen.

$$\text{BC2} \quad \left[\frac{dT}{dr}\right]_{r=0} = 0 \quad \text{at } r = 0 \ \text{ when } t \geq 0, \tag{E.4.11.3}$$

$$\text{IC } T = T_0. \tag{E.4.11.4}$$

In a moving boundary problem it is necessary to take into account the continuous change in the nodal positions due to the movement of the interface. Total derivative dT/dt may be expressed as

$$\frac{dT}{dt} = \frac{\partial T}{\partial z_{\text{crust}}}\frac{\partial z_{\text{crust}}}{\partial t} + \frac{\partial T}{\partial t}. \tag{E.4.11.5}$$

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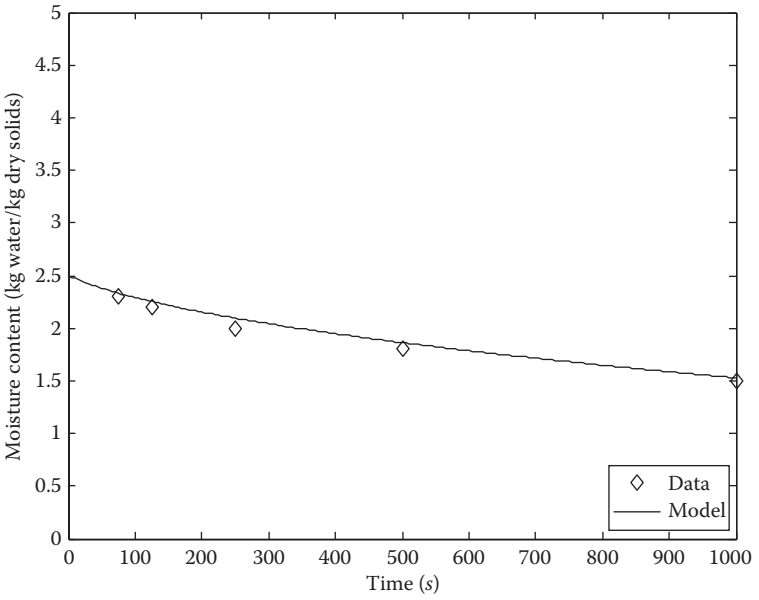


FIGURE E.4.11.3
Comparison of Equation 4.40 with the data obtained during immersion frying of an infinite potato slab with 25.4 mm thickness; oil temperature was 180°C. (Adapted from Farkas, B. E., Singh, R. P., and Rumsey, T. R., *Journal of Food Engineering*, 29, 227–48, 1996.) Parameters ε and k_{crust} were estimated from the data. (Other parameters from Farid, M., *Chemical Engineering and Processing*, 41, 5419–27, 2001.)

Equation E.4.11.1 may be combined with Equation E.4.11.5 as

$$\frac{dT}{dt} = \frac{\partial T}{\partial z_{crust}} \frac{\partial z_{crust}}{\partial t} + \frac{\partial}{\partial r}\left(\alpha \frac{\partial T}{\partial r}\right). \tag{E.4.11.6}$$

Equation E.4.11.6 may be expressed as

$$\frac{\partial T}{\partial t} = \alpha \frac{\partial^2 T}{\partial z^2} - \frac{\rho_{vapor} c_{vapor}}{\rho_{crust} c_{crust}} \frac{\partial z_{crust}}{\partial T} \frac{\partial T}{\partial z}. \tag{E.4.11.7}$$

The order of magnitude analysis shows that the second term from the left is negligible (Farid 2002). Therefore Equation E.4.11.1 is a reasonably good approximation of the problem. Farid (2001) employed $h = 500$ W/m²s during frying of the potato slab in a process with $L = 1.27$ cm, $T_0 = 20$°C, $T_{oil} = 180$°C. The initial phase change point of water, $T_c = 100$°C. The other physical properties are (Farid 2001)

	Crust	Core
c_p(J/kg K)	2.375	3.450
k (W/mK)	0.14	0.554
ρ (kg/m³)	1330	1132

MATLAB® code E.4.11.c produces the temperature profiles along the slab 5 minutes after the beginning of the process.

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MATLAB® CODE E.4.11.c

Command Window:

```
clear all
close all

m=0; % for slab
z = linspace(0,0.0127,20);
t = linspace(0,200,50);

sol = pdepe(m,@pdex2pde,@pdex2ic,@pdex2bc,z,t);
% Extract the first solution component as Temperature T.
T = sol(:,:,1);

% prepare the surface plot.
surf(z,t,T)
title('Temperature distribution during frying')
xlabel('z, distance from the center plane (m)')
ylabel('Time (min)')
zlabel('Temperature (K)')
```

M-file1:

```
function [c,f,s] = pdex2pde(r,t,T,DTDr)
if ( T >= 373) % (K)
   cp = 3450;
   rho = 1132;
   k = 0.554;
else
   cp = 2375;
   rho = 1330;
   k = 0.14;
end;

c = rho*cp;
f = k*DTDr;
s = 0;
```

M-file2:

```
function T0 = pdex2ic(r)
T0 = 395; % (K)
```

M-file3:

```
function [pl,ql,pr,qr] = pdex2bc(rl,Tl,rr,Tr,t)
h=500;
Text=453; % (K)
pl = 0;
ql = 1;
pr = h*(Text-Tr);
qr = -1;
```

When we run the code Figure E.4.11.4 will appear on the screen.

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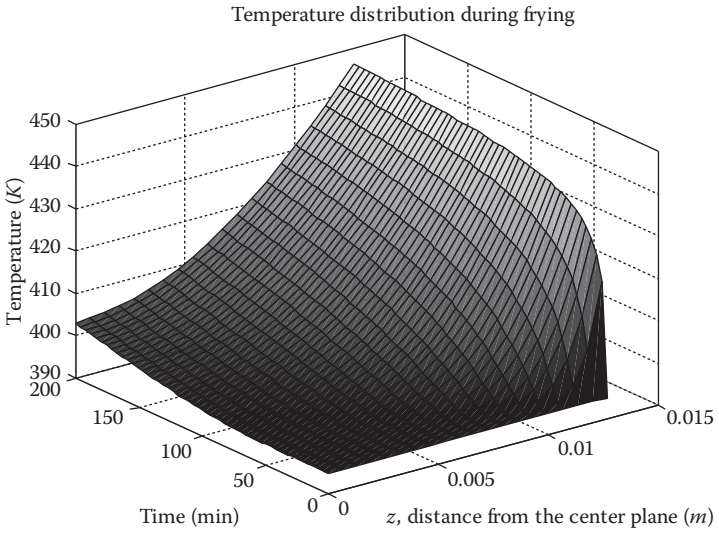


FIGURE E.4.11.4
Temperature profile along the slab during frying.

In a drying process almost all water present in the food is removed through vaporization. It is usually the final step before packaging to improve the microbial and chemical stability of the food. In a drying process, the phase change of water may be achieved with heat supplied by the heated air (convective drying), direct contact with a hot surface (conduction heating), radiation, or microwaves. Water molecules in the food might be bound to the ionic groups or make hydrogen bonds with the food solids. Unbound free water molecules make hydrogen bonds with each other. In a drying process, the energy requirement for evaporation of unbound free water is less than that required for evaporation of hydrogen bound water. Water molecules that are bound to the ionic groups require the largest energy and it may be so large that destructive reactions may occur in the food before they are removed. Drying data is usually expressed as the amounts of water carried per unit dry mass of a process stream:

$$x = \frac{\text{mass of water}}{\text{mass of dry solids}} \quad \text{or} \quad \mathcal{H} = humidity = \frac{mass \text{ of water}}{\text{mass of dry air}}.$$

The drying rate may be defined as

$$R_d = -\frac{1}{A}\frac{dx_f}{dt}, \tag{4.41}$$

where R_d = drying rate per unit weight of the dry solids, A = surface area of the food per unit dry weight of the solids, and t = time. Free moisture content per unit weight of the dry solids may be calculated as $x_f = x - x^*$, where $x = (W - W_s)/W_s$ = total moisture content of the food per unit dry weight of the solids, W = total weight of the food, W_s = weight of the dry solids in the food, x^* = equilibrium moisture content of the food per unit weight of the dry solids. It should be noticed that Equation 4.41 was originally defined

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in nonfood applications and may not be used in food processing. Most food materials contain more than 70% water and may experience drastic shape changes upon drying and that make it almost impossible to evaluate A as a function of time easily; then bulk parameter drying rate expressions may be used after combining R and A in the same bulk parameter.

In a drying process, first the solids are charged into the dryer and heated up if the temperature of the dryer is higher than that of the wet solids. If the surface is covered with a continuous film of water it attains the wet-bulb temperature at the end of the heating period. The evaporation rate from the surface at the wet-bulb temperature is constant. When the surface remains fully covered with the water film and evaporation is the rate determining step, the process is referred to being in the constant rate drying period. Water movement during the constant rate period is assumed to be controlled by several factors, including capillary suction and diffusion. The capillaries extend from small reservoirs of water in the solid to the drying surface. As drying proceeds, moisture moves by capillary to the surface rapidly enough to maintain a uniform wetted surface. Surface tension of the liquid is a controlling factor on the rate of water flow due to capillary suction (Labuza and Simon 1970). When the food attains the critical moisture content, dry spots start appearing on the surface indicating the beginning of the first falling rate period. In this stage of the drying process the water supply rate to the surface is not sufficient, therefore the dry spots enlarge and the water film decreases continuously. When the water film on the surface disappears the second falling rate period starts, where evaporation occurs below the food surface and the diffusion of vapor occurs from the place of vaporization to the surface (Treybal 1980). The drying process stops when equilibrium is established between the food and the ambient air. A variation of the drying rate during the drying process of nixtamal (lime solution treated, cooked, and dried raw maize) is depicted in Example 4.12.

With the depletion of the subsurface water reservoirs, the mechanical structure collapses and the food undergoes shrinkage. In foods where shrinkage occurs, the shortening of the path length for water migration may offset the reduction in matrix porosity (Labuza and Simon 1970). If the food should be subject to too high temperatures at the beginning of the second falling rate period, the entrance of the partially empty capillaries may shrink rapidly and prevent removal of the remaining water at the deeper locations. This is called *case hardening*. This entrapped moisture may diffuse to the surface during storage and may cause microbial spoilage. Case hardening may be prevented by using moderately moist or warm air for drying.

The mechanism in slow drying nonporous materials (such as soap, gelatin, glue) and in the later stages of drying (clay, wood, textiles, leather, paper, foods and starches) is liquid diffusion (Geankoplis and Toliver 2003). Diffusion of liquid water may result because of the concentration of gradients between the depths of the solid, where the concentration is high, and the surface where it is low. These gradients are set up during drying from the surface (Treybal 1980).

Heat and mass transfer in an immersion-fat frying process has been reviewed by Singh (1995), where conductive heat transfer occurs in the food and convective heat transfer occurs on the interface between the solid food and the surrounding oil. The water vapor bubbles escaping from the surface of the food cause considerable turbulence in the oil, on the other side their accumulation on the underside of the food may prevent effective heat transfer. Moisture transfer from the food to the surroundings is the principle physical phenomena in both drying and frying processes; where the surrounding media are air

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and oil in drying and frying processes, respectively, therefore these processes have a lot of common characteristics and are discussed in a similar manner.

In the analogy of drying, a frying process is composed of four distinct stages (Singh 1995)

i. **Initial heating period** lasts until the surface of the food is elevated to the boiling temperature of the oil. This stage lasts a few seconds and the mode of heat transfer between the oil and the food is natural convection. No vaporization of water occurs from the surface of the food.
ii. **Surface boiling period** is signaled by evaporation on the surface of the food. The crust begins to form at the surface and the dominant mode of heat transfer on the surface is forced convection due to the considerable turbulence on the surface.
iii. **Falling rate period** in frying is similar to the falling rate period observed in drying processes. The internal core temperature rises to the boiling point, then gelatinization and cooking takes place. The crust layer continues to increase in thickness.
iv. **Bubble end point** is observed after a long time of frying, when moisture removal diminishes and no more bubbles are seen leaving the surface.

In both drying and frying processes the crust is formed at the outer layer of the food after losing all of its unbound water.

Example 4.12: Drying Rates of Nixtamal

Nixtamalization typically refers to a process for the preparation of maize (corn) in which the grain is soaked and cooked in limewater, then hulled. Dried nixtamal grains are among the popular ingredients of Mexican foods. Experimental data of the fractions of water remaining in nixtamal during drying at 60°C were adapted from the literature. MATLAB® code E.4.12 converts the data into free moisture contents by using Equation 4.41. The drying rates were computed by using Equation 4.40. A numerical differentiation MATLAB® function was tried first, but there were unacceptably high levels of fluctuation in the results. A polynomial function was fit into the data as the second choice; and the polynomial was differentiated algebraically in MATLAB® code E.4.12. Figure E.4.12.1 describes variation of the fraction of the free moisture content with time. Figures E.4.12.2 and E.4.12.3 describe the variation of the drying rates with the free moisture content and time, respectively.

MATLAB® CODE E.4.12

Command Window:

```
clear all
close all
format compact

% enter the data
xData=[0.92 0.87 0.83 0.75 0.70 0.63 0.58 0.55 0.50 0.47 0.45 0.42
0.38 0.37 0.33 0.31 0.30 0.29 0.28 0.27 0.25 0.23 0.23 0.22 0.21
0.21 0.20 0.19 0.18 0.18 0.17 0.17 0.16 0.15 0.15 0.14 0.14 0.14
0.13 0.13 0.12 0.13 0.12]; % T=60 oC
```

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```
tData=[0:5:210]; % time (min)

% enter the data
xBound=0.10; % fraction of the bound moisture
xDataFreeMoisture=xData-xBound; % determine the fractions of the
free moisture
A=0.01; %  (estimated from the data, m2)

% plot the data
plot (tData,xDataFreeMoisture,'*'); hold on;
xlabel ('t (s), Time');
ylabel ('x (g water/g dry solids)')

%  fit a polynomial empirical model to the data
N=4; % determine N by trial and error to obtain good agreement
between model & data
c = polyfit(tData,xDataFreeMoisture,N)

tModel=1:1:210;
xModel=polyval(c,tModel);
plot (tModel,xModel,'-'); hold on;
legend('data','model','Location','SouthWest')

%  compute the drying rates
for i=1:1:length(tModel)
R(i)=(c(1)*(tModel(i).^((c(1)-1)))+ c(2)*(tModel(i).^((c(2)-1)))+
c(3)*(tModel(i).^((c(3)-1))))/A;
end;

figure
plot (xModel,R,'-'); hold on;
xlabel ('x (g water/g dry solids)')
ylabel ('R (g water/g dry solids m2 s)')
text(0.2,0.001, 'second falling rate period'), % insert text to the
figure (0.2 is the distance from the bottom)
text(0.02,0.0005, 'x_e'), % insert text to the figure (0.2 is the
distance from the bottom)
text(0.6,0.007, 'first falling rate period'), % insert text to the
figure (0.007 is the distance from the x axis)
text(0.75,0.0015, 'x_c')

figure
plot (tModel,R,'-'); hold on;
xlabel ('t (s)')
ylabel ('R (g water/g dry solids m2 s)')
text(7,0.008, 'first falling rate period'), % insert text to the
figure (0.007 is the distance from the x axis)
text(75,0.001, 'second falling rate period'), % insert text to the
figure (0.2 is the distance from the bottom)
text(200,0.0005, 'x_e'), % insert text to the figure (0.2 is the
distance from the bottom)
text(15,0.0009, 'x_c')
```

When we run the code Figures E.4.12.1–E.4.12.3 will appear on the screen.

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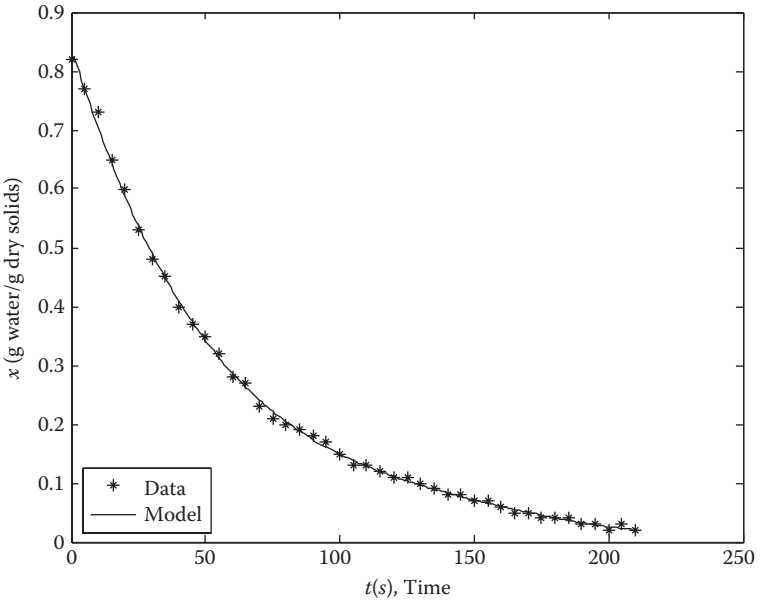


FIGURE E.4.12.1
Variation of the fraction of the free moisture in nixtamal during drying. (Adapted from Gasson-Lara, J. H., *Food Dehydration*, Vol. 89, 85–89, IAChE Symposium Series, 1993.)

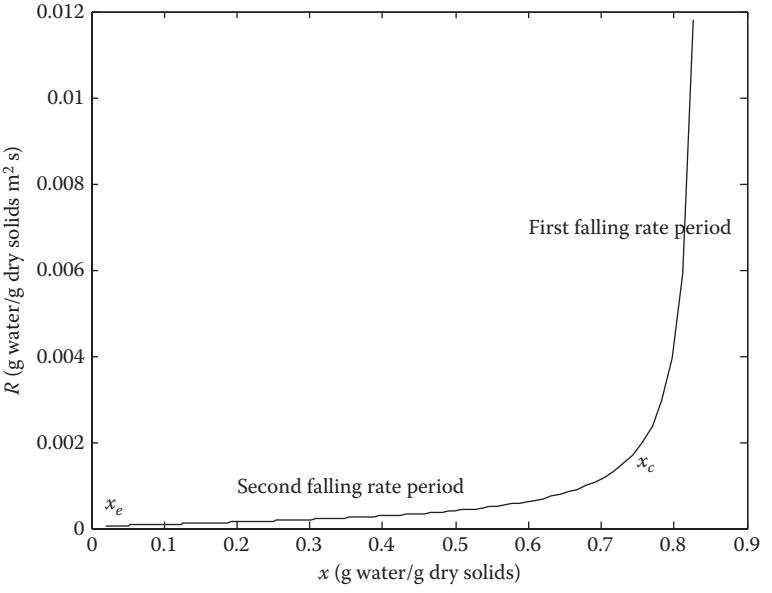


FIGURE E.4.12.2
Variation of the drying rates of nixtamal with the free moisture content during drying. There is no constant rate drying period in this plot. The location marked as x_c is the roughly defined value of x, where transition occurs from the first falling rate period to the second falling rate period. Parameter x_e denotes the end of the drying process, where a fraction of the free moisture of the nixtamal attains equilibrium with the moisture of air. It is not possible to continue removing water from the nixtamal after reaching x_e. (Adapted from Gasson-Lara, J. H., *Food Dehydration*, Vol. 89, 85–89, IAChE Symposium Series, 1993.)

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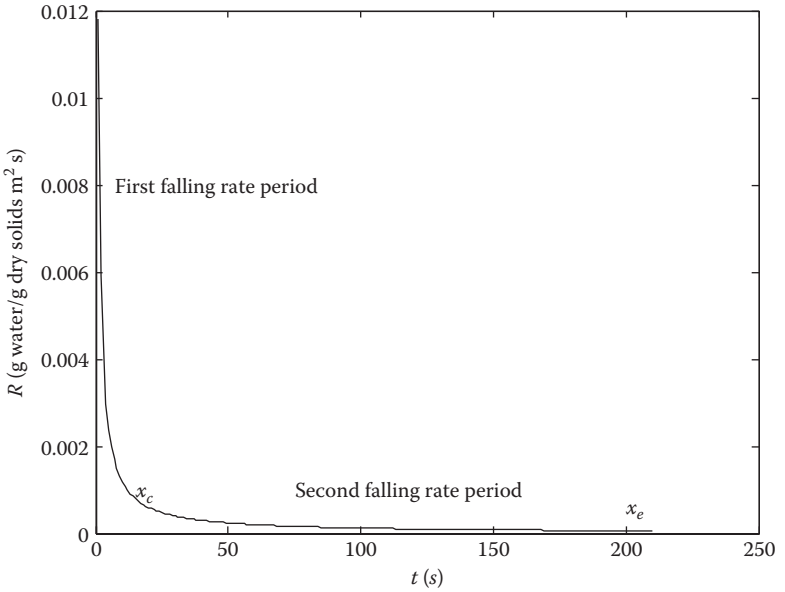


FIGURE E.4.12.3
Variation of the drying rates of nixtamal with time during drying. (Adapted from Gasson-Lara, J. H., *Food Dehydration*, Vol. 89, 85–89, IAChE Symposium Series, 1993.)

Example 4.13: Drying Behavior of Thin Biscuits During Baking Process

Biscuits with $7 \times 5 \times 0.25$ cm dimensions are baked in an oven at a constant temperature. Drying phenomena during baking in the falling rate period may be simulated with the simplified form of the equation of continuity in a rectangular coordinate system as (Turhan and Özilgen 1991)

$$\frac{\partial x}{\partial t} = D\frac{\partial^2 x}{\partial z^2}, \tag{E.4.13.1}$$

where D = diffusivity of water in the biscuit and z = distance along the shortest dimension of the biscuit. The solution to Equation E.4.13.1 is

$$\frac{x - x^*}{x_0 - x^*} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2}\exp\left\{-\frac{(2n+1)^2\pi^2}{4}\frac{Dt}{L^2}\right\}, \tag{E.4.13.2}$$

where L = thickness of the biscuit. When D/L^2 is a constant, Equation E.4.13.2 may be approximated with a single term while simulating the long drying times, and rearranged as

$$\ln(x - x^*) = \ln\left[(x_0 - x^*)B\right] - Kt, \tag{E.4.13.3}$$

where $B = 8/\pi^2$ and $k = \pi^2 D/4L^2$. Parameter K may be referred to as the drying rate constant. When a biscuit was baked at a constant temperature, Equation E.4.13.3 was found to agree with the data (Figure E.4.13.1). MATLAB® code E.4.13.a presents the details of the computations.

Mathematical models appear to be more complicated than Equation E.4.13.2 when the process itself is complicated. Giner and Calvelo (1987), while drying early harvested wheat with about

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MATLAB® CODE E.4.13.a

Command Window:

```
clear all
close all
format compact

% enter the times
t=[0:5:30];

% enter the drying rate constants
K(1)=0.070; %s-1 (T=100 oC)
K(2)=0.120; %s-1 (T=125 oC)
K(3)=0.182; %s-1 (T=150 oC)
K(4)=0.275; %s-1 (T=175 oC)
B=8/pi^2;

% enter & plot the data
lnX100=[-1.1 -1.4 -1.75 -2 -2.3 -2.6 -2.9]; % ln(x-x*) @ 100 C
t100=[0 5 10 15 20 25 30]; % time @ 100
plot(t100,lnX100,'p'), hold on

lnX125=[-1.1 -1.7 -2.1 -3 -3.2 -3.8]; % x-x* @ 125 C
t125=[0 5 10 15 20 25]; % time @ 125 C
plot(t125,lnX125,'o'), hold on

lnX150=[-1.1 -1.9 -2.6 -3.95 -4.6]; % x-x* @ 150 C
t150=[0 5 10 15 20]; % time @ 150 C
plot(t150,lnX150,'*'), hold on

lnX175=[-1.1 -2.3 -3.7 -5.4]; % x-x* @ 175 C
t175=[0 5 10 15]; % time @ 175 C
plot(t175,lnX175,'^'), hold on

legend('100 oC','125 oC','150 oC', '175
oC',3,'Location','SouthWest')
xlabel('Time (min)')
ylabel('ln(x-x*)')

% compute and plot the model
for i=1:4
x(i,:)=(-1.1)*B-K(i).*t; % x=ln(x-x*)
end

plot(t,x(1,:)); hold on
plot(t,x(2,:)); hold on
plot(t,x(3,:)); hold on
plot(t,x(4,:)); hold on
```

When we run the code Figure E.4.13.1 will appear on the screen.

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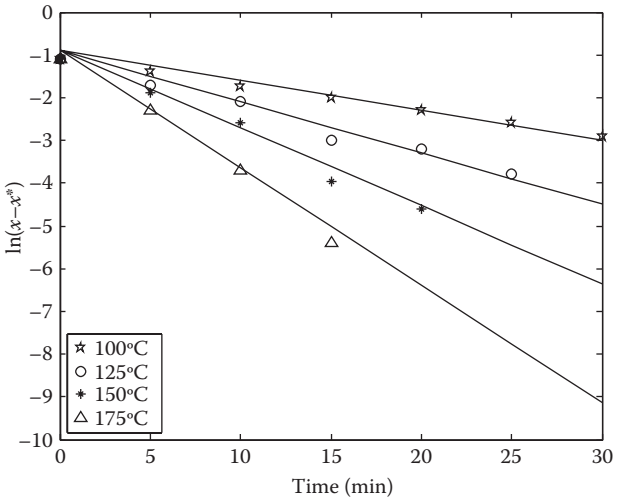


FIGURE E.4.13.1
Comparison of Equation E.4.13.3 with the experimental data. (Experimental data adapted from Turhan, M., and Özilgen, M., *Acta Alimentaria*, 20, 197–203, 1991.)

25% of initial moisture content in fluidized beds, suggested the following equation after assuming an internal control of water movement and short drying times:

$$\frac{\bar{x}-x^*}{x_0-x^*}=1-2a_v\sqrt{\frac{Dt}{\rho}}+0.33a_v^2Dt, \tag{E.4.13.4}$$

where a_v is the area per unit volume of the wheat. MATLAB® code E.4.13.b compares the model with the data (Figure E.4.13.2).

Example 4.14: Drying Behavior of the Cookies With Finite Convective Heat Transfer at the Surface

Demirkol, Erdogdu, and Palazoglu (2006) reported that when there is a convective heat transfer on the surface of the cookie, moisture transport from an infinite slab cookie (thickness = 2*L*) may be expressed with an equation of continuity as

$$\frac{\partial c}{\partial t}=D\frac{\partial^2 c}{\partial z^2}, \tag{E.4.14.1}$$

$$c(z,t)_{t=0}=c_i \quad \text{(IC)}, \tag{E.4.14.2}$$

$$-D\left[\frac{\partial c(z,t)}{\partial(z)}\right]_{z=0}=h\left(c(z,t)_{z=L}-c_\infty\right)\ \text{(BC)}, \tag{E.4.14.3}$$

where D = diffusivity of water in the cookie and z = distance along the shortest dimension. The solution to Equation E.4.17.1 with the given IC and BC is

$$\frac{c(z,t)-c_\infty}{c_i-c_\infty}=\sum_{n=0}^{\infty}\frac{2\sin(\lambda_n)}{\lambda_n+\sin(\lambda_n)\cos(\lambda_n)}\cos\left(\lambda_n\frac{z}{L}\right)\exp\left\{-\lambda_n^2\frac{z}{L}\right\}, \tag{E.4.14.4}$$

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MATLAB® CODE E.4.13.b

Command Window:

```
clear all
close all

% enter the data
XratioData1=[0.96 0.93 0.89 0.84 0.78 0.72 0.67]; % Tair=40 oC
tData1=[0.3e-3 0.8e-3 1.5e-3 2.8e-3 4.1e-3 5.2e-3 7.2e-3]; %
Tair=40 oC
XratioData2=[0.92 0.89 0.87 0.82 0.73 0.67 0.60]; % Tair 60=oC
tData2=[0.2e-3 0.6e-3 0.7e-3 1.1e-3 1.8e-3 2.6e-3 3.8e-3]; %=Tair
60 oC
XratioData3=[0.91 0.86 0.79 0.76 0.69 0.66 0.62]; % Tair 75=oC
tData3=[0.2e-3 0.6e-3 0.9e-3 1.1e-3 1.7e-3 2.2e-3 2.8e-3]; %=Tair
75 oC

av = 18.2;
D = [0.035 0.11 0.16];

% plot the data
plot(tData1,XratioData1,'^', tData2,XratioData2,'o',
tData3,XratioData3,'+') ; hold on;
legend(' Tair=40 oC',' Tair=60 oC',' Tair=75
oC',3,'Location','Best')
xlabel('Time (min)')
ylabel(' (x-x*/x_o-x*)')

% modeling
for j = 1:3;
    for i = 0:90
        t(i+1) = i*0.0001;
        X(i+1) = 1 - (2 * av * ((D(j) * t(i+1) / pi)^0.5)) + 0.33 *
(av^2) * D(j) * t(i+1);
    end
    plot(t,X); hold on;
    axis([0 9e-3 0.5 1.1]);
end
```

When we run the code Figure E.4.13.2 will appear on the screen.

where

$$\lambda \tan(\lambda) = \frac{hL}{D} = \text{Bi}. \tag{E.4.14.5}$$

Equation E.4.14.4 may be modified to express the variation of the average moisture content of the cookies with time as

$$\frac{c_{avg} - c_\infty}{c_i - c_\infty} = \sum_{n=0}^{\infty} \frac{2}{\lambda_n} \left[\frac{\sin^2(\lambda_n)}{\lambda_n + \sin(\lambda_n)\cos(\lambda_n)} \right] \exp\left\{ -\lambda_n^2 \frac{Dt}{L^2} \right\}. \tag{E.4.14.6}$$

MATLAB® codes E.4.14.a determines the Bi and λ_n first (Figure E.4.14.1), then MATLAB® code E.4.14.b compares Equation E.4.14.6 with the experimental data (Figure E.4.14.2).

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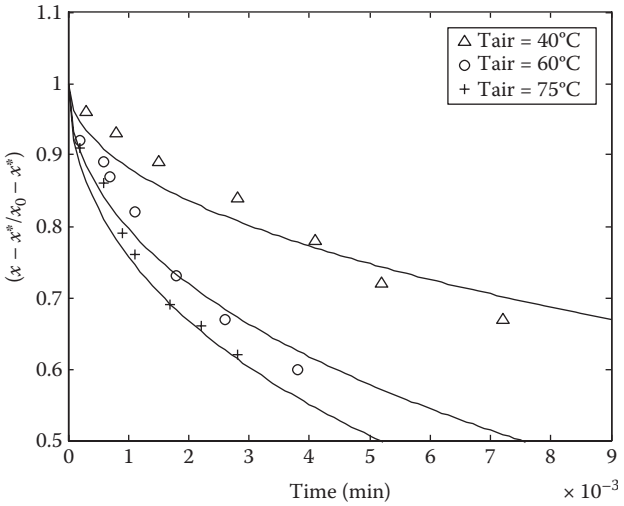


FIGURE E.4.13.2
Comparison of Equation E.4.13.4 with the experimental data at different inlet air temperatures. (Experimental data adapted from Giner, S. A., and Calvelo, A., *Journal of Food Science,* 52, 1358–63, 1987.)

MATLAB® CODE E.4.14.a

Command Window:

```
clear all
close all

%  determine the values of lambda(n)
lambda(1)=0.0001;
BiEst=0.0007; % estimated Biot number
k=1;
for n=2:1:1500
lambda(n)=1.1*lambda(n-1);
Bi(n)=lambda(n)*tan(lambda(n));
if Bi(n)>=0.9*BiEst
if Bi(n)<=1.1*BiEst
xxx(k)=lambda(n);
k=k+1;
fprintf('lambda=%4.4f \n',xxx)
end
end
end
plot(lambda(2:n),Bi(2:n))
xlabel('lambda(n)')
ylabel('Bi')
```

When we run the code the following lines and Figure E.4.14.1 will appear on the screen:

```
lambda=0.0252
lambda=0.0252
lambda=0.0277
```

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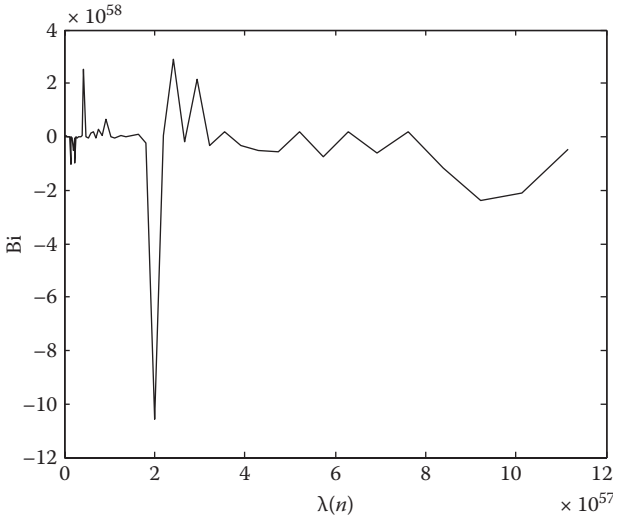


FIGURE E.4.14.1
Variation of a Biot number with λ_n. The Biot number was estimated by a trial and error procedure. The Biot numbers were computed from Equation E.4.14.5, and plotted against $\lambda(n)$. Within the range scanned, only $\lambda = 0.0252$ appeared to be a real root of Equation E.4.14.5 when $Bi_{est} = 0.0007$.

MATLAB® CODE E.4.14.b

Command Window:

```
clear all
close all
format compact

% enter the data
D0=4e-3; % m2/min
a=0.0002;
L=7.8e-3; % m
lambda=[ 0.0252];

% Cratio=(Caverage(t)-Cinf)/(Ci-Cinf)
CratioData1=[-0.1 -0.15 -0.3 -0.4 -0.6 -0.8 -1.1 -1.2 -1.5 -1.75];
% T=190 oC
tData1=[2 4 6 8 10 12 14 16 18 20]; % baking time(min)

% modeling
timeM=[0:0.1:20];
for i=1:200
D(i)=D0+a*timeM(i);
   for n=1:1:length(lambda)
     LAM=lambda(n);
      SIN=sin(lambda(n));
     COS=cos(lambda(n));
    Cterm(n)=((2*SIN^2)/(LAM*(LAM+SIN*COS)))*exp(-
(lambda(n)^2)*D(i)*timeM(i)/L^2);
   end
```

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```
 CratioM(i)=log(sum(Cterm));
end

plot(timeM(:,1:200),CratioM(:,1:200), '-' ,tData1,CratioData1, '+')
xlabel('Baking time(min)')
ylabel('Concentration Ratio')
```

When we run the code Figure E.4.14.2 will appear on the screen.

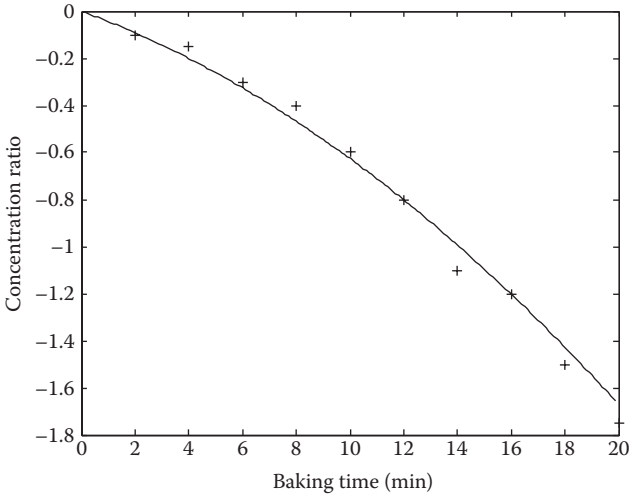


FIGURE E.4.14.2
Comparison of the model with the experimental data of baking time of cookies at 190°C. A linearly increasing diffusivity with time was used in the model. (Adapted from Demirkol, E., Erdogdu, F., and Palazoglu, T. K., *Journal of Food Engineering*, 72, 364–71, 2006.)

Expressions for the effective diffusivity of water in food systems has been given in Chapter 2 and also in Examples 4.13 and 4.14. The diffusivity of water in bakery products is generally expressed with an Arrhenius type expression as

$$D_{eff} = D_0 \exp\left(-\frac{E}{RT}\right). \tag{2.36}$$

Constants of Equation 4.42 may be expressed as a function of the moisture content. The major operation during the production of noodles is drying and the majority of the process occurs during the falling rate period. The drying process is achieved under the careful control because the quality of the product is affected by the drying behavior, therefore the drying behavior of pasta products has been studied by many research groups and the following constants for Equation 4.42 were reported: $D_0 = 7.8 \times 10^{-2}x^2 + 1.67 \times 10^{-2}x + 1.5 \times 10^{-3}$ m^2/s, $E = 48{,}580$ J/mole (Andrieu et al 1988); $D_0 = 3.1 \times 10^{-7}x - 9.1 \times 10^{-9}$ m^2/s, $E = 21{,}600$ J/mole (Andrieu and Stamatopoulos 1986).

The following expressions were reported for the effective diffusivities of bakery products in the temperature range of $293 \le T \le 373$K (Tong and Lund 1990):

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Bread ($0.10 \le x \le 0.75$):

$$D_{eff} = 28945 \times 10^{-4} \exp\left\{1.26x - 2.76x^2 + 4.96x^3 - \left(6117.4/T\right)\right\}. \quad (\mathrm{m}^2/\mathrm{s})$$

Biscuit ($0.10 \le x \le 0.60$):

$$D_{eff} = 9211.4 \times 10^{-4} \exp\left\{0.45x - \left(6104.5/T\right)\right\}. \quad (\mathrm{m}^2/\mathrm{s})$$

Muffin ($0.10 \le x \le 0.95$):

$$D_{eff} = 61672.9 \times 10^{-4} \exp\left\{0.39x - \left(6664.0/T\right)\right\}. \quad (\mathrm{m}^2/\mathrm{s})$$

Example 4.15: Modeling Heat and Mass Transfer to Cookies During the Baking Process

During the baking process, thermal energy balance around a cookie may be presented as

$$c_{\text{cookie}} V \bar{\rho} \frac{d\bar{T}}{dt} = \left(A_{\text{upper}} + A_{\text{sides}}\right) h_{\text{upper and sides}} \left(T_{\text{air}} - T_{\text{side surfaces}}\right) + A_{\text{bottom}} h_{\text{bottom}} \left(T_{\text{conveyor}} - T_{\text{bottom surfaces}}\right) +$$
$$\left(A_{\text{upper}} + A_{\text{sides}}\right) \gamma_{\text{air}} \left(T_{\text{air}}^4 - T_{\text{side surfaces}}^4\right) + \gamma_{wall} \left(T_{\text{wall}}^4 - T_{\text{side surfaces}}^4\right) + V \Delta H_{\text{vapor}} \bar{\rho} \frac{d\bar{x}}{dt}, \quad \text{(E.4.15.1)}$$

where A and T represent the surface area of the cookies and the temperature of the cookies (or the oven), respectively (areas and temperatures pertinent to different locations of the cookies or the oven are depicted at the subscripts); c_{cookie}, V, and $\bar{\rho}$ are the specific heat, volume, and average density of the cookies, respectively; parameter h is the convective heat transfer coefficients on the surface of the cookies at the subscripted locations, γ_{air} and γ_{wall} are constants of the radiative heat exchange that is equal to the product of the absorbance of oven walls or air geometric correction factor and the Stefan–Boltzmann constant. Parameter ΔH_{vapor} is the apparent latent heat of vaporization and $\bar{x}$ is the average moisture content (g water/g dry matter) of the cookies. Each term of Equation E.4.15.1 represents the followings:

$c_{\text{cookie}} V \bar{\rho} \frac{d\bar{T}}{dt}$	Rate of the enthalpy change of a cookie
$(A_{\text{upper}} + A_{\text{sides}}) h_{\text{upper and sides}} (T_{\text{air}} - T_{\text{side surfaces}})$	Convective heat transfer on the upper and side surfaces of a cookie
$A_{\text{bottom}}\, h_{\text{bottom}}\, (T_{\text{conveyor}} - T_{\text{bottom surface}})$	Heat transfer at the bottom surface of a cookie in contact with the conveyor band (radiation heat transfer from the bottom of the cookie are also implicitly included into this term, therefore h_{bottom} is actually an apparent constant)
$(A_{\text{upper}} + A_{\text{sides}}) \gamma_{\text{air}} \left(T_{\text{air}}^4 - T_{\text{side surface}}^4\right)$	Radiative heat transfer from the hot air
$\gamma_{\text{wall}} \left(T_{\text{air}}^4 - T_{\text{side surfaces}}^4\right)$	Radiative heat transfer from the side wall of the oven located in the upper space of the conveyor
$V \Delta H_{\text{vapor}} \bar{\rho} \frac{d\bar{x}}{dt}$	Energy consumed to evaporate water in the cookie

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The moisture balance around a cookie is

$$V\bar{\rho}_{\text{dry matter}}\frac{d\bar{x}}{dt}=\left(A_{\text{upper}}+A_{\text{sides}}\right)k_{\text{upper and sides}}(\bar{x}-x^*)+A_{\text{bottom}}k_{\text{bottom}}(\bar{x}-x^*). \quad \text{(E.4.15.2)}$$

After rearranging Equation E.4.15.2 we will have

$$\frac{d\bar{x}}{dt}=\left(\left(A_{\text{upper}}+A_{\text{sides}}\right)k_{\text{upper and sides}}\left(\bar{x}-x^*\right)+A_{\text{bottom}}k_{\text{bottom}}\left(\bar{x}-x^*\right)\right)/\left(V\bar{\rho}_{\text{dry matter}}\right), \quad \text{(E.4.15.3)}$$

where $\bar{\rho}_{dry\ \text{matter}}$ is the average density of the dry matter of the biscuits, and k and x are the mass transfer coefficient and the moisture content (g water/g dry matter) at the locations indicated by the subscripts. Initial conditions of Equations E.4.15.1 and E.4.15.3 are

$$\bar{x}=x_0 \quad \text{at} \quad t=0 \quad \text{(E.4.15.4)}$$

and

$$\bar{T}=T_0 \quad \text{at} \quad t=0. \quad \text{(E.4.15.5)}$$

Hayakawa and Hwang (1981) solved these equations to simulate a commercial baking process in a 90 m long commercial oven. They have determined the operating conditions at various locations of the oven and presented detailed analysis for the evaluation of the apparent model constants, then presented their results in tables and compared the model with the experimental data. MATLAB® code E.4.15 presents the solution of Equations E.4.15.1 and E.4.15.3 with the initial conditions (Equations E.4.15.4 and E.4.15.5) to simulate the variation of the average temperature

MATLAB® CODE E.4.15

Command Window:

```
clear all
close all
format compact

global V rho Au Ab As
V=2;  % volume of the cookie (cm3), (diameter=2 cm, height=0.5 cm)
rho=12; % density of the cookie (g/cm3)
Au=3.20;  % upper surface area of the cookie (cm2)
Ab=3.14;  % bottom surface area of the cookie (cm2)
As=3.14;  % side surface area of the cookie (cm2)

% modeling
Y0=[38 305];
[t,x]=ode45 ('CookieBaking', [0 200 ],Y0);
mModel=x(:,1);
Tmodel=x(:,2);
[AX,H1,H2] = plotyy(t, mModel, t, Tmodel); hold on
xlim([0 200])
```

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```
set(H1, 'LineStyle',':')
set(H2,'LineStyle','-')
xlabel('time spent in the oven (s)')
ylabel('m ((g moisture/g dry matter)*100)')
set(get(AX(2),'ylabel'), 'string', 'Temperature (\circ C)')
legend('average moisture content of the cookie', 'average
temperature of the cookie','Location','Best')
```

M-File:

```
function dYdt=CookieBaking(t,Y);
global V rho Au Ab As
% constants of the model (although single values are assigned in
this example, in a real baking oven these parameters varies with
location and have diffeerent values at each section of the oven)
ku=6*10^-2 ;
kb=0.1*10^-4;
gammaWall=1;
gammaAir=1;
xs=5;
hu=3800; % W/m2K
hb=300; % W/m2K
Ta=423;
Tc=300;% K
Tb=298;% K
Tw=273;% K
delHevap=2430; % apparent latent heat of evaporation of water
c=2*10^9;
x=Y(1);
T=Y(2);
dxdt=-((Au+As)*ku*(x-xs)+Ab*kb*(x-xs))/(rho*V);
dTdt=(((Au+As)*hu*(Ta-T))+((Ab*hb)*(Tc-
Tb))+((Au+As)*gammaAir*((Ta^4)-(T^4)))+gammaWall *((Tw^4)-
(T^4))+(V*rho*delHevap*dxdt))/(c*V*rho);
dYdt=[dxdt; dTdt];
```

When we run the code Figure E.4.15 will appear on the screen.

and average moisture content of a cookie undergoing a baking process (Figure E.4.15) where the assigned values of the physical and operating parameters prevail.

Example 4.16: Temperature Profiles in a Cylindrical Cookie During Baking

The equation of energy Equation 2.17 may be simplified to describe the temperature profiles in a cylindrical cookie during baking as

$$\frac{\partial T}{\partial t} = \alpha\left[\frac{\partial^2 T}{\partial r^2} + \frac{1}{r}\frac{\partial T}{\partial r} + \frac{\partial^2 T}{\partial z^2}\right]. \tag{E.4.16.1}$$

The IC and the BCs are

$$\text{IC: } T = T_0 \text{ at } t = 0, \tag{E.4.16.2}$$

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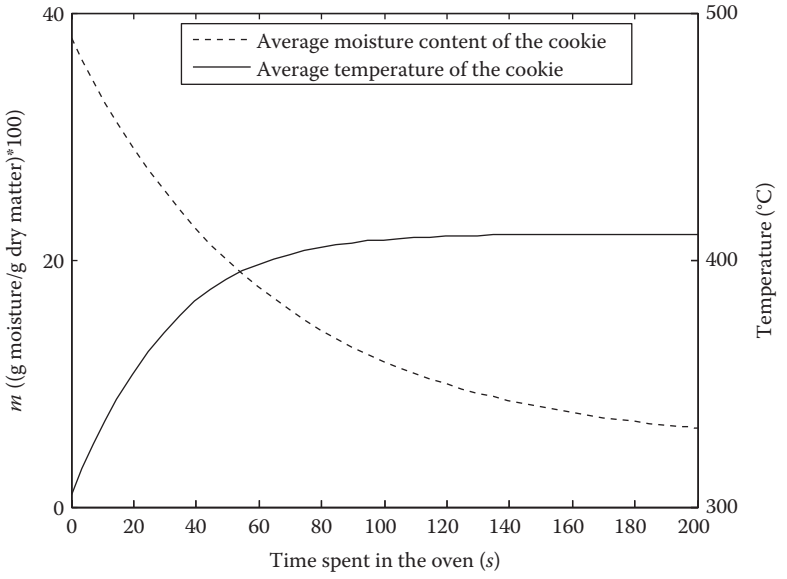


FIGURE E.4.15
Variation of the predicted values of the average moisture content and average temperature of a cookie during baking process in an oven where the operating and physical parameters assigned in the MATLAB® code prevail.

$$\text{BC1: } \left[\frac{dT}{dz}\right]_{r=0} = 0 \quad \text{at} \quad r = 0 \text{ for } t \geq 0, \tag{E.4.16.3}$$

$$\text{BC2: } \left[k\frac{dT}{dz}\right]_{r=R} = hA\left(T_R - T_\infty\right) \text{ at } r = R \text{ for } t \geq 0. \tag{E.4.16.4}$$

The graphical user interface of the toolbox can be started by typing pdetool in the MATLAB® command window. The geometry of the cookie can be sketched as a rectangle and discretized with an unstructured mesh as shown in Figure E.4.16.1.

The heat transfer PDE in MATLAB is formulated as follows:

$$\rho c\frac{\partial T}{\partial t} - div\left(k \cdot grad(T)\right) = Q + h\left(T_{ext} - T\right) \tag{E.4.16.5}$$

Since in this example the geometry of the cookie is simplified as a cylinder, cylindrical coordinates are used. Therefore, the equation should be transformed as follows:

$$\rho cr\frac{\partial T}{\partial t} - \frac{\partial}{\partial r}\left(kr\frac{\partial T}{\partial r}\right) - \frac{\partial}{\partial z}\left(kr\frac{\partial T}{\partial z}\right) = Qr + hr\left(T_{ext} - T\right) \tag{E.4.16.6}$$

The x and y axes in MATLAB represent the z and r axes in our problem, respectively. The values of the coefficients defining the PDE and boundary conditions should be set accordingly. Enter the coefficients in the PDE specification dialog box as

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k	240*y
h	18*y
c	963*y
ρ	2800
Q	0

The boundary conditions are Neumann on the boundary $r = 0$, which is the symmetry axis, and a Dirichlet boundary condition is set on the other faces, where surface temperature is equal to the oven temperature.

Now the PDE can be solved for different oven temperatures. Temperature distribution through the cookie is shown in Figure E.4.16.2. Figure E.4.16.3 shows the experimental and calculated temperature profiles at the center of the cookie with respect to baking time.

Similar figures to Figure E.4.16.2 were plotted with time intervals and their center temperatures were employed to plot the model (Figure E.4.16.3) by using MATLAB® code E.4.16.

In a freeze-drying process a food is frozen, than water is removed by transfer from the solid state to the vapor state by sublimation. A vapor pressure versus temperature phase diagram for free water is shown in Figure 4.2. The process 1 → 2 is conventional drying under constant pressure, where liquid water is evaporated. The process 3 → 4 represents freeze drying, where ice is converted directly into vapor. It should be noticed that freeze drying requires a vacuum and conducted at lower temperatures, therefore, expensive equipment and long processing times are needed, which increases the cost of the process.

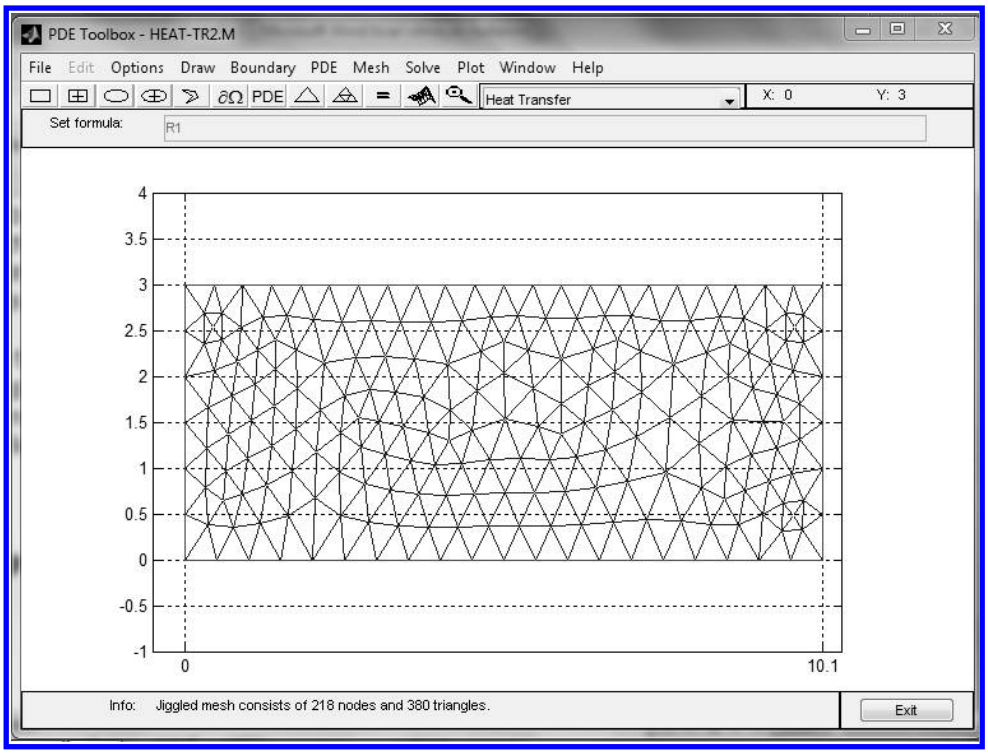


FIGURE E.4.16.1
The grid system in the cylindrical cookie.

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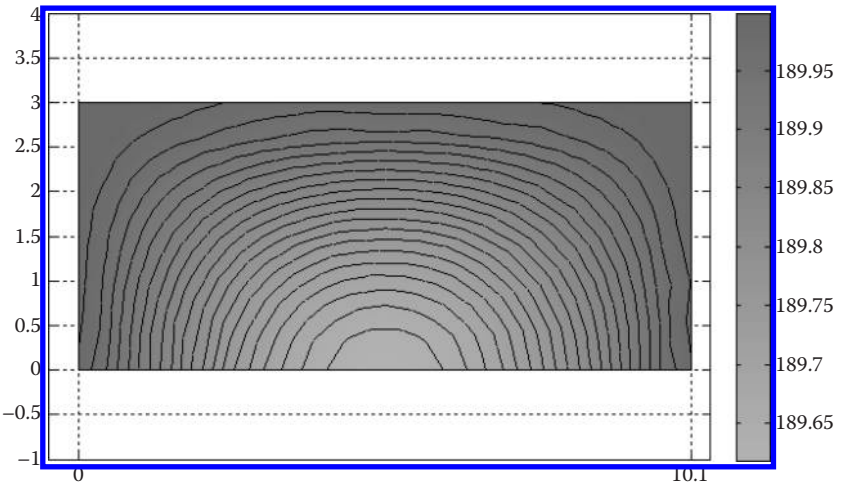


FIGURE E.4.16.2
Temperature distribution in a cylindrical cookie (y axis describes r and x axis describes the length of the cylinder) at $t = 90$ min ($T_{ext} = 190$°C).

MATLAB® CODE E.4.16

Command Window:

```
clear all
close all

Tdata190num=[25 61 117 152 170 180 184 187 189 190];
Tdata190=[25 60 103 130 150 163 175 180 185 192]; % temperature at
the center of the cookie  (Toven=190 oC)
tData=[0 10 20 30 40 50 60 70 80 90]; % times the data were recorded
(min)

Tdata130=[25 42 63 80 96 106 112 120 124 128]; % temperature at the
center of the cookie  (Toven=130 oC)
Tdata130num=[25 44 81 104 117 123 126 128 129 129.5];

plot(tData,Tdata190,'o',tData,Tdata190num,'-',tData,Tdata130,'s',tDa
ta,Tdata130num,'-') ; hold on
xlabel('Time (min)')
ylabel('Tcenter')
legend('data,190 ^oC','model, 190 ^oC','data, ^o 130 ^oC', 'model,
130 ^oC', 'Location','SouthEast')
```

When we run the code Figure E.4.16.3 will appear on the screen.

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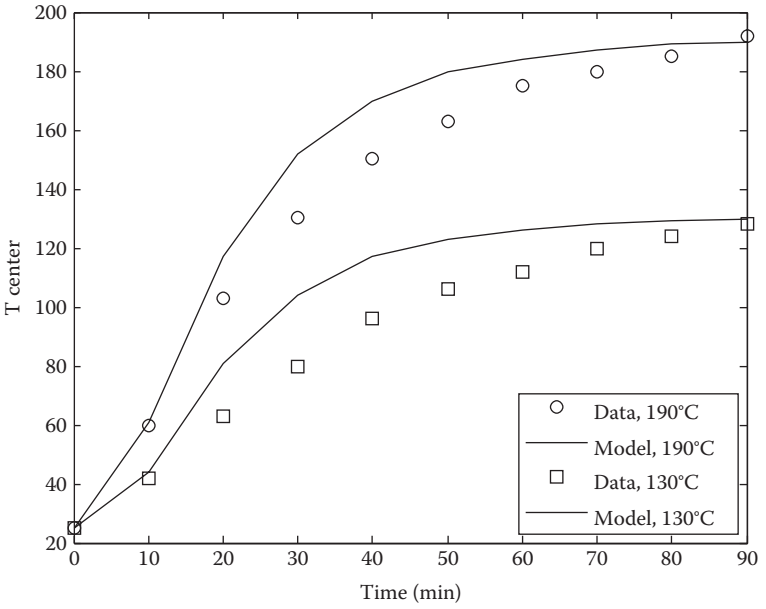


FIGURE E.4.16.3
Comparison of the model center temperatures with the data. (Adapted from Sakin, M., Kaymak-Ertekin, F., and Ilıcalı, C., *Journal of Food Engineering*, 94, 344–49, 2009.)

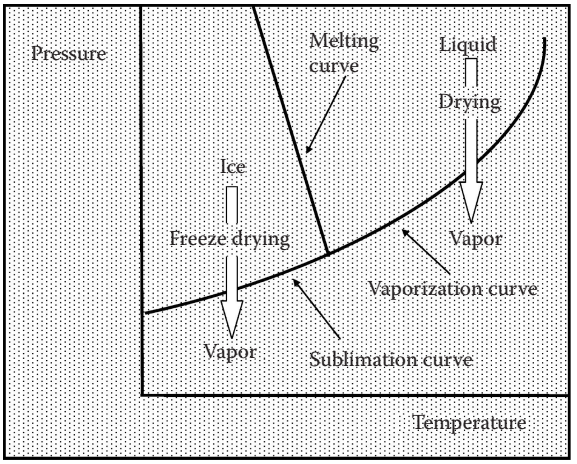


FIGURE 4.2
A qualitative vapor pressure versus temperature phase diagram for free water.

Example 4.17: Heat and Mass Transfer Rate Limited Periods in Freeze Drying

In the process described in Figure E.4.17.1 heat is transferred from the heater plate to the unfrozen core, then to the core–crust interface, where ice is converted into vapor via sublimation under vacuum. Water vapor is transferred along the crust with diffusion, which leaves the food after reaching to the crust–air interface. At the beginning of the process the crust is not established yet and the core is thick, therefore heat transfer is expected to be the rate limiting step. At the later

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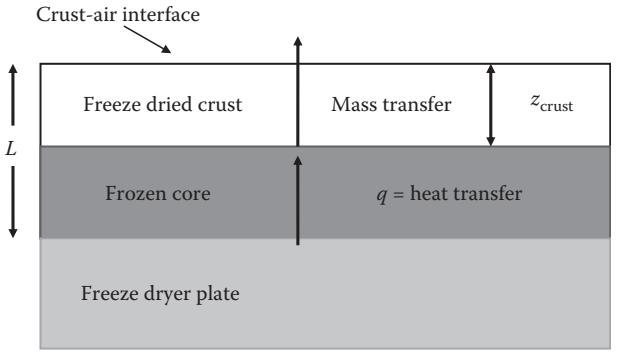


FIGURE E 4.17.1
Freeze-drying process of the foods on a plate freeze dryer.

stages of freeze drying when the unfrozen core becomes thinner and the crust becomes thicker, the path of heath transfer decreases and the path of mass transfer increases, therefore mass transfer rate is expected to become the rate limiting process.

Mathematical models for computing the amounts of moisture remaining in the foods during the freeze-drying process are based on the rate limiting steps. When heat transfer is the rate limiting step, the heat transfer rate from the plate to the unfrozen core–crust interface is

$$q = -k_{\text{core}} \frac{\left(T_{\text{plate}} - T_{\text{phase change}}\right)}{L - z_{\text{crust}}} = -\left(V_{\text{food}} \rho \Delta H_{\text{phase change}}\right) \frac{dx}{dt}, \tag{E.4.17.1}$$

after substituting $L - z_{\text{crust}} = Lx/x_0$ and $\kappa_1 = [x_0 \rho k_{\text{core}}(T_{\text{plate}} - T_{\text{phase change}})]/(L\Delta H_{\text{phase change}})$, Equation E.4.17.1 may be rearranged as

$$\frac{dx}{dt} = -\frac{\kappa_1}{x}. \tag{E.4.17.2}$$

Equation E.4.17.2 may be expressed in numerical form as

$$x(i+1) = x(i) - \frac{\kappa_1}{x(i)} \Delta t(i+1). \tag{E.4.17.3}$$

We may use Equation E.4.17.3 to estimate the fraction of water remaining in the food during the freeze-drying process or to compute the time required for freeze drying foods.

When mass transfer is the rate limiting step, mass transfer may be expressed as

$$N_{\text{water vapor}} = \frac{D_{\text{crust}}}{RT} \frac{P_{\substack{\text{core-crust} \\ \text{interface}}} - P_{\substack{\text{crust-chamber} \\ \text{interface}}}}{L - z_{\text{crust}}} = k_{\text{external}} \left(P_{\substack{\text{crust-chamber} \\ \text{interface}}} - P_{\text{chamber}} \right). \tag{E.4.17.4}$$

Equation E.4.17.4 may be rearranged as

$$N_{\text{water vapor}} = \left(x_0 L \rho_{\text{solids}}\right)\left(-\frac{dx}{dt}\right) = \frac{P_{\substack{\text{core-crust} \\ \text{interface}}} - P_{\text{chamber}}}{\dfrac{1}{k_{\text{external}}} + \dfrac{\left(L - z_{\text{crust}}\right)RT}{D_{\text{crust}}}}. \tag{E.4.17.5}$$

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After substituting $L - z_{crust} = Lx/x_0$ and assuming that the external resistance to mass transfer is much smaller than that of the core region, for example, $(1/k_{external}) << (((L - z_{crust})RT)/D_{crust})$ Equation E.4.17.5 may be rewritten as

$$\frac{dx}{dt} = -\frac{D_{crust}}{L^2 \rho_{solids} RT} \frac{P_{\substack{\text{core-crust} \\ \text{interface}}} - P_{chamber}}{x}, \tag{E.4.17.6}$$

after substituting $\kappa_2 = [D_{crust}(P_{crust\text{-}core\ interface} - P_{chamber})/(L^2 \rho_{solids} RT)]$, Equation E.4.17.6 may be rearranged as

$$\frac{dx}{dt} = -\frac{\kappa_2}{x}. \tag{E.4.17.7}$$

Equation E.4.17.2 may be expressed in numerical form as

$$x(i+1) = x(i) - \frac{\kappa_2}{x(i)} \Delta t(i+1), \tag{E.4.17.8}$$

although Equations E.4.17.3 and E.4.17.8 have similar forms, they are based on different rate limiting values, parameters κ_1 and κ_2 are also expected to have different values. Ranges of the heat transfer rate and mass transfer rate limited phases of the freeze-drying process of 1 and 3 mm thick carrot samples and capsicum with a natural layer are established with MATLAB® code E.4.17 (Figure E.4.17.2).

MATLAB® CODE E.4.17

Command Window:

```
clear all
close all
format compact

% enter the data
tData=[0 0.5 1 1.5 2 2.5 3 4 5 6 7];
x1mmCarrot=[1 0.7 0.48 0.33 0.22 0.18 0.11 0.08 0.04 0.02 0.01]; %
experimental data
x3mmCarrot=[1 0.88 0.75 0.64 0.56 0.48 0.42 0.31 0.22 0.18 0.13];
xCapsicum=[1 0.96 0.9 0.85 0.795 0.74 0.7 0.62 0.57 0.495 0.43];
plot(tData,xCapsicum,'s',tData,x3mmCarrot,'^',tData,x1mmCarrot,'o')
; hold on
legend('capsicum','3 mm thick carrot','1 mm thick carrot',
'Location','NorthEast')
xlabel('Time (h)')
ylabel('fraction of the remaining moisture')

% MODELING OF THE HEAT TRANSFER LIMITED RANGE
x0=1;
kappa1(1)=0.087; % capsicum;
tModel1(1)=0;
x1(1)=x0;
deltaTime=0.1; % (h)
for i=2:35
     tModel1(i)=i*deltaTime;
```

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```
     x1(i)=x1(i-1)-kappa1(1)*(deltaTime/x1(i-1));
end

kappa1(2)=0.2; % 3 mm carrot;
tModel2(1)=0;
x2(1)=x0;
deltaTime=0.1; % (h)
for i=2:20
     tModel2(i)=i*deltaTime;
     x2(i)=x2(i-1)-kappa1(2)*(deltaTime/x2(i-1));
end

kappa1(3)=0.5; % 1 mm carrot;
tModel3(1)=0;
x3(1)=x0;
deltaTime=0.1; % (h)
for i=2:9
     tModel3(i)=i*deltaTime;
     x3(i)=x3(i-1)-kappa1(3)*(deltaTime/x3(i-1));
end
 plot(tModel1,x1,':', tModel2,x2,':', tModel3,x3,':'); hold on

% MODELING OF THE MASS TRANSFER LIMITED RANGE

kappa2(1)=0.035; % capsicum;
tModel1(35)=3.5;
x1(35)=0.65;
deltaTime=0.1; % (h)
for i=36:70
     tModel1(i)=i*deltaTime;
     x1(i)=x1(i-1)-kappa2(1)*(deltaTime/x1(i-1));
end

kappa2(2)=0.013; % capsicum;
tModel2(35)=3.5;
x2(35)=0.32;
deltaTime=0.1; % (h)
for i=36:70
     tModel2(i)=i*deltaTime;
     x2(i)=x2(i-1)-kappa2(2)*(deltaTime/x2(i-1));
end

kappa2(3)=0.0012; % capsicum;
tModel3(29)=2.9;
x3(29)=0.10;
deltaTime=0.1; % (h)
for i=30:70
     tModel3(i)=i*deltaTime;
     x3(i)=x3(i-1)-kappa2(3)*(deltaTime/x3(i-1));
end

plot(tModel1(36:70),x1(36:70),'-', tModel2(36:70),x2(36:70),'-',
tModel3(30:70),x3(30:70),'-'); hold on
```

When we run the code Figure E.4.17.2 will appear on the screen.

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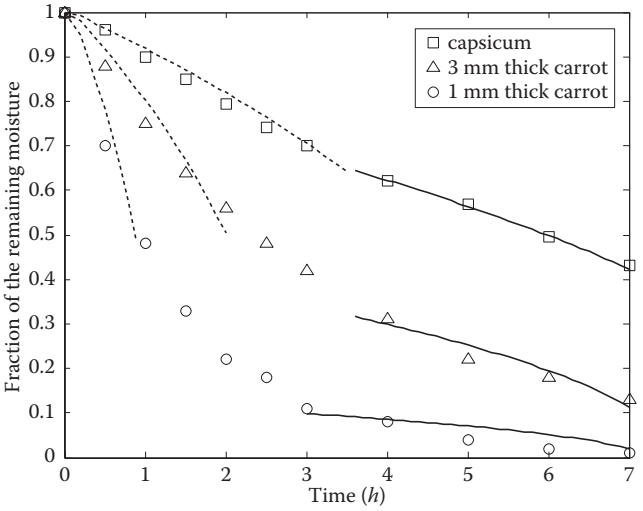


FIGURE E 4.17.2
Predicted moisture contents remaining in the plant tissues during the freeze-drying process. Dashed lines represent the heat transfer limiting phase (at the beginning). The solid lines represent the mass transfer limiting phase (at the end). The range where no models were presented represents the transition period from the heat transfer limiting to mass transfer limiting regime. (Experimental data adapted from George, J. P., and Datta, A. K., *Journal of Food Engineering*, 52, 89–93, 2002.)

In a freezing process the moment that the interface reaches the thermal center is referred to as the freezing time and calculated after rearranging Equation 4.37 or Equation 4.38 as

$$t_F = \frac{\rho \Delta H_{\text{product}}}{T_{\text{freezing}} - T_{\text{coolant}}} \left\{ P \frac{2L}{h} + R \frac{4L^2}{k} \right\}. \tag{4.42}$$

Equation 4.39 is referred to as the Plank's equation (Plank 1941) and it is the best known analytical expression for freezing time calculations. Parameter L is half the thickness of an infinite slab. Parameter r is replaced by radius r in the cylinder or sphere problems. Dimensions of a brick-shaped food are usually given as $2L \times \beta_1 2L \times \beta_2 2L$, with $2L$ being the shortest dimension. Parameters β_1 and β_2 are employed in freezing time calculations. Parameters $P = 1/2$, $R = 1/8$ for infinite slab; $P = 1/4$, $R = 1/16$ for infinite cylinder and $P = 1/6$, $R = 1/24$ for sphere. Equation 4.42 may be expressed in terms of dimensionless numbers as

$$Fo = \frac{R}{Ste} + \frac{P}{(Bi)(Ste)}, \tag{4.43}$$

where $\text{Fo} = k_{\text{crust}} t / \rho c_p L^2$ is the Fourier number, $\text{Ste} = c_p (T_{\text{fluid}} - T_{\text{phase change}}) / \omega_0 \Delta H_{\text{phase change}}$ is the Stefan number, and $\text{Bi} = hL/k_{\text{crust}}$ is the Biot number. Plank's equation does not account for the sensible enthalpy change since the sensible enthalpy change to bring the food from its initial temperature to the freezing temperature and from the freezing temperature to its final temperature is usually very small when compared to the enthalpy of

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phase change. There may be some cases where the sensible enthalpy changes may not be neglected. The Cleland and Earle model may be regarded as an improved version of Plank's equation and used when sensible enthalpy change is not negligible (Cleland and Earle 1982):

$$t_F = \frac{\Delta H_{\text{beginning-final}}}{\left(T_{\text{beginning}} - T_{\text{coolant}}\right)\left(N_{EHTD}\right)}\left\{P\frac{2L}{h} + R\frac{4L^2}{k_{\text{frozen}}}\right\}. \tag{4.44}$$

With the brick-shaped foods

$$P = 0.5\left[1.026 + 0.5808Pk + \text{Ste}\left(0.226Pk + 0.1050\right)\right],$$

$$R = 0.125\left[1.202 + \text{Ste}\left(3.410Pk + 0.7336\right)\right],$$

$$N_{EHDT} = 1 + W_1 + W_2.$$

where

$$Pk = c_{\text{unfrozen}}\left(T_{\text{initial}} - T_{\text{beginning}}\right)/\Delta H = \text{Plank number}$$

$$\text{Ste} = c_{\text{frozen}}\left(T_{\text{beginning}} - T_{\text{end}}\right)/\Delta H = \text{Stefan number}$$

$$W_1 = \left(\frac{\text{Bi}}{\text{Bi}+2}\right)\left(\frac{5}{8\beta_1^3}\right) + \left(\frac{\text{Bi}}{\text{Bi}+2}\right)\left(\frac{2}{\beta_1\left(\beta_1+1\right)}\right),$$

$$W_2 = \left(\frac{\text{Bi}}{\text{Bi}+2}\right)\left(\frac{5}{8\beta_1^3}\right) + \left(\frac{\text{Bi}}{\text{Bi}+2}\right)\left(\frac{2}{\beta_2\left(\beta_2+1\right)}\right), \text{ and}$$

$$\text{Bi} = \frac{2hL}{k_{\text{frozen}}}$$

T_{initial} = initial temperature of the food
$T_{\text{beginning}}$ = temperature where freezing starts
T_{final} = final temperature of the food after freezing
T_{coolant} = temperature of the coolant
c_{unfrozen} = volumetric specific heat of the unfrozen food (J/m^3 °C)
c_{frozen} = volumetric specific heat of the fully frozen food (J/m^3 °C)
N_{EHTD} = number of equivalent heat transfer dimensions (N_{EHTD} = 1 for an infinite slab, N_{EHTD} = 2 for an infinite cylinder, N_{EHTD} = 3 for a sphere)
$\Delta H_{\text{beginning-final}}$ = enthalpy change between the beginning and the end of the freezing process including the sensible and phase change enthalpies
k_{frozen} = thermal conductivity of the fully frozen product

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The Mascheroni and Calvelo (1982) model is also suggested after Plank's model to include the sensible enthalpy change as

$$t_F = \frac{\rho_{unfrozen} x \Delta H^0_{phase\ change} \omega L^2}{\left(T_{beginning} - T_{coolant}\right) k_{frozen}} \left[\frac{1}{Bi_{frozen}} + \frac{1}{2}\right], \tag{4.45}$$

$\rho_{unfrozen}$ = density of the unfrozen food
x = water content of the food on a wet basis
ω = average of the ice content (weight of ice/initial weight of water) of the product at temperatures T_{final} and $T_{coolant}$

$$\Delta H^0_{phase\ change} = \text{enthalpy of freezing of water at } 0°C$$

$$Bi_{frozen} = 2hL/k_{frozen}$$

In industrial use either the temperature driving force or Biot number at different sides of the food may be different, which results in nonsymmetric freezing. In some cases the food may be frozen in boxes, where the air space at the top of the box may also be a source of the nonsymmetric behavior. When freezing of the objects is not symmetric, parameter L of Equation 4.45 may be the distance between the thermal center (latest freezing point) and the surface. Thermal center may be estimated intuitively by comparing the Biot numbers and the temperature driving forces of different sides. An interested reader may refer to De Michelis and Calvelo (1982) for a better estimate.

Example 4.18: Freezing Time Calculations

a. Beef carcass (average dimensions 150 × 60 × 7 cm, $k_{average}$ = 1.04 W/mK, ρ = 1060 kg/m^3, ω = 75%, c_p = 3.5 kJ/kg K and at the initial freezing temperature of the beef = –2.8°C) is being frozen in an air-blast freezer (h = 22 W/m^{2}K) with air at –30°C, where the latent heat of fusion of water to ice is about 334 kJ/kg. Determine the freezing time of the carcass.

Solution: Equation 4.42 may be used with infinite slab shape factors P = 1/2 and R = 1/8. The latent heat of freezing of the product is defined as (Heldman 1983):

$$\Delta H_{product} = \omega \Delta H_{F,water}. \tag{E.4.18.1}$$

After substituting the numbers we will obtain $\Delta H_{product}$ = 250.5 kJ/kg. The characteristic length L = 0.035 m. After substituting the data in Equation 4.42 we will obtain

$$t_F = \frac{(1060\text{kg/m}^3)(250.5\text{kJ/kg})}{(270.2-243)\text{K}} \left[\frac{1}{2}\frac{2(0.035\text{m})}{22\text{W/m}^2\text{K}} + \frac{1}{8}\frac{4(0.035\text{m})^2}{1.04\text{W/mK}}\right]\left(\frac{\text{Ws}}{\text{J}}\right)\left(\frac{1000\text{J}}{\text{kJ}}\right)\left(\frac{1h}{3600s}\right) = 5.9h.$$

b. Determine the freezing time of the individual units after the carcass is converted into the following products (you may assume that the properties of the products are almost the same as that of the carcass and use the Plank's equation):

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i. Sausages (diameter = 1.5 cm, length = 10 cm)
ii. Meat balls (diameter = 3 cm)
iii. Hamburger patties (thickness = 1 cm, diameter = 7 cm)
iv. Fifty hamburger patties are packaged with paper (thickness = Δx = 3 mm, $k_{apparent}$ = 0.14 W/mK). Individual patties are separated with paper. The effective convective heat transfer coefficient may be calculated as

$$\frac{1}{h_{eff}} = \frac{1}{h} + \frac{\Delta x}{k_{\text{apparent}}}. \tag{E.4.18.2}$$

a. A sausage with 1.5 cm diameter and 10 cm length may be regarded as an infinite cylinder (characteristic dimension L = 0.75 cm). Equation 4.42 may be used with shape factors P = 1/2 and R = 1/16:

$$t_F = \frac{(1060\,\text{kg/m}^3)(250.5\,\text{kJ/kg})}{(270.2-243)\text{K}}\left[\frac{1}{2}\frac{2(0.075\text{m})}{22\text{W/m}^2\text{K}} + \frac{1}{16}\frac{4(0.075\text{m})^2}{1.04\,\text{W/mK}}\right]$$
$$\left(\frac{\text{Ws}}{\text{J}}\right)\left(\frac{1000\,\text{J}}{\text{kJ}}\right)\left(\frac{1h}{3600\,s}\right) = 57.7h.$$

b. The meat balls are spherical (characteristic dimension L = 1.5 cm). The shape factors are P = 1/6 and R = 1/24. After substituting the numbers in Plank's equation (e.g., Equation 4.44), we will obtain

$$t_F = \frac{(1060\text{kg/m}^3)(250.5\text{kJ/kg})}{(270.2-243)\text{K}}\left[\frac{1}{6}\frac{2(0.015\text{m})}{22\text{W/m}^2\text{K}} + \frac{1}{24}\frac{4(0.015\text{m})^2}{1.04\,\text{W/mK}}\right]$$
$$\left(\frac{\text{Ws}}{\text{J}}\right)\left(\frac{1000\,\text{J}}{\text{kJ}}\right)\left(\frac{1h}{60\,s}\right) = 42.8\text{min}.$$

c. The hamburger patties may be considered as an infinite slab with a characteristic length L = 0.5 cm. The shape factors are P = 1/2 and R = 1/8. After substituting the data in Plank's equation (e.g., Equation 4.42), we will obtain

$$t_F = \frac{(1060\text{kg/m}^3)(250.5\text{kJ/kg})}{(270.2-243)\text{K}}\left[\frac{1}{2}\frac{2(0.005\text{m})}{22\text{W/m}^2\text{K}} + \frac{1}{8}\frac{4(0.005\text{m})^2}{1.04\,\text{W/mK}}\right]$$
$$\left(\frac{\text{Ws}}{\text{J}}\right)\left(\frac{1000\,\text{J}}{\text{kJ}}\right)\left(\frac{1h}{60\,s}\right) = 38.9\text{min}.$$

d. The package may be regarded as an infinite cylinder (characteristic dimension L = 3.5 cm). The shape factors are P = 1/2 and R = 1/16. The effective convective heat transfer coefficient is calculated as

$$\frac{1}{h_{eff}} = \frac{1}{h} + \frac{\Delta x}{k_{\text{apparent}}} = \frac{1}{22} + \frac{0.003}{0.14}.$$

therefore h_{eff} = 14.95 W/m^{2}K. After substituting the numbers in Plank's equation (e.g., Equation 4.42), we will obtain

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$$t_F = \frac{(1060\text{kg/m}^3)(250.5\text{kJ/kg})}{(270.2-243)\text{K}}\left[\frac{1}{2}\frac{2(0.075\text{m})}{14.95\text{W/m}^2\text{K}} + \frac{1}{16}\frac{4(0.035\text{m})^2}{1.04\,\text{W/mK}}\right]$$
$$\left(\frac{\text{Ws}}{\text{J}}\right)\left(\frac{1000\,\text{J}}{\text{kJ}}\right)\left(\frac{1h}{3600\,s}\right) = 6.5h.$$

e. The 0.59 × 0.38 × 0.15 m cartons of deboned beef are frozen in a tunnel freezer. The thermal center was estimated to be approximately 9 cm from the bottom and 6 cm from the top. The relevant data for the process were $T_{initial} = 10°C$, $T_{beginning} = -2°C$, $T_{final} = -15°C$, $T_{coolant} = -21°C$, $k_{frozen} = 1.6$ W/m°C, $\Delta H_{beginning\text{-}final} = 240 \times 10^{-6}$ J/m^3 between 10°C and –15°C, $C_{unfrozen} = 3.6 \times 10^6$ J/m^3 °C and $c_{frozen} = 1.9 \times 10^6$ J/m^3 °C, $h = 12.9$ W/m^2 °C. Determine the freezing time of the beef.

Solution: Cleland and Earle's model (Cleland and Earle 1982) will be used for prediction of the freezing times. The thermal center appears to be 9 cm from the bottom, therefore the process is actually equivalent to freezing a carton with $L = 9$ cm.

$$Pk = \frac{c_{unfrozen}\left(T_{initial} - T_{beginning}\right)}{\Delta H} = 0.180,\ \text{Ste} = \frac{c_{frozen}\left(T_{beginning} - T_{coolant}\right)}{\Delta H} = 0.15$$

P = 0.5[1.026 + 0.5808Pk + Ste(0.226Pk + 0.1050)] = 0.576 and R = 0.125[1.202 + Ste(3.410Pk + 0.7336)] = 0.176. We may calculate W_1 and W_2 with $Bi = 2hL / k_{solid} = 1.45$, $\beta_1 = 0.38 / 0.18 = 2.11$, and $\beta_2 = 0.59 / 0.18 = 3.28$ as $W_1 = (\text{Bi/Bi} + 2)(5/8\beta_1^3) + (\text{Bi/Bi} + 2)(2/\beta_1(\beta_1 + 1)) = 0.20$ and $W_2 = (Bi/Bi + 2)(5/8\beta_1^3) + (Bi/Bi + 2)(2/\beta_2(\beta_2 + 1)) = 0.09$. We also have $N_{EHTD} = 1 + W_1 + W_2 = 1.29$. After substituting the numbers in Equation 4.44 we will obtain

$$t_F = \frac{\Delta H_{beginning-final}}{(T_{beginning} - T_{final})(N_{EHTD})}\left[P\frac{L}{h} + R\frac{L^2}{k_{solid}}\right] = 31.6h.$$

Example 4.19: Freezing Time Calculation with the Mascheroni and Calvelo Equation

A slab of meat (water content = 74%, fat content = 5%, ρ = 1060 kg/m^3, thickness = 5 cm, initially at 8°C) is placed in a blast freezer ($h_1 = 36$ W/m^{2}K, $T_1 = -30°C$, $h_2 = 32$ W/m^{2}K, $T_2 = -25°C$). Determine the time required to reduce the thermal center to –10°C).

Solution: We will use equation 4.35 with $T_{coolant} = [(-30) + (-25)]/2 = -27.5°C$ and $T_{frozen} = [(-2.8) + (-27.5)]/2 = -15.5°C$. Thermal conductivity is commonly related to the moisture content of nonfat meat when heat flow is nonperpendicular to the fibers as (Pham and Willix 1989):

$$k_{unfrozen} = 0.080 + 0.52x \tag{2.47a}$$

$$k_{frozen} = -0.28 + 1.9x - 0.0092T, \tag{2.47b}$$

where $x = 74/26 = 2.86$ kgH_2O/kg dry matter, thermal conductivity k has the units of W/mK. After substituting x in Equations 2.47a and 2.47b we will calculate $k_{unfrozen} = 1.56$ W/mK and $k_{frozen} = 2.76$ W/mK. At the lowest medium temperature ($T_1 = -30°C$) thermal conductivity was $k_{low} = 2.89$ W/mK. The average thermal conductivity is $k_{average} = (k_{frozen} + k_{unfrozen})/2 = 2.16$ W/mK. The Biot numbers are $Bi_1 = 2h_1L/k_{frozen} = 0.65$, $Bi_2 = 2h_2L/k_{frozen} = 0.58$ and $Bi = 2h_1L/k_{low} = 0.62$. The temperature driving force of side 1 is 20% larger than that of side 2 and convective heat transfer coefficient of side 1 is 10% larger than that of side 2. Both the temperature driving force and the convective

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heat transfer function enhances the rate of the heat transfer rate on side 1 when compared to that of side 2. Since both of these effects are additive in nature we may estimate the thermal center to move toward the side by about 25%. Half of the slab thickness is 2.5 cm, with a 25% shift we may estimate $L = 2.5 \times 1.25 = 3.1$ cm $= 0.031$ m. Siebel's equation will be used to assume the specific heat as

$$c_{\text{unfrozen}} = 1674.72\omega_f + 837.36\ \omega_s + 4186.8\ \omega_w, \tag{2.45a}$$

$$c_{\text{frozen}} = 1674.72\ \omega_f + 837.36\ \omega_s + 2093.4\ \omega_w, \tag{2.45b}$$

where $\omega_f = 0.05$ (mass fraction of fat), $\omega_s = 0.21$ (mass fraction of nonfat solids), $\omega_w = 0.74$ (mass fraction of water) in the food. After substituting the numbers we will calculate $c_{\text{unfrozen}} = 3357.8$ J/kg K and $c_{\text{frozen}} = 1808.7$ J/kg K. We also calculate that $c_{\text{average}} = (c_{\text{frozen}} + c_{\text{unfrozen}})/2 = 2583.3$ J/kg K.

MATLAB® code E.4.19 uses Equation 4.45 with the outlined parameter values and estimates the time required to bring the thermal center from T_{initial} to $T_{\text{phase change}}$ (referred to as $t_{\text{precooling}}$) and

MATLAB® CODE E.4.19

Command Line:

```
clear all
close all
format compact

%  For meat
wc=0.74;  % water content
fc=0.05;  % fat content
d=1060;  % density, kg/m3
w=0.05;  % thickness, m
To=8;  % initial temperature, C
W=0.70; % average of ice content

%  For freezer
h1=36;  % W/m2.K
T1=-30; % C
h2=32; % W/m2.K
T2=-25; % C
Tc= -27.5; % Tcoolant=(T1+T2)/2, C
Tf=-15.5; % Tfrozen=(-27.5+(-2.8))/2, C
Tfr=0;  % Temperature for freezing beginning
kuf=1.56; % kunfrozen, W/m.K
kf=2.76; % kfrozen=, W/m.K
kl=2.89; % klow @ -30 C, W/m.K
kavg=2.16; % kaverage=(kfrozen+kunfrozen)/2, W/m.K
Bi1=0.65; % Bi1=2*h1*L/kfrozen
Bi2=0.58; % Bi2=2*h2*L/kfrozen
Bil=0.62; % Bil=2*h1*L/klow
cuf=3357.8; % cunfrozen, J/kg.K
cf=1808.7; % cfrozen, J/kg.K
cavg=2583.3; % caverage=(cfrozen+cunfrozen)/2, J/kg.K
```

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```
% For phase change
L=0.031; % m
H=333500;% J/kg
tpc=d*wc*H*W*L^2/((Tfr-Tc)*kf)*((1/Bi1)+1/2)

%  For pre-cooling
alpha=kavg/(d*cavg)
A=(Tfr-Tc)/(To-Tc)

% For tempering
Tfi=-10; % Final temperature attained by thermal center
B=(Tfi-Tc)/(Tfr-Tc)
%  Bi_min = 1 / (Min. Bi)
% Bi_max = 1 / (Max. Bi)
Bi_min = 0.1; Bi_max = 2; Bi_stp = 0.20;
Fo_min = 0; Fo_max = 4;
for b = (Bi_min):(Bi_stp):(Bi_max)
    Bi = 1/b;
if Bi >= 50
    Dt = 1.6;
elseif Bi >= 10
    Dt = 0.7;
elseif Bi >= 1
    Dt = 0.1;
elseif Bi >= 0.1
    Dt = 0.01;
elseif Bi >= 0.01
    Dt = 0.003;
end
G = 0; j = 0;
for i= 1:10000
    r = i / 1000;
    k(i) = r / cot(r);
    if (Bi - Dt) <= k(i)
        if k(i) <= (Bi + Dt)
            j = j + 1;
            G(j) = r;
        end
    end
    t(i) = r;
end
n = 1;
R(n) = G(1);
for l = 2:j
    if G(l) > (1.2*G(l-1))
        n = n + 1;
        R(n) = G(l);
    end
end

% Solve for 3 roots
for Fo = Fo_min:Fo_max
    sum = 0;
    for i = 1:3
        sum = sum + 2* exp(-(R(i)^2) * (Fo)) * (sin(R(i))*cos(R(i))
/ (R(i) + sin(R(i)) * cos(R(i))));
```

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```
    end
    Q(Fo+1) = sum;
    f(Fo+1) = Fo;
end
semilogy(f,Q); hold on;
end
xlabel('alpha*t/L^2')
ylabel('(T(t)-Tfinal)/(Tinitial-Tfinal)')
% insert texts to the figure
text(3.2, 0.018, '1/Bi=1.50'), % 3.2 and 0.018 are the distances
from the y and axis, respectively
text(3.2, 0.004, '1/Bi=1.70')
text(3.2, 0.0002, '1/Bi=1.90')
tpcmin=tpc/60;
fprintf('\n tphase change is %3.2f min\n',tpcmin)
```

When we run the code the following lines and Figure E.4.19 will appear on the screen:

```
tpc =
  4.7262e+003
alpha =
  7.8881e-007
A =
    0.7746
B =
    0.6364

 tphase change is 78.77 min
```

after freezing from the $T_{\text{phase change}}$ to T_{final} (referred to as $t_{\text{tempering}}$) with the following expression after substituting $z/L = 1$:

$$\frac{T(t)-T_{\text{final}}}{T_{\text{initial}}-T_{\text{final}}} = \sum_{n=1}^{\infty} \frac{\sin(\lambda_n)\cos(\lambda_n z/L)}{\lambda_n + \sin(\lambda_n)\cos(\lambda_n)} \exp\left(-\frac{\lambda_n^2 \alpha t}{(z/L)^2}\right), \tag{E.4.19.1}$$

where λ_n is the nonzero roots of

$$\lambda_n \tan(\lambda_n) = hL/k, \tag{E.4.19.2}$$

and computes the total freezing time t_F from the expression:

$$t_F = t_{\text{precooling}} + t_{\text{phase-change}} + t_{\text{tempering}}. \tag{E.4.19.3}$$

Use c_{average} in a while computing α of the tempering time.

Calculation of the precooling time: From the Figure E.4.19 for $(T_{\text{beginning of freezing}} - T_{\text{cooling medium}}) / (T_{\text{initial}} - T_{\text{cooling medium}}) = 0.77$ and $(1/\text{Bi}) = 1.5$ we will read $(\alpha t)/(z/L)^2 = 0.25$. Since $\alpha = 7.88 \times 10^{-7}$ m^2/s and $\alpha t/L^2 = 0.25$, we will end up with $t_{\text{precooling}} = 5.08$ minutes.

The calculation of the tempering time: from the Figure E.4.19 for $(T_{\text{thermal center}} - T_{\text{cooling medium}}) / (T_{\text{phasechange}} - T_{\text{final}}) = 0.64$ and $(1/\text{Bi}) = 1.5$, we will read $(\alpha t)/(z/L)^2 = 0.5$ and end up calculating $t_{\text{tempering}} = 10.16$ minutes.

It was already computed that $t_{\text{phase change}} = 78.77$ minutes, therefore $t_F = t_{\text{precooling}} + t_{\text{phase change}} + t_{\text{tempering}} = 5.08 + 78.77 + 10.16 = 94$ min.

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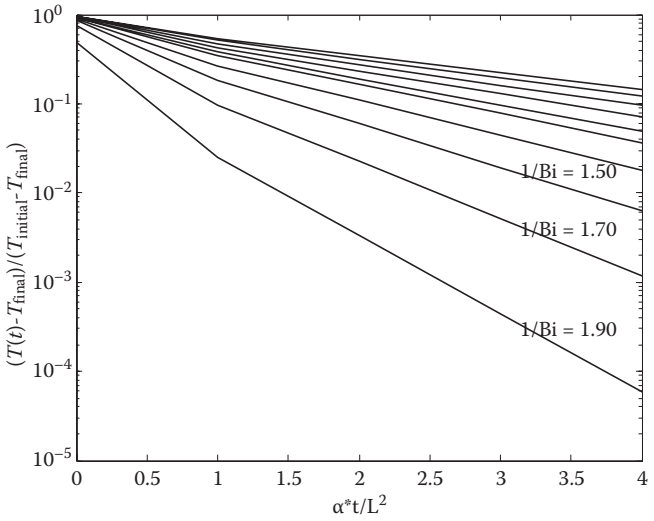


FIGURE E.4.19
Figure for precooling and tempering time calculations.

Example 4.20: Prediction of Freezing Temperature Profiles Along a Sphere During Freezing

During freezing and thawing processes, the energy balance around a sphere may be stated with the IC and BCs as

$$\rho c_p \frac{\partial T}{\partial t} = \frac{1}{r^2}\frac{\partial}{\partial r}\left(kr^2\frac{\partial T}{\partial r}\right), \tag{E.4.20.1}$$

$$\text{BC1a } k\left[\frac{dT}{dr}\right]_{r=R} = h\left(T_a - T_s\right) \text{ convective BC}, \tag{E.4.20.2}$$

$$\text{BC2 } \left[\frac{dT}{dr}\right]_{r=0} = 0 \text{ at } r = 0 \text{ when } t \geq 0, \tag{E.4.20.3}$$

$$\text{IC } T = T_0. \tag{E.4.20.4}$$

Mannapperuma and Singh (1988) determined $h = 300$ W/m²s during freezing a sphere of Tylose in a process with $R = 0.75$ cm, $T_0 = 15$°C, $T_a = -40$°C. The initial freezing point of Tylose, $T_f = -0.6$°C. The following values of the physical properties are adapted from Otero et al. (2006) and Norton et al. (2009):

	Unfrozen	Frozen
c_p(kJ/kg K)	3.78	2.10
k (W/mK)	0.49	1.67
ρ (kg/m³)	950	1015

Determine the temperature profile along the sphere of Tylose until the center reaches –25°C.

MATLAB® code E.4.20 presents the solution of the problem.

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MATLAB® CODE E.4.20

Command Window:

```
clear all
close all

m=2; % for sphere
r = linspace(0,0.75,20);
t = linspace(0,200,50);

sol = pdepe(m,@pdex1pde,@pdex1ic,@pdex1bc,r,t);
% Extract the first solution component as Temperature T.
T = sol(:,:,1);

% A surface plot is often a good way to study a solution.
surf(r,t,T)
title('Temperature distribution during freezing with varying
thermodynamic properties')
xlabel('r (cm)')
ylabel('Time (min)')
zlabel('Temperature (K)')

% Plot the temperature profile at the final time step.
figure
plot(r,T(end,:))
title('Solution at t = 200')
xlabel('r (cm)')
ylabel('Temperature (K)')
```

M-file1:

```
function [c,f,s] = pdex1pde(r,t,T,DTDr)
if ( T >= 267.15)
   cp = 3.78;
   rho = 950;
   k = 0.49;
else
   cp = 2.10;
   rho = 1015;
   k = 1.67;
end;

c = rho*cp;
f = k*DTDr;
s = 0;
```

M-file2:

```
function T0 = pdex1ic(r)
T0 = 288.15;
```

M-file3:

```
function [pl,ql,pr,qr] = pdex1bc(rl,Tl,rr,Tr,t)
h=300;
Text=233.15;
```

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```
pl = 0;
ql = 1;
pr = h*(Text-Tr);
qr = -1;
```

When we run the code Figures E.4.20.1 and E.4.20.2 will appear on the screen.

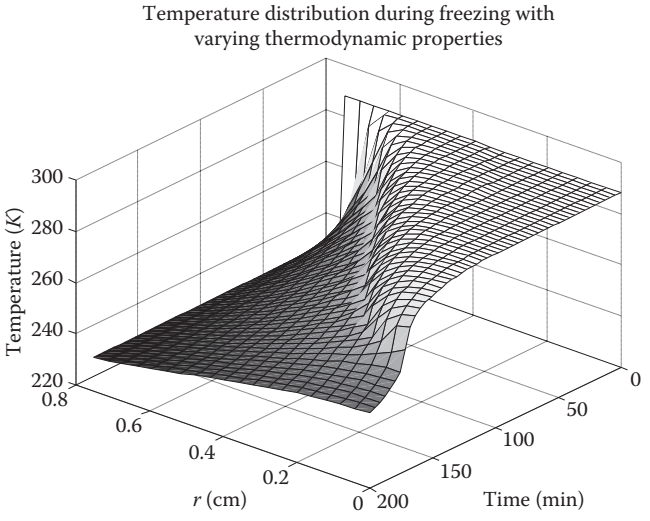


FIGURE E.4.20.1
Temperature distribution with respect to time and distance.

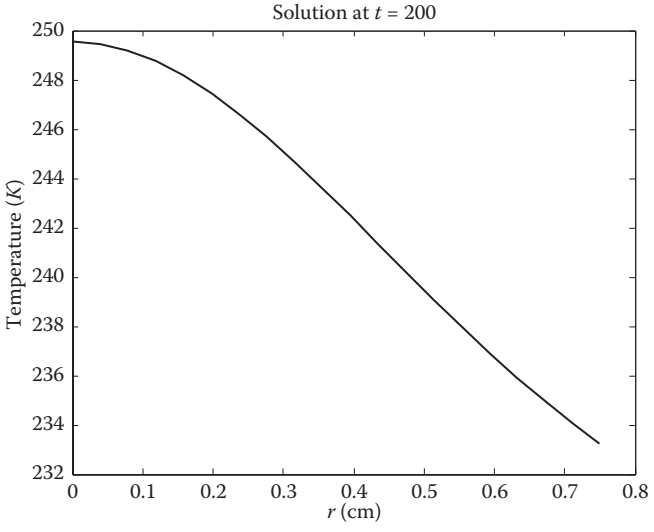


FIGURE E.4.20.2
Variation of the temperature along the radius when the center temperature reaches to –25°C (253 *K*).

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Example 4.21: Modeling of the Temperature Variations in a Slab-Shaped Food With an Enthalpy Method During the High Pressure Freezing Process

Under high pressure, the freezing point and the phase change enthalpy of water decreases, therefore the phase change is achieved in a shorter time as the pressure increases. Variation of the freezing point, ΔT, may be related with the pressure increase applied on the food ΔP as

$$\Delta T = \frac{\beta TV}{c_u}\Delta P, \tag{E.4.21.1}$$

where T is the freezing temperature at pressure P before applying the pressure increase, ΔP, and V is the specific volume of the food at T and P. Parameter β is the thermal expansion coefficient of water and its value changes with temperature. Parameter c_u is the specific heat of the unfrozen food. Equation E.4.21.1 may also be written as

$$T_{op} = T_0 - m(P - P_{atm}), \tag{E.4.21.2}$$

where T_{op} is the freezing temperature under applied pressure P and P_{atm} is the atmospheric pressure, m is a constant.

Enthalpy of foods may be calculated with the Schwartzberg equation below their initial freezing temperature T_o as

$$h = (T - T_r)\left[A + \frac{B}{(T_o - T)(T_o - T_r)}\right], \tag{E.4.21.3}$$

where A and B are constants, T is the temperature below the freezing point of water and T_r is the reference temperature of the enthalpy calculations. The enthalpy of unfrozen food may be calculated over the freezing point (0°C) as

$$h = h_0 + c_u T, \tag{E.4.21.4}$$

where h_0 is the enthalpy of the food at the freezing point. The heat of phase change (latent heat) at the atmospheric pressure may be calculated as

$$L = h_0 + T_f c_u - A(T_f - T_r). \tag{E.4.21.5}$$

Thermal conductivity of ice is larger than that of liquid water. Equation E.4.21.6 may be used to express the thermal conductivity at the temperatures below the initial freezing point:

$$k = k_f + (k_u - k_f)\left(\frac{T_0 - T_f}{T_0 - T}\right). \tag{E.4.21.6}$$

Density of the product below the initial freezing point may be calculated as

$$\rho = \rho_f + (\rho_u - \rho_f)\left(\frac{h - A(T_f - T_r)}{L_p}\right), \tag{E.4.21.7}$$

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where subscripts *u* and *f* refer to frozen and unfrozen states, respectively. Thermal energy balance around the food requires

$$\frac{\partial h}{\partial t} = \frac{1}{r^p}\frac{\partial}{\partial r}\left(kr^p\frac{\partial T}{\partial r}\right), \tag{E.4.21.8}$$

where $p = 0$ for an infinite slab, $p = 1$ for an infinite cylinder, or $p = 2$ for a sphere with

IC: $T = T_i$ when $t = 0$ for all r

BC1: $\dfrac{dT}{dR} = 0$ at $r = 0$ when $t > 0$

BC2: $\left[-k\dfrac{dT}{dR}\right]_{r=R} = h_c\left[T(R,t) - T_\infty\right]$ at $r = R$ when $t > 0$.

Equation E.4.21.8 is converted into a finite difference equation. At the center plane

$$\Delta h_{t,1} = \frac{4k_{t,1}\left(T_{t-1,2} - T_{t-1,1}\right)}{\rho_{t,1}(\Delta r)^2}\Delta t, \tag{E.4.21.9}$$

at the interior points:

$$\Delta h_{t,i} = \frac{k_{t,i}\left(T_{t-1,i+1} - T_{t-1,i}\right)\left(i + \frac{1}{2}\right) - k_{t,i-1}\left(T_{t-1,i} - T_{t-1,i-1}\right)\left(i - \frac{1}{2}\right)}{i\rho_{t,i}(\Delta r)^2}\Delta t, \tag{E.4.21.10}$$

on the surface:

$$\Delta h_{t,n} = 2\frac{h_c\left(T_\infty - T_{t-1,n}\right) - k_{t,n}\left(T_{t-1,n} - T_{t-1,n-1}\right)}{\rho_{t,n}\Delta r}\Delta t, \tag{E.4.21.11}$$

then we may compute enthalpies at any point as

$$h_{t,n} = h_{t-1,n} + \Delta h_{t,n}. \tag{E.4.21.12}$$

Equation E.4.21.12 may be rearranged to determine

$$T_{t,n} = (h_{t,n} - h_o)/c_u. \tag{E.4.21.13}$$

Initial enthalpy of the food was

$$h_{1,i} = c_u T_{1,i} + h_o. \tag{E.4.21.14}$$

Equations E.4.21.1 through E.4.21.14 are combined, solved, and compared with the experimental data in MATLAB® code E.4.21.

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MATLAB® CODE E.4.21

Command Window:

```
clear all
close all

% OBTAIN AN EXPRESSION FOR THERMAL EXPANSION COEFFICIENT (beta) of
WATER AS A FUNCTION OF THEMPERATURE
Tbeta=[0.01 1 4 5 10 15 20 30]; % temperatures where beta of water
were recorded (data)
beta=[-7e-6 -50e-6 0 16e-6 88e-6 151e-6 207e-6 303e-6]; % values of
beta (data)
plot(Tbeta, beta, '*') ; hold on; % plot beta versus temperature
(data)
xlabel('T (^o C)');
ylabel('beta (1/K)');

% fit a polynomial empirical model to the data
N=6; % determine N by trial and error to obtain good agreement
between model & data
c1=polyfit((Tbeta+273),beta,N);
betaModel=polyval(c1,(Tbeta+273));
plot(Tbeta, betaModel, ':') ; hold on;
legend('data', 'best fitting curve', 'Location','SouthEast')

%  MODELING TEMPERATURE HISTORIES DURING HIGH PRESSURE SHIFT
tData209 = [0 20 40 50 60 70 80 100 120 140 180 190 210 240 270 300
310 320 330 340 350 380 420 460 500 540 600 700]; % times data
recorded at 209 MPa (s)
Tdata209 = [3 2.5 1.5 0.5 -1 -3 -5 -8 -13 -17 -22 -24 -24 -25 -25
-26 -27 -30 -33 -35 -37 -38 -40 -40.5 -41 -42 -43 -44]; %
temperature data recorded at 209 MPa (oC)

tData140 =[20 30 40 50 60 75 80 100 105 130 150 170 185 220 230 235
240 270 300 310 340 350 355 360 365 370 375 380 390 420 450 480 510
540 560 580 600 630 660 680 710]; % times data recorded at 140 MPa
(s)
Tdata140 =[13 13 12.5 10.5 9.5 3 5 4 2.2 -0.7 -5 -9.5 -10.5 -15 -16
-16.5 -14.5 -14.5 -14.5 -15 -16 -17.5 -19 -21.5 -25 -26.5 -28 -28.5
-30.5 -31.7 -32 -33 -34 -34.1 -34.2 -34.5 -34.5 -35 -35.5 -37 -38];
% temperature data recorded at 140 MPa (oC)

% plot the data
figure
plot(tData209, Tdata209, '*', tData140, Tdata140, 'o') ; hold on;
xlabel('Time (s)');
ylabel('Temperature (C)');
legend('P=209 MPa', 'P=140 MPa', 'Location','NorthEast')
ylim([-50 20]);

% experimental conditions
Pa=[209 140]; % pressure (MPa)
tSurface=[270 290]; % time when the surface attained Tinfa (s)
Tia=[2 12]; % initial temperature of the food (oC)
Tinfa=[24 16]; % temperature of the fluid surrounding the food (oC)
```

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```
Tsa=[46 39]; % surface temperature the food (oC)

% constants of the model
Cu=3.78; % unfrozen specific heat (kJ/kg K)
RhoU=1006; % density of the unfrozen food (kg/m3)
RhoF=950; % % density of the frozen food (kg/m3)
A=2083; % Schwartzberg constant (kJ/kg K)
B=134; % Schwartzberg constant (kJ/kg K)
V=0.001; % specific volume kg/m3
ku=[0.499 0.49]; % thermal conductivity of unfrozen matter (W/mK)
kf=[1.74 1.645]; % thermal conductivity of unfrozen matter (W/mK)
ho=3e5; % enthalpy at 0 oC (kJ/kg)
Patm=101e3; % atmospheric pressure (MPa)
m=-0.0001; % constant in equation [E.4.21.2]
hc=250; % convective surface heat transfer coefficient (W/m2 K)

for r=1:2 % r=1 experiments with P=209 kPa, r=2 experiments with
P=140 kPa,

    deltaP=Pa(r); % pressure after increase (MPa)
    tlim=730; % duration of the process (s)
    dp=deltaP/tlim; n=5; P=101e3+dp;
    dr=0.1; dt=1;

    Ti=273+Tia(r); % initial temperature of the food (K)
    Tr = Ti; % reference temperature (K)
    To = -0.6; % initial freezing point under the atmospheric
pressure (oC)
    Tinf=273-Tinfa(r); % temperature of the surrounding freezing
medium  (K)
    Tfr =273-1.1; % freezing temperature (K)
    Ts=273-Tsa(r); % surface temperature (K)

   for i=1:n % initial condition
      T(1,i)=Ti; % initial temperature of the food
      h(1,i)=Cu*T(1,i)+ho; % initial enthalpy of the food
      Tf(1,i)=Tfr; % surface attains the freezing temperature
immediately
   end

BETA=c1(1)*T(1,n)^6+c1(2)*T(1,n)^5+c1(3)*T(1,n)^4+c1(4)*T(1,n)^3+c1(
5)*T(1,n)^2+c1(6)*T(1,n)+c1(7); % thermal expansion coefficient
(1/K)
deltaT=dp*Ti*V*BETA/Cu; % change in the freezing point due to deltaP
(K)
T(1,n)=T(1,n)-deltaT; % temperature of the food after the pressure
shift at t=0

Lp=ho+Tfr*Cu- m*(P-Patm)*Cu-A*(Tf-Tr); % enthalpy of phase change
under pressure (kJ/kg)
a=4; % parameter for new freezing point of sample

for t = 2:tlim

    if t > tSurface(r)
        Tinf=Ts;
```

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```
    end

    P=P+dp;
    Top=To+m*(P-Patm)+273; % initial freezing temperature under
pressure (K)
    Lp=ho+Tf((t-1),1)*Cu-m*(P-Patm)*Cu-A*(Tf((t-1),1)-Tr); %
enthalpy of phase change under pressure (kJ/kg)
    k(t,1)=kf(r)+(ku(r)-kf(r))*((Top-Tf((t-1),1))/(Top-T((t-1),1)));
% thermal conductivity for temperatures below the initial freezing
point (W/mK)
    Rho(t,1)=RhoF+(RhoU-RhoF)*((h((t-1),1)-A*(Tf((t-1),1)-Tr))/Lp);
% density of the product below the initial freezing point (kg/m3)
    dh(t,1)=4*k(t,1)*(T((t-1),2)-T((t-1),1))*dt/(Rho(t,1)*(dr^2));
    h(t,1)=h((t-1),1)+dh(t,1);
    T(t,1)=(h(t,1)-ho)/Cu;
    BETA=c1(1)*T(t,1)^6+c1(2)*T(t,1)^5+c1(3)*T(t,1)^4+c1(4)*T(t,1)^3
+c1(5)*T(t,1)^2+c1(6)*T(t,1)+c1(7); % thermal expansion coefficient
(1/K)
    deltaT=dp*T(t,1)*V*BETA/Cu; % change in the freezing point due
to deltaP (K)
    T(t,1)=T(t,1)-deltaT;
    Tf(t,1)=Tf((t-1),1)-deltaT*a;

    for i=2:(n-1)
           if t>tSurface(r)
              Tinf=Ts;
           end
        Lp=ho+Tf((t-1),i)*Cu-m*(P-Patm)*Cu-A*(Tf((t-1),i)-Tr); %
enthalpy of phase change under pressure (kJ/kg)
        k(t,i)=kf(r)+(ku(r)-kf(r))*((Top-Tf((t-1),i))/(Top-T((t-
1),i))); % thermal conductivity for temperatures below the initial
freezing point (W/mK)
        Rho(t,i)=RhoF+(RhoU-RhoF)*((h((t-1),i)-A*(Tf((t-1),i)-Tr))/
Lp); % density of the product below the initial freezing point (kg/
m3)
        dh(t,i) = (k(t,i)*(T((t-1),(i+1))-T((t-1),i))*(i+(1/2))-
k(t,(i-1))*(T((t-1),i)-T((t-1),(i-1))) *(i-(1/2)))*dt/
(i*Rho(t,i)*(dr^2));
        h(t,i)= h((t-1),i)+dh(t,i);
        T(t,i)=(h(t,i)-ho)/Cu;
        BETA=c1(1)*T(t,i)^6+c1(2)*T(t,i)^5+c1(3)*T(t,i)^4+c1(4)*T(t,
i)^3+c1(5)*T(t,i)^2+c1(6)*T(t,i)+c1(7); % thermal expansion
coefficient (1/K)
        deltaT=dp*T(t,i)*V*BETA/Cu; % change in the freezing point
due to deltaP (K)
        T(t,i)=T(t,i)-deltaT;
        Tf(t,i)=Tf((t-1),i)-deltaT*a;

    end

           if t>tSurface(r)
              Tinf=Ts;
           end

    Lp=ho+Tf((t-1),i)*Cu-m*(P-Patm)*Cu-A*(Tf((t-1),i)-Tr); %
enthalpy of phase change under pressure (kJ/kg)
```

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```
    k(t,n)=kf(r)+(ku(r)-kf(r))*((Top-Tf((t-1),n))/(Top-T((t-1),n)));
% thermal conductivity for temperatures below the initial freezing
point (W/mK)
    Rho(t,n)=RhoF+(RhoU-RhoF)*((h((t-1),n)-A*(Tf((t-1),n)-Tr))/Lp);
% density of the product below the initial freezing point (kg/m3)
    dh(t,n)=2*(hc*(Tinf-T((t-1),n))-k(t,n)*((T((t-1),n)-T((t-
1),(n-1)))/dr))*dt/(Rho(t,n)*dr);
    h(t,n)=h((t-1),n)+dh(t,n);
    T(t,n)=(h(t,n)-ho)/Cu;
    BETA=c1(1)*T(t,n)^6+c1(2)*T(t,n)^5+c1(3)*T(t,n)^4+c1(4)*T(t,n)^3
+c1(5)*T(t,n)^2+c1(6)*T(t,n)+c1(7); % thermal expansion coefficient
(1/K)
    deltaT=dp*T(t,n)*V*BETA/Cu; % change in the freezing point due
to deltaP (K)
    T(t,n)=T(t,n)-deltaT;
    Tf(t,n)=Tf((t-1),n)-deltaT*a;

end

%  plot the model temperatures
    if r==1 plot(T(:,1)-273,':'); hold on; end
    if r==2 plot(T(:,1)-273,'-'); hold on; end

end
```

When we run the code Figures E.4.21.1 and E.4.21.2 will appear on the screen.

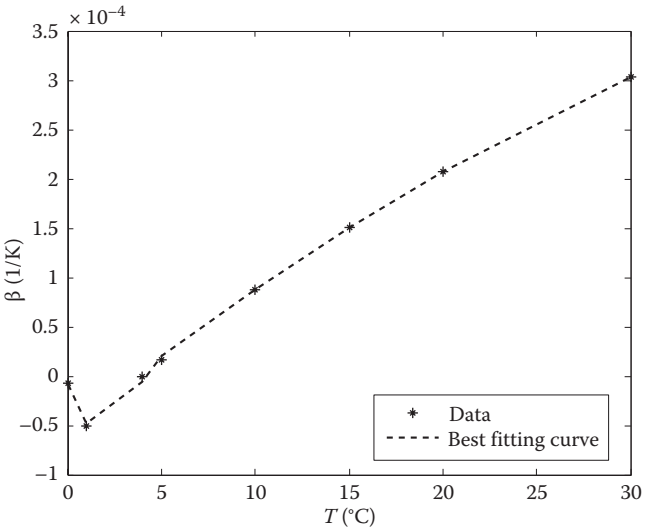


FIGURE E.4.21.1
Variation of the thermal expansion coefficient (*b*) of water with temperature.

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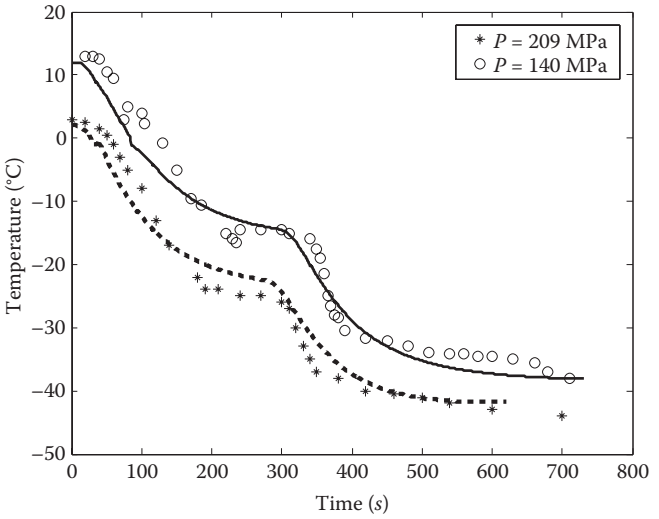


FIGURE E.4.21.2
Temperature histories for the pressure-aided freezing process of a potato sample. Experimental data adapted from Norton, T., Delgado, A., Hogan, E., Grace, P., and Sun, D., *Journal of Food Engineering*, 91, 260–68, 2009.)

4.3 Kinetic Modeling of Crystallization Processes

There are two basic types of crystallization processes involved in food processing: Crystallization from a solution and crystallization from a melt. The typical examples to crystallization from a solution are crystal sugar production, crystallization of sugar in jams, potassium acid tartarate precipitation in wines, crystallization of high melting point glycerides in vegetable oils, and so on. The major example to crystallization from a melt is the freezing and freeze concentration processes.

Crystallization occurs in two distinct steps: *Nucleation* and *crystal growth*. Various kinds of nucleation have been identified. Spontaneous or primary nucleation occurs due to high supersaturation in the absence of crystals. The approximate supersolubility curve for sucrose is shown in Figure 4.3. Nucleus formation starts above the supersolubility curve. In the metastable zone, crystals may grow but nucleation can not occur. Crystals dissolve when concentration is below the solubility curve.

Secondary nucleation is caused by the presence of particles of a material that is being crystallized. Adding seed crystals to a solution in the metastable zone is a typical application of the secondary nucleation process. *Contact nucleation*, a special case of the secondary nucleation, is the formation of new nuclei from a parent crystal of the material being crystallized. Crystals may collide with each other or with the surface of the crystallization equipment and give birth to new crystals. A solution may be brought into a labile or metastable zone after cooling at a constant concentration or concentrating at a constant temperature. Evaporators are used to achieve the later process.

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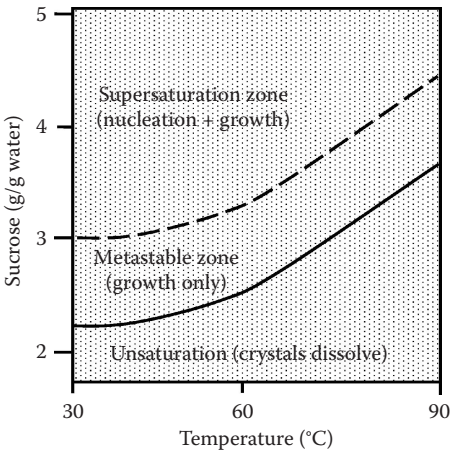


FIGURE 4.3
Approximate supersolubility curve for sucrose.

During *homogeneous nucleation* molecules combine spontaneously, without the presence of any foreign molecules, to form an embryo, which may grow further and form the nucleus:

$$A + A \underset{\leftarrow}{\overset{\rightarrow}{}} A_2,$$

$$A_2 + A \underset{\leftarrow}{\overset{\rightarrow}{}} A_3,$$

and

$$A_{n-1} + A \underset{\leftarrow}{\overset{\rightarrow}{}} A_n.$$

Embryos smaller than a critical size may not grow and dissociate. During *heterogeneous nucleation*, the embryos are formed on the catalytic surfaces of foreign particles.

Example 4.22: Critical Embryo Size for Stable Ice Nucleation

The total Gibbs free energy of formation of an embryo (ΔG) is (Franks 1982)

$$\Delta G = \frac{4}{3}\pi r^3 \Delta G_v + 4\pi r^2 \sigma, \tag{E.4.22.1}$$

where r = radius of the embryo, ΔG_v = Gibbs energy of forming the bulk solid from the liquid phase, and σ is the interfacial tension between water and the embryo. The term $(4/3)\pi r^3 \Delta G_v$ is

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always negative below 0°C, therefore favors nucleation. It becomes increasingly more negative as the radius of the particle increases. This term relates mostly to the decrease in Gibbs energy when hydrogen bonds form during the association of water molecules in an ordered particle. The term $4\pi r^2\sigma$ is the Gibbs free energy of the formation of the interface between the embryo and water. It is always positive and does not favor nucleation. It becomes increasingly larger as the radius of the particle increases. Figure E.4.22 shows a variation of ΔG during the formation of an embryo as a function of r. At the maximum:

$$\frac{\partial(\Delta G)}{\partial r} = 4\pi r^2 \Delta G_v + 8\pi r\sigma, \tag{E.4.22.2}$$

implying that the *critical radius* is

$$r_c = \frac{2\sigma}{\Delta G_v}. \tag{E.4.22.3}$$

The maximum represents the *Gibbs free energy of activation* for nucleation at the temperature under consideration. After substituting Equation E.4.22.3 in Equation E.4.22.1 we will obtain the Gibbs free energy of activation as

$$\Delta G^* = \frac{16\pi\sigma^2}{3\Delta G_v^2}. \tag{E.4.22.4}$$

MATLAB® code E.4.22 exemplifies the use of Equations E.4.22.1 through E.4.22.4 to compute the critical radius r_c.

MATLAB® CODE E.4.22

Command Window:

```
clear all
close all

% introduce the data
DeltaGv=-4*10^10; % j/m3
sigma=250*10^-2; % j/m2
R=0;
DeltaR=0.5*10^-12;

%  compute the volume, surface and total Gibbs free energies of the
clusters
for i=1:800
r(i)=R;
VolumeEnergy(i)=(4/3)*3.14*(r(i).^3)*DeltaGv;
SurfaceEnergy(i)=4*3.14*(r(i).^2)*sigma;
DeltaG(i)= VolumeEnergy(i) + SurfaceEnergy(i);
R=R+DeltaR;
end

%  prepare the figure
plot(r,VolumeEnergy,':'); hold on
plot(r,SurfaceEnergy,'--'); hold on
```

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```
plot(r,DeltaG, '-')
legend('Volume Energy', 'Surface Energy', 'Total Energy',
3,'Location','SouthWest')
xlabel('r (nm)');
ylabel('DeltaG (J)');

%  find the maximum energy barrier that the cluster passed through
DeltaGmax=max(DeltaG);

%  search for the critical cluster radius
R=0;
for i=1:800
r(i)=R;
VolumeEnergy(i)=(4/3)*3.14*(r(i).^3)*DeltaGv;
SurfaceEnergy(i)=4*3.14*(r(i).^2)*sigma;
DeltaG(i)= VolumeEnergy(i) + SurfaceEnergy(i);
Error=abs((DeltaGmax-DeltaG(i))/DeltaGmax);
   if (Error<1e-008)
     Rc=R;
   end
R=R+DeltaR;
end
fprintf('\n\nRc= %.2g m\n', Rc)
```

When we run the code the following line and Figure E.4.22 will appear on the screen:

```
Rc= 1.2e-010 m
```

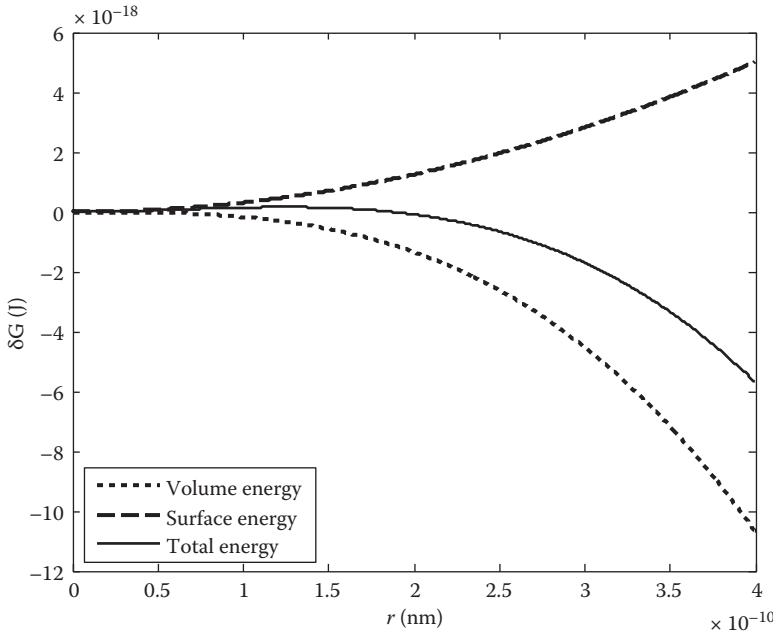


FIGURE E.4.22
Variation of the volume, surface, and total Gibbs free energy of a cluster with radius during nucleation.

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At a critical cluster size, by gaining a further molecule, the free energy of transfer from bulk to a cluster becomes negative and the nucleation process becomes spontaneous. The homogeneous nucleation rate is determined by the rate by which the clusters of critical size gain a further molecule. Hoffman (1958) and (Buckle 1961) have shown that the homogeneous nucleation rate may be expressed as

$$J = A\exp(B\tau_\theta), \tag{4.46}$$

where τ_θ is a function of reduced temperature θ.

$$\tau_\theta = \frac{1}{\theta^3(1-\theta)^2} \tag{4.47}$$

in which $\theta = T/T_m$, where T = process temperature, T_m = equilibrium melting point.

Example 4.23: Kinetics of Nucleation

Charoenrein and Reid (1989) studied homogeneous ice nucleation in water and sucrose solutions. Water or a sucrose solution was dispersed in continuous phase (silicone oil) to obtain $10^6 - 10^7$ drops per unit volume. Growth of the ice crystals is rapid compared to nucleation, therefore the rate of the nucleation process was assumed to be the same as droplet freezing and determined after measuring the heat released in a differential scanning calorimeter. It is believed that heterogeneous nucleation is predominant and more important than homogeneous nucleation in foods. Özilgen and Reid (1993) applied the same procedure as (Charoenrein and Reid 1989) to study heterogeneous nucleation kinetics by using *Pseudomonas syringae* as the nucleating agent in the D-alenine solutions. The rate of both homogeneous and heterogeneous nucleation per unit volume was simulated with Equation 4.46. MATLAB® code E.4.23.a compares the model with the experimental data.

MATLAB® CODE E.4.23.a

Command Window:

```
clear all
close all
format compact

% enter the homogeneous nucleation data
tau1Data=[729 759 788 833 891 950 994 1068 1125];
tau2Data=[288 303 306 318 332 347];
lnJ1data=[34.8 34.7 34.6 34.4 34.2 34.0 33.8 33.6 33.7];
lnJ2data=[34.4 34.0 33.9 33.7 33.4 32.9];

% plot the data
plot(tau1Data,lnJ1data,'o') ; hold on
plot(tau2Data, lnJ2data,'*') ; hold on
legend('15 % sucrose','50 % sucrose',2,'Location','SouthEast')
xlabel('tau')
ylabel('log(J)   (nuclei/s)')
title('Homogeneous Nucleation')
```

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```
% determine the model coefficients,
f1= polyfit(tau1Data,lnJ1data,1);
fp1= polyval(f1, tau1Data);
B1= f1(1)
A1=exp(f1(2))

f2= polyfit(tau2Data,lnJ2data,1);
fp2= polyval(f1,tau2Data);
B2= f2(1)
A2=exp(f2(2))

% compute and plot the model
J1model=A1*(exp(B1*tau1Data));
lnJ1model=log(J1model);
plot(tau1Data,lnJ1model,' :'); hold on

J2model=A2*(exp(B2*tau2Data));
lnJ2model=log(J2model);
plot(tau2Data, lnJ2model,' -') ; hold on

% enter the heterogeneous nucleation data
tau3Data=[420 450 480 520 550];
tau4Data=[420 450 480 520 550];
lnJ3data=[-1.1 -1.3 -1.5 -1.8 -2.18];
lnJ4data=[ -1.4 -1.45 -1.57 -1.6 -1.65];

figure
% plot the data
plot(tau3Data,lnJ3data,'o') ; hold on
plot(tau4Data, lnJ4data,'*') ; hold on
legend('no D-alanine','1.5 M/L D-alanine',2,'Location','SouthEast')
xlabel('tau')
ylabel('log(J)   (nuclei/s)')
title('Heterogeneous Nucleation')

% determine the model coefficients,
f3= polyfit(tau3Data,lnJ3data,1);
fp3= polyval(f3, tau3Data);
B3= f3(1)
A3=exp(f3(2))

f4= polyfit(tau4Data,lnJ4data,1);
fp4= polyval(f4, tau4Data);
B4= f4(1)
A4=exp(f4(2))

% compute and plot the model
J3model=A3*(exp(B3*tau3Data));
lnJ3model=log(J3model);
plot(tau3Data,lnJ3model,' :'); hold on

J4model=A4*(exp(B4*tau4Data));
lnJ4model=log(J4model);
plot(tau4Data, lnJ4model,' -') ; hold on
```

When we run the code the following lines and Figures E.4.23.1 and E.4.23.2 will appear on the screen:

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```
B1 =
   -0.0031
A1 =
  1.2291e+016
B2 =
   -0.0242
A2 =
  9.1988e+017
B3 =
   -0.0081
A3 =
   10.2565
B4 =
   -0.0020
A4 =
    0.5549
```

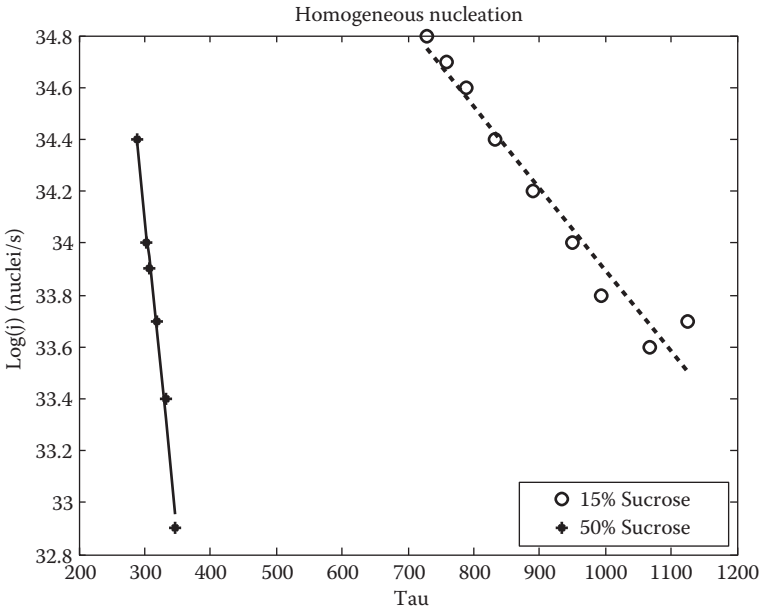


FIGURE E.4.23.1
Variation of the homogeneous ice nucleation rate ln(*J*) as a function of parameter τ_θ in solutions *of sucrose in water*. (From Charoenrein, S. and Reid, D. S., *Thermochimica Acta*, 156, 373–81, 1989.)

Shi, Liang, and Hartel (1990) suggested the following equations while studying the nucleation and growth rates of lactose monohydrate in a continuous cooling crystallizer:

$$J_N = B/M_t = K_1 \exp\{-K_2/RT\}(S-1)^{1.9}, \tag{E.4.23.1}$$

$$J_G = K_3 \exp\{-K_4/RT\}(S-1)^{2.5}, \tag{E.4.23.2}$$

where J_N and J_G are the nucleation (number of nuclei/g crystals min) and the linear growth (μm/min) rates, respectively. Parameter K_1 – K_4 are constants, B is the birth rate of the nuclei,

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and M_t is the suspension density of the crystals. Parameter S is the supersaturation ratio, defined as

$$S = \frac{c}{c_s - FK_m(c - c_s)}, \tag{E.4.23.3}$$

where c = total crystal concentration; c_s = equilibrium solubility of lactose; F = temperature dependent factor for depression of solubility of α-lactose by β-lactose and K_m = ratio of β/α lactose in a mutarotation equilibrium. MATLAB® code E.4.23.b compares Equations E.4.23.1 and E.4.23.2 with the experimental data and are depicted in Figures E.4.23.3 and E.4.23.4.

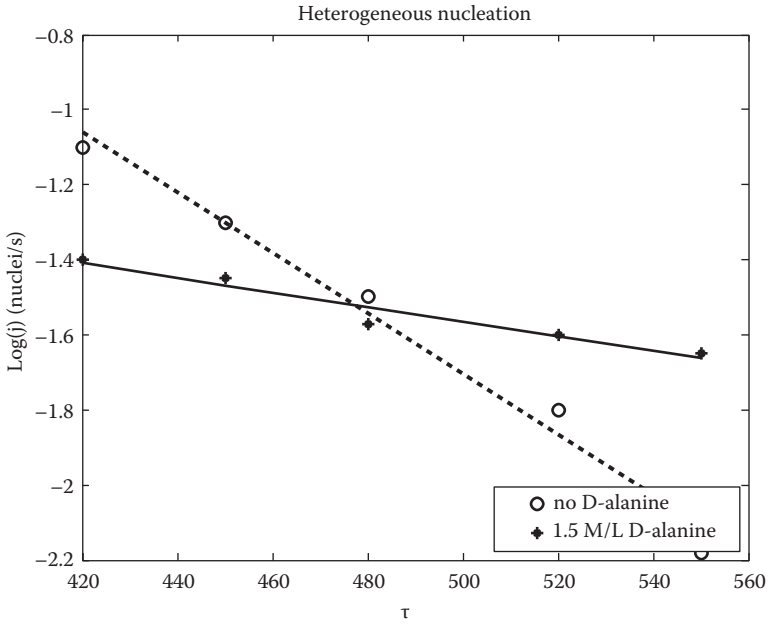


FIGURE E.4.23.2
Variation of the heterogeneous ice nucleation rate ln(J) as a function of parameter τ_θ in solutions *of Pseudomonas syringae* and D-alenine. (From Özilgen, S. and Reid, D. S., *Lebensmittel-Wissenschaft und Technologie*, 26, 116–20, 1993.)

MATLAB® CODE E.4.23.b

Command Window:

```
clear all
close all
format compact

R = 8.314; % gas constant J/mol K

% enter the nucleation and growth data at 333 K
sData1=[0.252 0.275 0.293 0.32 0.361 0.391 0.415]; % (S-1) at 333K
```

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```
MtData1=[1.74e-3 8.25e-3 6.77e-3 53.1e-3 7.69e-3 0.525e-3 3.78e-3];
% suspension density (g crystal/mL suspension)
BData1=[1078 22413 17034 83994 8851 2262 11143]; % nucleation rates
at 333K (number/mL min)
JnData1= log(BData1./ MtData1); % nucleation rates normalized by
suspension density at 333K (number/g min)
JgData1=[0.59 0.66 1.11 1.29 1.73 2.65 2.95]; % crystal growth rates
at 333K (micrometer/min)

% enter the nucleation and growth data at 313 K
sData2=[0.392 0.488 0.52 0.631 0.639 0.754 0.837 0.924 1.0 1.089
1.138]; % (S-1) at 313K
MtData2=[0.051 0.92 1.03 52.7 9.55 28.6 8.2 2.8 10.0 0.465 4.04]; %
suspension density (g crystal/mL suspension)
BData2=[27 181 1095 48104 8289 86821 10039 2988 42596 2709 14715]; %
nucleation rates at 313K (number/mL min)
JnData2= log(BData2./ MtData2); % nucleation rates normalized by
suspension density at 313K (number/g min)
JgData2=[0.28 0.41 0.54 0.83 1.02 1.2 1.26 1.85 2.14 2.42 3.71]; %
crystal growth rates at 313K (micrometer/min)

% plot the nucleation data
plot(sData1,JnData1,'o') ; hold on
plot(sData2,JnData2,'d') ; hold on
legend('333 K','313 K',2,'Location','SouthEast')
xlabel('Supersaturation (S-1)')
ylabel('ln(Nucleation Rate)')

% compute and plot the nucleation model at 333 K
T=333; % K
increment=0.5/length(sData1);
for i=1:length(sData1);
sModel1(i)=increment*i;
JnModel1(i)=log((1.99e7)*(exp(-71.1./(R*T))).*((sModel1(i)).^1.9));
end

plot(sModel1, JnModel1,' :'); hold on

T=313; % K
increment=1.2/length(sData2);
for i=1:length(sData2)
sModel2(i)=increment*i;
JnModel2(i)=log((1.99e3)*(exp(-71.1./(R*T))).*((sModel2(i)).^1.9));
end

plot(sModel2, JnModel2,' -'); hold on
xlim([0.2 1.2]); % limits of the x-axis

% plot the crystal growth data
figure
plot(sData1,log(JgData1),'o') ; hold on
plot(sData2,log(JgData2),'d') ; hold on
legend('333 K','313 K',2,'Location','SouthEast')
xlabel('Supersaturation (S-1)')
ylabel('ln(Crystal Growth Rate)')
```

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```
% compute and plot the crystal growth model at 333 K
T=333; % K
increment=0.5/length(sData1);
for i=1:length(sData1);
sModel1(i)=increment*i;
JgModel1(i)=log((12)*(exp(-92.4./(R*T))).*((sModel1(i)).^1.9));
end

plot(sModel1, JgModel1,' :'); hold on

T=313; % K
increment=1.2/length(sData2);
for i=1:length(sData2)
sModel2(i)=increment*i;
JgModel2(i)=log((1.99)*(exp(-92.4./(R*T))).*((sModel2(i)).^1.9));
end

plot(sModel2, JgModel2,' -'); hold on
xlim([0.2 1.2]); % limits of the x-axis
```

When we run the code Figures E.4.23.3 and E.4.23.4 will appear on the screen.

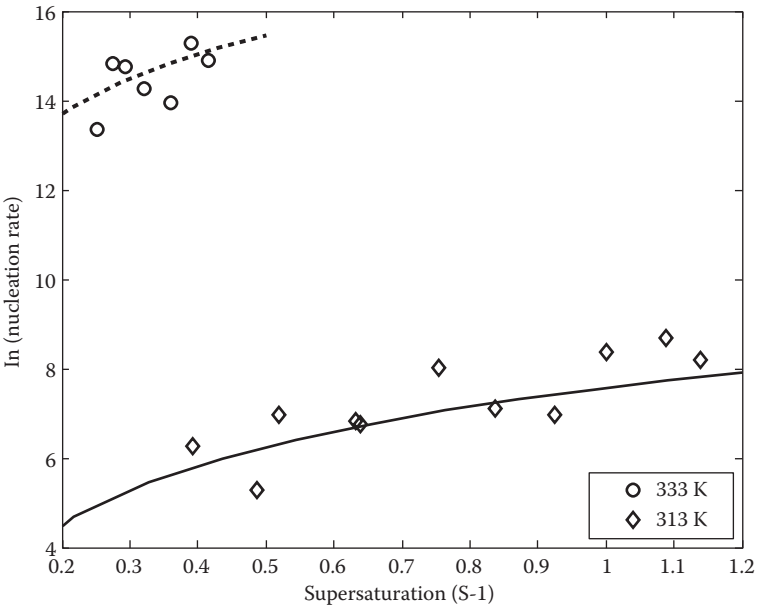


FIGURE E.4.23.3
Comparison of the nucleation rate (normalized by suspension density) models (lines) with the data (symbols) at 333 and 313 K. (Adapted from Shi, Y., Liang, B., and Hartel, R. W., *Journal of Food Science*, 55, 817–20, 1990.)

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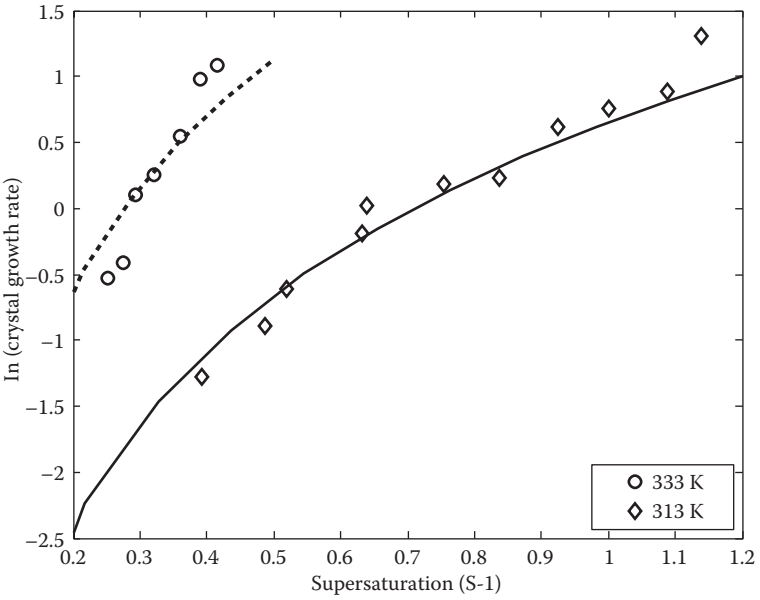


FIGURE E.4.23.4
Comparison of the crystal growth rate models (lines) with the data (symbols) at 333 and 313 K. (Adapted from Shi, Y., Liang, B., and Hartel, R. W., *Journal of Food Science,* 55, 817–20, 1990.)

The rate of growth of a crystal in a solution is dependent on temperature and concentration of liquid at the crystal face. Qualitative temperature and concentration profiles near the crystal surface are depicted in Figures 4.4a and 4.4b.

During crystal growth in a solution, solute molecules diffuse through the laminar film surrounding the crystal and join the lattice with a surface reaction. Crystal growth rate may be expressed as a function of the mass transfer as (Richardson, Backhurst, and Harker 2002):

$$\frac{dm}{dt} = kA\left(c_A - c_B\right), \tag{4.48}$$

where A = interfacial area. Mass transfer coefficient k may be expressed by using the film model (Example 2.16) as

$$k = \frac{D}{\delta}, \tag{4.49}$$

where D = diffusivity of the solute, δ = hypothetical film thickness. The surface reaction rate on the interface is directly proportional to the supersaturation at the interface (Richardson, Backhurst, and Harker 2002):

$$\frac{dm}{dt} = K_s A\left(c_B - c_S\right)^n, \tag{4.50}$$

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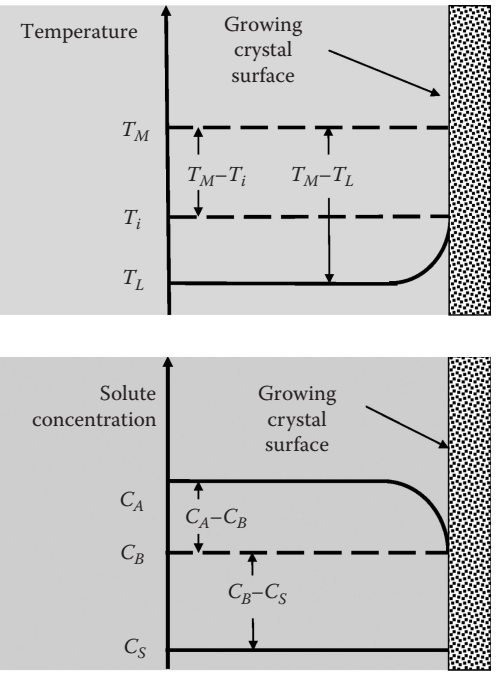


FIGURE 4.4
(a) Qualitative temperature profile for crystallization from a melt T_i = temperature of the interface, T_L = temperature of the liquid, T_M = melting point. (b) Qualitative concentration profile for crystallization from a solution. The c_A = concentration of the solute in the bulk liquid, c_B = concentration of the solute on the crystal surface, and c_S = concentration of the saturated liquid.

where K_s = surface reaction rate constant and n = constant. When $n = 1$ after combining Equations 4.48, 4.49, and 4.50 we will obtain an expression for the crystal growth rate in a solution when both the surface reaction and the mass transfer rates are not negligible as

$$\frac{dm}{dt} = \frac{A(c_A - c_S)}{\frac{\delta}{D} + \frac{1}{K_S}}. \tag{4.51}$$

Example 4.24: Kinetics of Potassium Bitartrate Crystallization From Wines

When the mass transfer on the crystal surface is the rate limiting step, the rate of potassium bitartrate removal from wines with crystallization was described as (Dunsford and Boulton 1981)

$$-\frac{dm}{dt} = k_D \frac{DA}{\delta}(c - c^*), \tag{E.4.24.1}$$

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where $-dm/dt$ is the rate of solute disappearance, k_D is a constant, D is the diffusivity of the solute, A is the surface area of the crystal, δ is the film thickness, and $(c - c^*)$ is the degree of supersaturation. When the rate determining step is the reaction of the solute molecules to join the lattice, the rate of solute removal from the solution would be

$$-\frac{dm}{dt} = k_S (c - c^*)^2. \tag{E.4.24.2}$$

It was concluded that the crystallization of potassium bitartrate from table wines generally displays rate limiting steps controlled by nucleation, surface reaction, and mass transport at various points in time. The length of time for which each process is controlling is determined by the particle size, crystal loading, and to a lesser extent, the level of agitation (Dunsford and Boulton 1981). With the Pinot noir wine, the test for the mass transport limiting stage (Figure E.4.24.1) shows that with the 400 μm and 200 μm particles the surface reaction rate controlling regime starts after approximately 4 and 8 minutes, respectively. The crystallization rates were controlled by the nucleation rates before the beginning of the mass transfer rate controlling step reaction rates. The surface reaction rate controlling regions with the Pinot noir wine are depicted in Figure E.24.2. MATLAB® code E.4.24 gives the details of the computations. It should be noticed that c^* was assumed to be negligibly small in both of the models.

The equilibrium between the crystals and the surrounding liquid is dynamic. Some ions leave the crystal, while new ones join it. Since the net number of the ions leaving the crystal is the same as the ones joining, there is no net change between the phases. The solubility, S, of a solid sphere of an ionic compound with the general formula M_mX_x and diameter D is related to that of a flat surface, S_0, with the *Kelvin equation* (Hiemenz and Rajagopalan 1997) as

$$S = S_0 \exp\left\{\frac{\gamma MW}{(m+x)RT\rho D}\right\}, \tag{4.52}$$

where γ = interfacial tension, MW = molecular weight of the solid, ρ = density of the solid, R = gas constant, and T = absolute temperature. Equation 4.52 implies that the solubility

MATLAB® CODE E.4.24

Command Window:

```
clear all
close all
format compact

% enter the data
c400Data=[9.28e-3 9.19e-3 9.10e-3 9.01e-3 8.92e-3 8.83e-3 8.74e-3
8.67e-3 8.50e-3 8.40e-3 8.30e-3 8.23e-3 8.13e-3 7.79e-3]; % particle
size 400 micrometer
t400Data=[7 12 17 25 32 40 45 50 70 80 95 110 120 150]; % particle
size 400 micrometer
```

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```
c200Data=[9.01e-3 8.92e-3 8.83e-3 8.74e-3 8.65e-3 8.48e-3 8.32e-3
8.20e-3 8.06e-3 7.91e-3 7.84e-3 7.79e-3]; % particle size 200
micrometer
t200Data=[1 17 25 33 40 49 55 70 80 95 105 118]; % particle size 200
micrometer

% NUCLEATION PHASE
%  rearrange the data
lnC200Data=log(c200Data);
lnC400Data=log(c400Data);

%  determine the duration of the nucleation process
LIMIT=0.04; % maximum acceptable standard error
SIZE=400; % micrometer
[M1 slope1 intercept1]= NUCLEATION(SIZE,LIMIT,t400Data,lnC400Data);

SIZE=200; % micrometer
[M2 slope2 intercept2]= NUCLEATION(SIZE,LIMIT,t200Data,lnC200Data);

% plot the data
for i=1:M1
t400D(i)=t400Data(i);
lnC400D(i)=lnC400Data(i);
end
plot(t400D, lnC400D,'o') ; hold on

for i=1:M2
t200D(i)=t200Data(i);
lnC200D(i)=lnC200Data(i);
end
plot(t200D, lnC200D,'*') ; hold on

legend('400 micrometer particles','200 micrometer particles',2,'Loca
tion','SouthWest')
xlabel('time (minutes)')
ylabel('ln(c)')

% plot the model
for i=1:M1
lnC400Model(i)=intercept1+slope1.*t400D(i);
end
plot(t400D, lnC400Model,'-') ; hold on

for i=1:M2
lnC200Model(i)=intercept2+slope2.*t200D(i);
end
plot(t200D, lnC200Model,':') ; hold on

% CRYSTAL GROWTH PHASE
%  rearrange the data
M3= length(t400Data);
for i=M1:1:M3
t400CrstlGrwthD(i)= t400Data(i);
invC400Data(i)=1./c400Data(i);
end
```

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```
M4= length(t200Data);
for j=M2:1:M4
invC200Data(j)=1./c200Data(j);
t200CrstlGrwthD(j)= t200Data(j);
end

% plot the data
figure
plot(t400CrstlGrwthD(M1:M3), invC400Data(M1:M3),'o') ; hold
plot(t200CrstlGrwthD(M2:M4), invC200Data(M2:M4),'*') ; hold
legend('400 micrometer particles','200 micrometer particles',2,'Loca
tion','NorthWest') ; hold
xlabel('time (minutes)') ; hold
ylabel('1/c') ; hold

% modeling
N=1;
X= t400CrstlGrwthD(M1:M3);
Y= invC400Data(M1:M3);
[intercept3 slope3 S3 R3]=LineFitting(X,Y,N);

N=1;
X= t200CrstlGrwthD(M2:M4);
Y= invC200Data(M2:M4);
[intercept4 slope4 S4 R3]=LineFitting(X,Y,N);

% plot the model
for i=M1:1:M3
InvC400Model(i)=intercept3+slope3.* t400CrstlGrwthD(i);
end

for j=M2:1:M4
InvC200Model(j)=intercept4+slope4.* t200CrstlGrwthD(j);
end

plot(t400CrstlGrwthD(M1:M3), InvC400Model(M1:M3),'-') ; hold on
plot(t200CrstlGrwthD(M2:M4), InvC200Model(M2:M4),':') ; hold on
```

M-file:

```
function [Counter SLP INTRCPT]=NUCLEATION(size,Limit,tData,cData)
% search for the moment of thee trend change with the  particles of
the chosen size
N=1;
for i=2:length(tData)
X=tData(1:i);
Y=cData(1:i);
[A1 B1 S R]=LineFitting(X,Y,N);
intercept(i)=A1;
slope(i)=B1;
s(i)=S;
r(i)=R;
if i>=4
if s(i)<Limit
tTrendChange=tData(i);
Counter=i;
end
```

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```
end
end
S=s(Counter);
R=r(Counter);
INTRCPT=intercept(Counter);
SLP=slope(Counter);
fprintf('\nNucleation lasts %g minutes with %g micrometer
particles\n',tTrendChange,size)
fprintf('Nucleation Model with %g micrometer particles is
ln(c)=%5.4f%5.4f*t with r=%2g Se=%3.2f\n',size, INTRCPT, SLP,R,S)
```

When we run the code the following lines and Figure E.4.24.1 and Figure E.4.24.2 will appear on the screen:

```
Nucleation lasts 50 minutes with 400 micrometer particles
Nucleation Model with 400 micrometer particles is ln(c)=-4.6711-
0.0015*t with r=-1 Se=0.04

Nucleation lasts 49 minutes with 200 micrometer particles
Nucleation Model with 200 micrometer particles is ln(c)=-4.7022-
0.0012*t with r=-1 Se=0.04
```

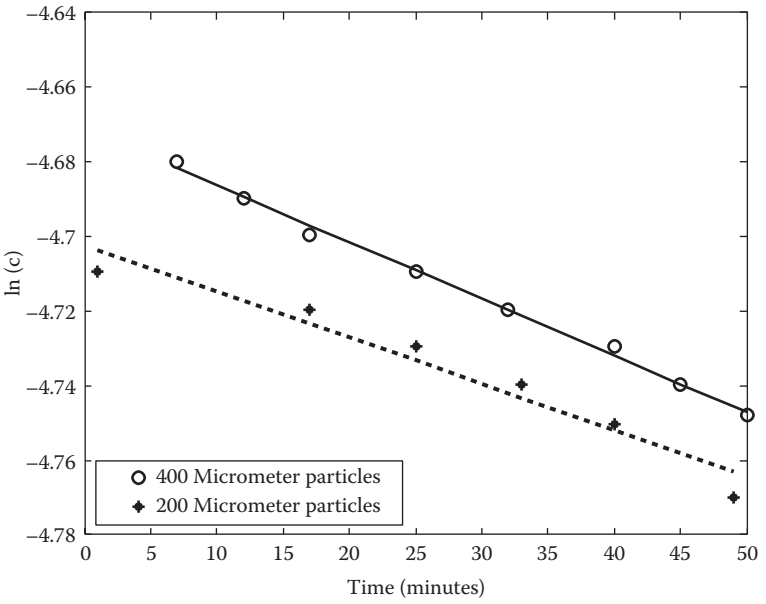


FIGURE E.4.24.1
Comparison of Equation E.4.24.1 with the experimental data in the nucleation phase. (Adapted from Dunsford, P., and and Boulton, R., *American Journal of Enology and Viticulture*, 32, 100–105, 1981.)

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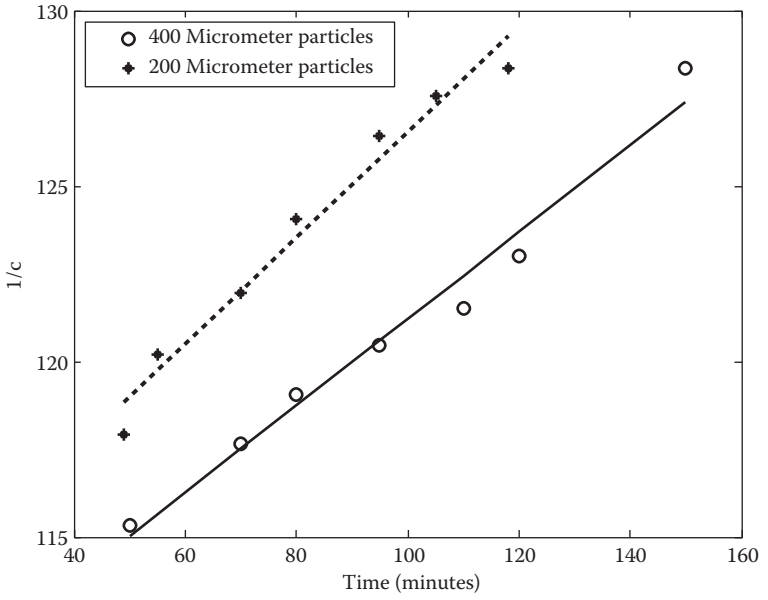


FIGURE E.4.24.2
Comparison of Equation E.4.24.2 with the experimental data in the crystal growth phase. Data were adapted from Dunsford, P., and Boulton, R., *American Journal of Enology and Viticulture*, 32, 100–105, 1981.)

increases exponentially with the decreasing particle diameter, therefore in dynamic equilibrium the smaller particles eventually disappear while the large ones get larger. This phenomena is called *recrystallization*.

One of the major industrial applications of recrystallization is a freeze concentration process where liquid foods or beverages are partially frozen, then the ice crystals (almost pure water) are removed to obtain a liquor with concentrated solutes. In a freeze concentration process, nucleation is started in a heat exchanger and crystal growth is achieved in a separate unit. During the ripening process, large crystals become larger and have a round shape while the small crystals disappear. Ripening makes ice removal easier and more efficient.

During the recrystallization process in a ripening tank, freezing temperatures for small ice crystals are slightly depressed because surface free energy per unit volume is larger for small crystals then for large crystals. Crystals of diameter D are in equilibrium when total free energy is minimized. This occurs at solution temperatures ΔT lower than equilibrium T for very large crystals:

$$\Delta T = \frac{4\sigma T}{\rho_s \Delta H D}, \tag{4.53}$$

where σ is the interfacial tension between the ice crystals and the surrounding medium, ΔH is the latent heat of crystallization and ρ_s is the density of ice. During the ripening process, a solution contains slurried ice crystals of mixed sizes. When the bulk temperature

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is T it adjusts to a value higher than that of the equilibrium temperature around the small crystals and lower than that around the large crystals. The small crystals melt, removing heat from the solution, which in turn, removes heat from large crystals, which consequently grow. If ripening is adiabatic, heat taken up by melting crystals with $D_p < D_n$ is generated by a growth of crystals with $D_p > D_n$, where D_n is the equilibrium particle size. After equating the rates of heat released and absorbed, we will have

$$\pi \int_0^{D_n} hD_p^2 \left(T_p - T_n\right) f(D_p) dD_p = \pi \int_{D_n}^{D_{\max}} hD_p^2 (T_p - T_n) f(D_p) dD_p, \tag{4.54}$$

where h is the heat transfer coefficient, $f(D_p)$ is the number of crystals in the diameter range between D_p and $D_p + dD_p$, T_p, and T_n are the respective equilibrium temperatures for particle sizes D_p and D_n. When $T_p = T + \Delta T_p$ and $T_n = T + \Delta T_n$ we will also have

$$(T_p - T_n) = (T + \Delta T_p) - (T + \Delta T_n) = (\Delta T_p - \Delta T_n). \tag{4.55}$$

When we combine Equations 4.53 and 4.55 we will have

$$\Delta T_p - \Delta T_n = \frac{4\sigma T}{\rho_s \Delta H}\left(\frac{1}{D_p} - \frac{1}{D_n}\right). \tag{4.56}$$

The total energy involved in a phase change of the particles in the diameter range between D_p and $D_p + dD_p$ is

$$\pi D_p^2 \frac{dD_p}{dt} \rho_s \Delta H = h\pi D_p^2 (T_p - T_n) = h\pi D_p^2 \frac{4\sigma T}{\rho_s \Delta H}\left(\frac{1}{D_p} - \frac{1}{D_n}\right). \tag{4.57}$$

After rearranging Equation 4.57 we will obtain an expression for the rate of particle size increase in the ripening process as

$$\frac{dD_p}{dt} = \frac{4\sigma hT}{\left(\rho_s \Delta H\right)^2}\left(\frac{1}{D_p} - \frac{1}{D_n}\right). \tag{4.58}$$

An interested reader may refer to Schwartzberg (1990) for a detailed discussion of the recrystallization kinetics.

Example 4.25: Kinetics of Recrystallization of Ice in Frozen Beef Tissue

Recrystallization is associated with the quality loss of frozen meats during storage and enhanced with temperature fluctuations. Figure E.4.25.1 is plotted by MATLAB® code E.4.25.a and show the

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variation of the mean and variance of the equivalent crystal diameters during the storage of the meat tissue.

A model describing the variation of the crystal size during the recrystallization process may be suggested in analogy with Equation 4.54 as

$$\frac{dD_{eq}}{dt} = K\left(\frac{1}{D_{eq}} - \frac{1}{D_{\infty}}\right), \tag{E.4.25.1}$$

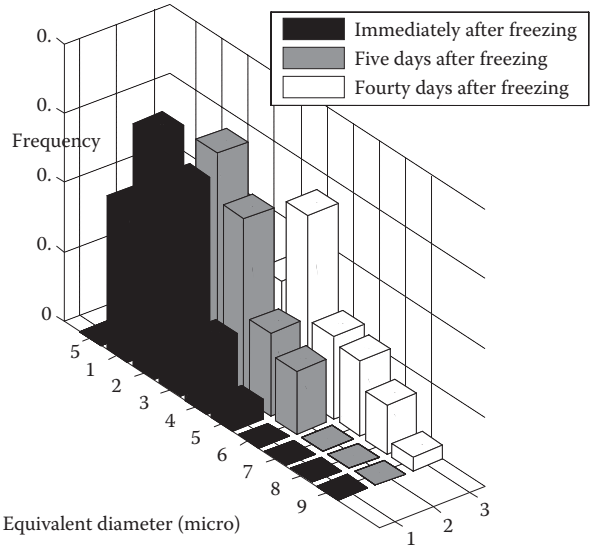


FIGURE E.4.25.1
Bar chart diagrams showing the increase in the crystal size distribution in the meat tissue during storage at –5°C. (a) Immediately after freezing, (b) after 5 days of storage, and (c) after 40 days of storage. (Adapted from Martino, M. N., and Zaritzky, N. E., *Journal of Food Science,* 53, 1631–37, 1649, 1988.)

MATLAB® CODE E4.25.a

Command Line:

```
clear all
close all

% introduce the data
Frequency=[0 0.22 0.35 0.30 0.10 0.03 0 0 0 0; 0 0.03 0.17 0.33 0.26
0.12 0.09 0 0 0; 0 0.03 0.11 0.12 0.15 0.27 0.12 0.11 0.07 0.02;];
EquivalentDiameter=[5 15 25 35 45 55 65 75 85 95];
FrequencyT=Frequency';
% prepare a bar chart of the data
bar3(FrequencyT,'detached');
grid on
set(gca, 'yTickLabels',EquivalentDiameter)
legend('Immediately After Freezing','Five Days After Freezing', '
Fourty Days After Freezing',3,'Location','NorthEast')
```

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```
zlabel('frequency')
ylabel('equivalent diameter (micro meter)')
colormap(gray)
```

When we run the code Figure E.4.25.1 will appear on the screen.

MATLAB® CODE E.4.25.b

Command Window:

```
clear all
close all
format compact

% enter the data
R = 8.314; % gas constant J/mol K
T = [-4.18 -10 -15 -20]; % C
invT=1./(T+273);
lnKdata=[5.8 5.26 4.94 4.64];
[Ea,lnK0,Se,r]=ARRHENIUS(T,lnKdata)
EaR=Ea/R;
% print the model, correlation coefficient and the standard error
fprintf('\nArrhenius relation is ln(K)= %.2g %2g/T and  r= %2g  se=
%2g  \n', lnK0, -EaR, r, Se)

% plot the model
for i=1:length(T)
lnKmodel(i)=lnK0-Ea/(R*(T(i)+273))
end
plot(invT, lnKmodel,'k:','LineWidth',2.5);
```

When we run the code the following line and Figure E.4.25.2 will appear on the screen:

```
Arrhenius relation is ln(K)= 24 -4938.35/T and  r= -0.991679  se=
0.110621
```

where k = rate constant. After integrating Equation E.4.25.1 we will obtain

$$\ln\left[\frac{D_\infty - D_0}{D_\infty - D_{eq}}\right] + \frac{D_0 - D_{eq}}{D_\infty} = \frac{K}{D_\infty^2}t, \tag{E.4.25.2}$$

where D_0 = mean equivalent initial diameter. Comparison of Equation E.4.25.2 with the experimental data is shown in Figure E.4.25.1.

The effect of temperature on the crystallization rate constant K may be expressed in terms of the Arrhenius expression (Martino and Zaritzky 1988):

$$K = K_0 \exp\left\{-\frac{E_a}{RT}\right\}. \tag{3.5}$$

MATLAB® code E.4.25.b compares Equation 3.5 with experimental data (Figure E.4.25.2).

MATLAB® code E.4.25.c depicts the effect of recrystallization on the mean equivalent diameter at different storage temperatures (Figure E.4.25.3).

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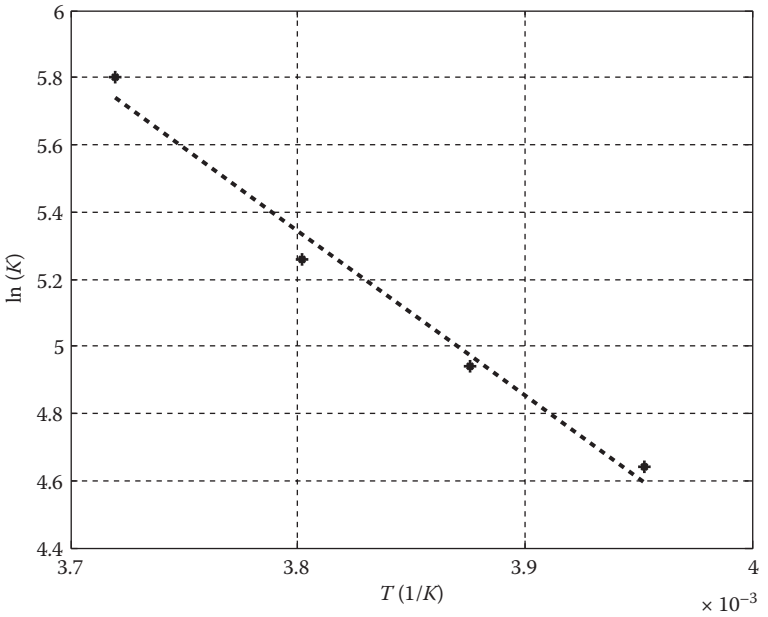


FIGURE E.4.25.2
Effect of temperature on recrystallization kinetic constant (K) in meat tissue. (Adapted from Martino, M. N., and Zaritzky, N. E., *Journal of Food Science,* 53, 1631–37, 1649, 1988.) Parameter K was expressed in μm^2/day.

MATLAB® CODE E.4.25.c

Command Line:

```
clear all
close all
format compact

% enter the data
T=[-20:5:-5]; % oC
D0=35; % micrometer
Dinfinity=61; % micrometer

DeltaTime=1;
R = 8.314;
Ko=0.273;
Ea=14562;
for i=1:1:length(T)
t(i,1)=0;
Deq(i,1)=D0;
EaRT(i)=Ea/(R.*(T(i)+273));
K(i)=Ko.*exp((EaRT(i)));
for k=1:1:80
t(i,k+1)=t(i,k)+DeltaTime;
Deq(i,k+1)= Deq(i,k)+(K(i).*(((1./Deq(i,k))-(1./
Dinfinity)))).*DeltaTime; % Deq=equilibrium diameter
end
end
```

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```
% plot the model
plot(t(1,:),Deq(1,:), '-'); hold on
plot(t(2,:),Deq(2,:), ':'); hold on
plot(t(3,:),Deq(3,:), '-.'); hold on
plot(t(4,:),Deq(4,:), '.'); hold on
xlabel('t (days)');
ylabel('Deq (micrometer)');
legend('- 20 oC','- 15 oC', '- 10 oC', '- 5 oC'
,4,'Location','SouthEast')
```

When we run the code Figure E.4.25.3 will appear on the screen.

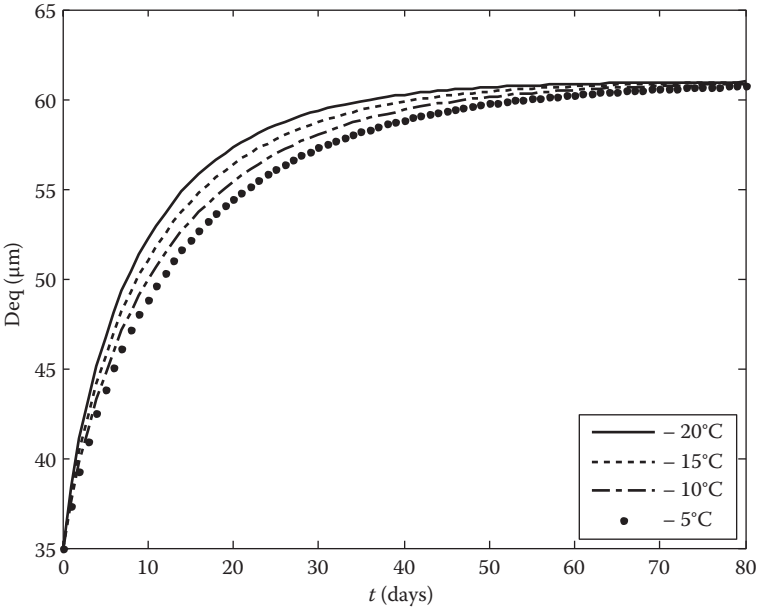


FIGURE E.4.25.3
Effect of recrystallization on mean equivalent diameter at different storage temperatures.

4.4 Unit Operation Models

4.4.1 Basic Computations for Evaporator Operations

In an evaporation process water is removed by vaporization to increase the concentration of nonvolatile solutes in a liquid food or beverage. It is the most economical and most widely used method of concentration (Karel 1975). Although the liquor fed into the evaporator may have the physical properties of water, as the concentration increases, the solution behaves differently. The density and the viscosity (or consistency) and the boiling point may increase with the solid content. Several rate processes are involved in evaporation, but the process may be simply considered as heat transfer from a heater to a boiling liquid.

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Heat-transfer analysis, combined with the mass and energy balance, is usually adequate for modeling the evaporation processes, provided that the boiling point and the physical properties of the liquid are known as a function of the pertinent temperatures and the solute concentrations. Most evaporators are heated by steam condensing in metal tubes. Usually steam is at a low pressure, below 3×10^5 Pa (absolute), often the boiling liquid is under vacuum, up to about 5×10^3 Pa (absolute). The vacuum reduces the boiling temperature of the liquid and increases the temperature difference, and subsequently heat transfer rates, between the steam and the liquid. Many food components are damaged when heated to moderate temperatures for relatively short times. The vacuum also helps to reduce the heat damage to the temperature sensitive food components. In a process consisting of series of evaporators each evaporator is called an *effect*. When a single evaporator is used, the vapor from the boiling liquid is discarded or used as a steam after recompression. This method is called *single-effect evaporation*. If the vapor from one evaporator is fed into the steam chest of a second evaporator and the vapor from the second effect to a condenser, the operation becomes double effect. This operational procedure may be generalized by using a higher number of evaporators and referred to as *multiple-effect evaporation*.

Example 4.26: Basic Computations for the Multieffect Tomato Paste Concentration Process

Tomato pulp at 35°C with 5% solids will be converted into tomato paste with 30% solids in a four-effect cascade as depicted in Table E.4.26.1. Saturated steam is supplied to the last effect under 143.3 kPa pressure ($T = 110$°C, $H = 2518$ kJ/kg, $h = 461.3$ kJ/kg). Input flow rate of the tomato pulp will change between 10 to 150 tons/h, but the fraction of the solids in the liquid streams leaving each effect will not change with the feed rate. Flow diagram of the cascade is given in Figure E.4.26.1.

i. How much water will be evaporated in each effect when the feed rate is 50 tons/h? Compute the amounts of liquid and vapor leaving each effect.

Solution: Total mass balance around the *i*th effect is

$$\frac{dM_{\text{total,i}}}{dt} = F_{L,i+1} - F_{V,i} - F_{L,i}, \tag{E.4.26.1}$$

where $M_{\text{total},i}$ is the amount of the total mass in the *i*th effect, $F_{L,i}$ and $F_{V,i}$ are the amounts of liquid and vapor, respectively, leaving the *i*th stage. Under the steady state operating conditions $dM_{\text{total},i} / dt = 0$ and

$$F_{L,i+1} - F_{V,i} - F_{L,i} = 0. \tag{E.4.26.2}$$

TABLE E.4.26.1

Operating Conditions of the Evaporators with 50 ton/h Tomato Pulp Input

n (effect number)	1	2	3	4
P (kPa)	67.7	36.5	23.8	16.5
T (°C)	55.6	63.8	74.3	89.3
x (g water/g solids)	0.25	0.20	0.10	0.05
τ (h)	0.15	0.20	0.31	0.75

Source: Pressure and the residence times are adapted from Simpson, R., Almonacid, S., Lopez, D., and Abakarov, A., Journal of Food Engineering, 89, 488–97, 2008.

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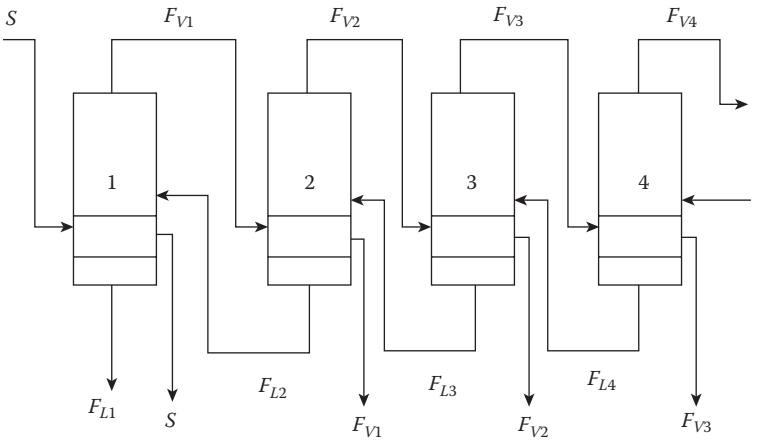


FIGURE E.4.26.1
The four-effect countercurrent evaporator system.

Equation E.4.26.4 may be rearranged to obtain

$$F_{V,i} = F_{L,i+1} - F_{L,i}. \tag{E.4.26.3}$$

Solids balance around the *i*th effect may be written the same way as

$$\frac{d\left(M_{\text{total},i}x_i\right)}{dt} = F_{L,i+1}x_{i+1} - F_{L,i}x_i. \tag{E.4.26.4}$$

Where we assume that no solids are entrained with the vapor stream. Under the steady state conditions Equation E.4.26.4 becomes

$$F_{L,i+1}x_{i+1} - F_{L,i}x_i = 0. \tag{E.4.26.5}$$

Equation E.4.26.4 may be rearranged to obtain

$$F_{L,i+1} = F_{L,i}\left(x_i/x_{i+1}\right). \tag{E.4.26.6}$$

MATLAB® code E.4.26.a employs Equations E.4.26.3 and E.4.26.6 to compute the amounts of liquid and vapor, which must be removed from each effect in order to attain the solid contents given in the problem statement when the feed rate is 50 tons/h.

ii. MATLAB® code E.4.26.b computes the variation of the amounts of liquid and vapor removed from each stage with the tomato pulp feed rates changing between 10 and 150 tons/h.

iii. The boiling point elevation may be related to the tomato solids concentration as

$$\Delta T_b = 0.175c^{1.11}\exp\left(-3.86c\right)P^{0.43}.$$

Operating temperature of the evaporator may be related to its pressure as

$$T_{vi} = 32.5515P^{0.2898} - 17.7778 \quad \text{when } 40°\text{C} < T_{vi} < 70°\text{C},$$

$$T_{vi} = 39.0514P^{0.2382} - 17.7778 \quad \text{when } 70°\text{C} < T_{vi} < 135°\text{C}.$$

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MATLAB® CODE E.4.26.a

Command Window:

```
clear all
close all
format compact

% enter the operating conditions
xL=[0.30 0.25 0.20 0.10 0.05];% fraction of solids after each effect
FL((1:15),5)=[10:10:150]; % feed rates of tomato paste under
different operating conditions
% FL(5,(1:5)),  FV(5,(1:5)) and  xL(5,(1:5)) refer to the operating
conditions when the feed rate is 50 ton/h
EffectNumber=[1 2 3 4 5]; % effect number 5 refers to the feed
%  fit a polynomial empirical model to the data
N=1; % degree of the fitted polynomial determine N
c = polyfit(EffectNumber, xL(1:5),N); % xL versus EffectNumber best
fit curve
EffectNumber=1:1:length(EffectNumber);
xLModel=polyval(c,EffectNumber);

% compute the flow rates of liquid stream after each effect
    FL(5,4)=FL(5,5)*xL(5)/xL(4); % FL(5,5)=feed entering the 4th
effect
    FL(5,3)=FL(5,4)*xL(4)/xL(3);
    FL(5,2)=FL(5,3)*xL(3)/xL(2);
    FL(5,1)=FL(5,2)*xL(2)/xL(1);

% compute the amount of vapor removed in each stage
    FV(5,1)=FL(5,2)-FL(5,1);
    FV(5,2)=FL(5,3)-FL(5,2);
    FV(5,3)=FL(5,4)-FL(5,3);
    FV(5,4)=FL(5,5)-FL(5,4);

%  fit a polynomial empirical model to the data
N=4; % degree of the fitted polynomial determine N
c = polyfit(EffectNumber,FL(5,(1:5)),N); % FL versus EffectNumber
best fit curve
EffectNumber=1:1:length(EffectNumber);
FLmodel=polyval(c,EffectNumber);

% plot the solids content and liquid leaving each stage versus the
effect number when the feed rate is 50 ton/h
 [AX,H1,H2] = plotyy(EffectNumber,FL(5,(1:5)),
EffectNumber,xL(1:5)); hold on
set(H1,'LineStyle','*')
set(H2,'LineStyle','o')
ylim(AX(2), [0.05 0.4])
ylim(AX(1), [5 50])
xlabel('effect number')
ylabel('amount of liquid leaving the effect (ton)')
set(get(AX(2),'ylabel'), 'string', 'fraction of solids (g solids/g
solution)')
legend('amount of  liquid', 'fraction of solids',
'Location','NorthWest') ; hold on;
```

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```
[AX,H1,H2] = plotyy(EffectNumber,FLmodel, EffectNumber,xLModel);
hold on
ylim(AX(2), [0.05 0.4])
ylim(AX(1), [5 50])
set(H1,'LineStyle','-')
set(H2,'LineStyle',':')

% plot the vapor leaving each stage versus the effect number when
the feed rate is 50 ton/h
figure
plot(EffectNumber(1:4),FV(5,(1:4)) ,'o'); hold on;
xlabel('effect number')
ylabel('amount of  vapor leaving the effect (ton)')
%  fit a polynomial empirical model to the data
N=2; % degree of the fitted polynomial determine N
c = polyfit(EffectNumber(1:4),FV(5,(1:4)),N); % FV versus
EffectNumber best fit curve
EffectNumber=1:1:length(EffectNumber);
FVmodel=polyval(c,EffectNumber(1:4));
plot (EffectNumber(1:4),FVmodel,'-'); hold on;
legend('computations','fitted curve','Location','NorthWest')
```

When we run the code Figures E.4.26.2 and E.4.26.3 will appear on the screen.

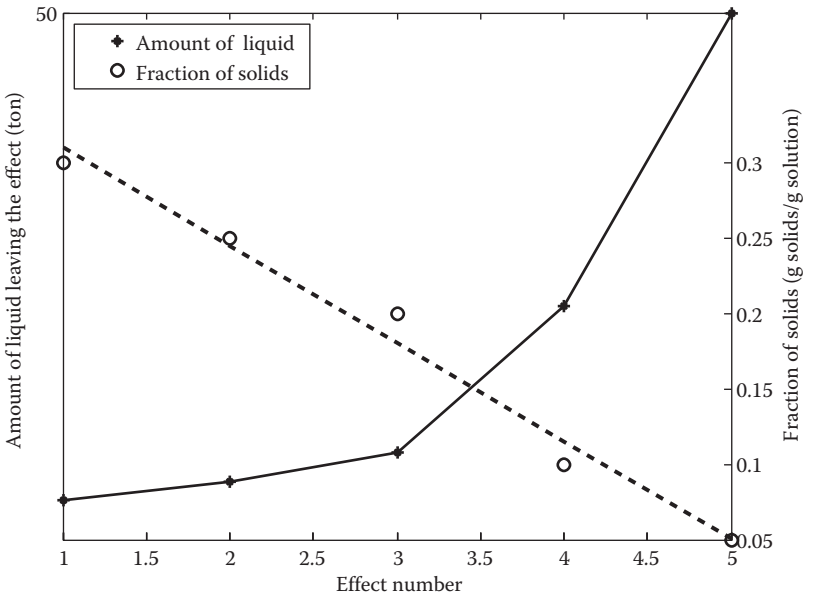


FIGURE E.4.26.2
Solids content of the tomato paste and the amount of liquid leaving each effect when the feed rate is 50 ton/h. Effect number 5 refers to the crushed fresh tomato pulp feed.

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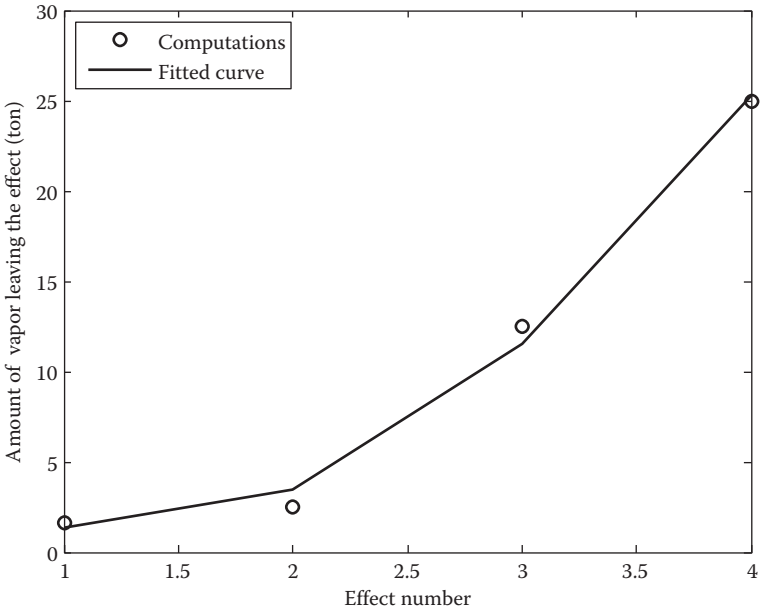


FIGURE E.4.26.3
Amount of vapor leaving each effect when the feed rate was 50 ton/h.

MATLAB® CODE E.4.26.b

Command Window:

```
clear all
close all
format compact

xL=[0.30 0.25 0.20 0.10 0.05];% fraction of solids after each effect

% compute the flow rates of liquid stream leaving each effect when
the feed rate is changing between 10 to 150 tons/h (solids contens
of the liquid streams do not change)

for i=1:15
FL(i,5)=10*i;

    FL(i,4)=FL(i,5)*xL(5)/xL(4); % FL(i,5)=feed entering the 4th
effect
    FL(i,3)=FL(i,4)*xL(4)/xL(3);
    FL(i,2)=FL(i,3)*xL(3)/xL(2);
    FL(i,1)=FL(i,2)*xL(2)/xL(1);

end

figure
plot (FL((1:15),5),FL((1:15),1),'-'); hold on;
plot (FL((1:15),5),FL((1:15),2),':'); hold on;
plot (FL((1:15),5),FL((1:15),3),'.-'); hold on;
```

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```
plot (FL((1:15),5),FL((1:15),4),'--'); hold on;
xlabel('feed rate (ton/h)')
ylabel('amount of liquid leaving the effect (ton)')
legend('first effect', 'second effect', 'third effect', 'fourth
effect','Location','NorthWest')

% compute the flow rates of vapour stream leaving each effect when
the feed rate is changing between 10 to 150 tons/h
for i=1:15

    FV(i,1)=FL(i,2)-FL(i,1);
    FV(i,2)=FL(i,3)-FL(i,2);
    FV(i,3)=FL(i,4)-FL(i,3);
    FV(i,4)=FL(i,5)-FL(i,4);
end

figure
plot (FL((1:15),5),FV((1:15),1),'-'); hold on;
plot (FL((1:15),5),FV((1:15),2),':'); hold on;
plot (FL((1:15),5),FV((1:15),3),'.-'); hold on;
plot (FL((1:15),5),FV((1:15),4),'--'); hold on;
xlabel('feed rate (ton/h)')
ylabel('amount of vapour leaving the effect (ton)')
legend('first effect', 'second effect', 'third effect', 'fourth
effect','Location','NorthWest')
```

When we run the code Figures E.4.26.4 and E.4.26.5 will appear on the screen.

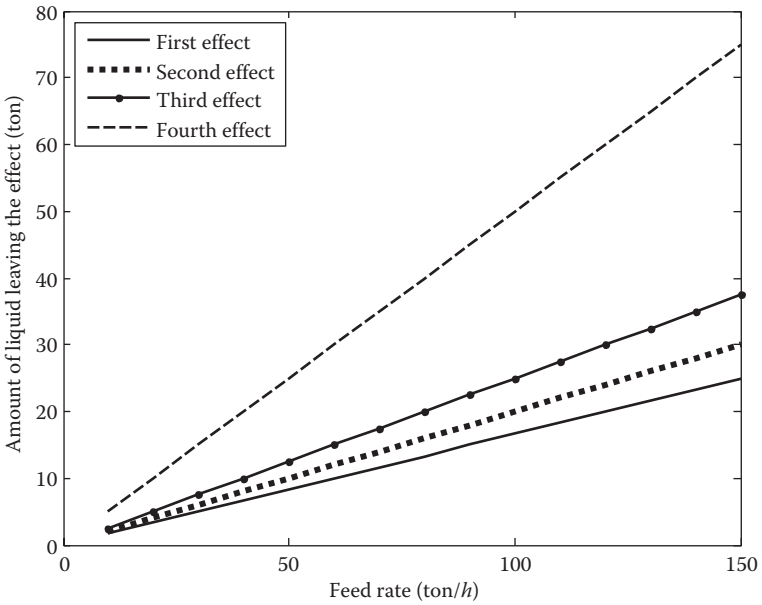


FIGURE E.4.26.4
Variation of the amount of liquid leaving each effect with the feed rate.

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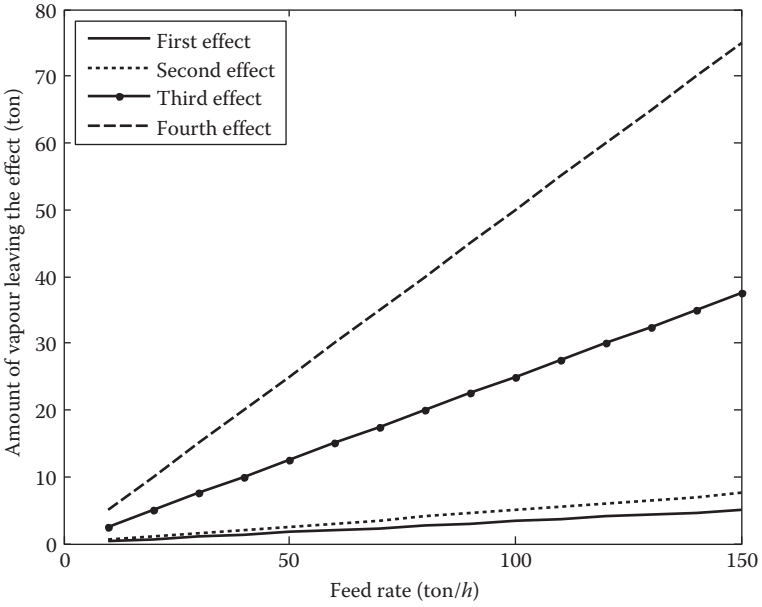


FIGURE E.4.26.5
Variation of the amount of vapor leaving each effect with the feed rate.

We want to keep the fraction of the solids in the liquid stream leaving each effect at a constant level, while increasing the feed rate.

Enthalpies of the vapor phase ($H_{v,i}$), condensed liquid phase ($H_{c,i}$) and tomato paste may be expressed as $H_{v,i} = 2509.2888 + 1.6747T_{vi}$ (kJ/kg), $H_{c,i} = 4.1868T_{c,i}$ (kJ/kg) where $T_{v,i}$ and $T_{c,i}$ are the temperatures of the vapor and the tomato paste in the ith effect, respectively. Enthalpy balance around the first effect is

$$SH_s + F_{L,2}h_{L,2} - F_{V,2}H_{V,2} - Sh_{S,1} - F_{L,1}h_{L,1} = 0. \tag{E.4.26.7}$$

Where S is the amount of the steam entering into the first effect, H_s and h_s are the enthalpies associated with S in the vapor and liquid phases, respectively, and $h_{L,i}$ is the enthalpy of the liquid stream leaving the ith effect. Equation E.4.26.7 may be rearranged to compute the steam requirement as

$$S = \frac{F_{L,1}h_{L,1} + F_{V,1}H_{v,1} - F_{L,2}h_{L,2}}{H_s - h_{S,1}}. \tag{E.4.26.8}$$

Steam economy (e) is defined as the total tons of water evaporated in the cascade per one ton of steam provided externally as

$$e = \frac{\sum_{i=1}^{n} F_{V,i}}{S}. \tag{E.4.26.9}$$

MATLAB® code E.4.26.c computes the relation between the apparent overall heat transfer coefficient, U, in each effect and the input rate of the tomato pulp to satisfy this requirement.

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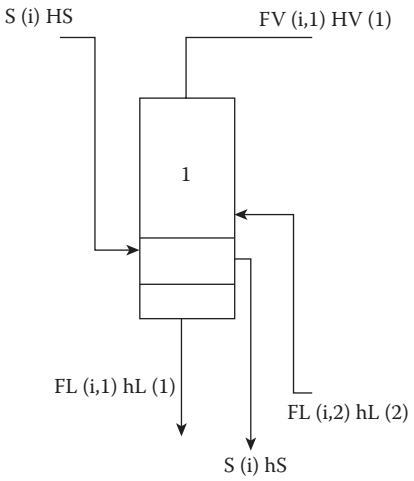


FIGURE E.4.26.6
Notation employed in the MATLAB® code E.4.26.c while making the enthalpy balance around the first effect.

MATLAB® CODE E.4.26.c

Command Window:

```
clear all
close all

Ts=110; % temperature of the steam provided to the last effect
(externally imposed design parameter)
xL=[0.30 0.25 0.20 0.10 0.05]; % fraction of the solids in the
liquid streams leaving each effect (externally imposed design
parameter)
P=[67.7 36.5 23.8 16.5]; % operating pressure of the first
evaporator (externally imposed design parameter)
T=[55.6 63.8 74.3 89.3]; % boiling temperature of the pure water at
the corresponding pressures
EffectNumber=[1 2 3 4 5]; % effect number 5 refers to the feed

% compute the temperature of the vapor in each stage
for i=1:4

     if i<=2
        TV(i)=32.5515*P(i)^0.2298-17.7778;
      end

     if i>2
       TV(i)=39.0514*P(i)^0.2382-17.7778;
     end
end

% determine the boiling point elevation and the boiling point of
liquid in each stage
for i=1:4
```

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```
      deltaTb(i)=0.175*xL(i)^1.11*exp(-3.86*xL(i))*P(i)^0.43; %
boiling point elevation
      Tboiling(i)=T(i)+deltaTb(i); % boiling point of the liquid in
each stage
end

%  best fitting linet o represent variation of  the fraction of the
solids with the effect number N=1; % degree of the fitted polynomial
determine N
c = polyfit(EffectNumber, xL(1:5),1); % xL versus EffectNumber best
fit curve
EffectNumber=1:1:length(EffectNumber);
xLModel=polyval(c,EffectNumber);

%  best fitting linet o represent variation of  the boiling point
elevation with the effect number
N=1; % degree of the fitted polynomial determine N
c = polyfit(EffectNumber(1:4), deltaTb(1:4),1); % xL versus
EffectNumber best fit curve
EffectNumber=1:1:length(EffectNumber);
deltaTbModel=polyval(c,EffectNumber);

% plot the solids fraction and the boiling point elevation in each
effect
[AX,H1,H2] = plotyy(EffectNumber(1:5),xL(1:5), EffectNumber(1:4),del
taTb(1:4)); hold on
ylim(AX(2), [0 0.1])
set(H1,'LineStyle','*')
set(H2,'LineStyle','o')
xlabel('effect number')
ylabel('fraction of the solids (kg solids/kg liquid)')
set(get(AX(2),'ylabel'), 'string', 'Temperature (^oC)')
legend('fraction of solids', 'boiling point elevation',
'Location','SouthWest') ; hold on;

% plot the best fitting lines to variation of solids fraction and
the boiling point elevation versus effect number plots
[AX,H1,H2] = plotyy(EffectNumber(1:5),xLModel(1:5), EffectNumber
(1:4),deltaTbModel(1:4)); hold on
ylim(AX(2), [0 0.1])
set(H1,'LineStyle','-')
set(H2,'LineStyle',':')
legend('fraction of solids', 'temperature', 'Location','SouthWest')
; hold on;

% compute the enthalpy of vapor leaving each stage
for i=1:4
      HV(i)=2509.2888+1.68747*TV(i); % enthalpy of vapor leaving the
stage (kJ/kg)
end

% compute the flow rates of liquid stream leaving each effect when
the feed rate is changing between 10 to 150 tons/h (solids contens
of the liquid streams do not change)
```

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```
for i=1:15
      FL(i,5)=10*i; % FL(i,5)=feed entering the 4th effect
      FL(i,4)=FL(i,5)*xL(5)/xL(4);
      FL(i,3)=FL(i,4)*xL(4)/xL(3);
      FL(i,2)=FL(i,3)*xL(3)/xL(2);
      FL(i,1)=FL(i,2)*xL(2)/xL(1);
end

% compute the flow rates of vapour stream leaving each effect when
the feed rate is changing between 10 to 150 tons/h

for i=1:15
    FV(i,1)=FL(i,2)-FL(i,1);
    FV(i,2)=FL(i,3)-FL(i,2);
    FV(i,3)=FL(i,4)-FL(i,3);
    FV(i,4)=FL(i,5)-FL(i,4);
end

% compute the heat exchange load in each stage
for i=1:15
   Q(i,1)=FV(i,1)*HV(1);
   Q(i,2)=FV(i,2)*HV(2);
   Q(i,3)=FV(i,3)*HV(3);
   Q(i,4)=FV(i,4)*HV(4);
end

% compute the temperature difference between both sides of the heat
exchanger in each effect
     T(5)=110; % temperature of the steam entering the fourth effect
for i=1:4
    deltaT(i)=T(i+1)-T(i);
end

% compute the heat transfer coefficients in each effect
A=16.4; % heat transfer area in each evaporator

for i=1:15
   U(i,1)=Q(i,1)/(A*deltaT(1));
   U(i,2)=Q(i,2)/(A*deltaT(2));
   U(i,3)=Q(i,3)/(A*deltaT(3));
   U(i,4)=Q(i,4)/(A*deltaT(4));
end

% plot the values of the heat transfer coefficients which are needed
to be achieved at different tomato pulp feed rates to achieve the
required solids concentration after each effect
figure
plot(FL((1:15),5),U((1:15),1),'-', FL((1:15),5),U((1:15),2),':',
FL((1:15),5),U((1:15),3), '.-', FL((1:15),5),U((1:15),4),'--')
xlabel('tomato pulp feed rate (ton/h)')
ylabel('U')
legend('first effect','second effect', 'third effect', 'fourth
effect','Location','NorthWest')

% compute the steam requirement
HS=2518; % enthalpy  of the steam provided to the 1st effect (kJ/kg)
```

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```
hS=461.3; % enthalpy of the saturated liquid (kJ/kg)

HV(1)=2509.2888+1.6747*T(1); % enthalpy of the vapor leaving the 1st
effect (kJ/kg)
HV(2)=2509.2888+1.6747*T(2); % enthalpy of the vapor leaving the 2nd
effect (kJ/kg)
hL(1)=4.1868*T(1); % enthalpy of the liquid leaving the 1st effect
(kJ/kg)
hL(2)=4.1868*T(2); % enthalpy of the liquid leaving the 2nd effect
(kJ/kg)

for i=1:15
   S(i)=(FL(i,1)*hL(1)+FV(i,1)*HV(1)-FL(i,2)*hL(2))/(HS-hS);
end

% plot the amounts of the steam required the at different tomato
pulp feed rates
figure
plot(FL((1:15),5),S(1:15), '-*')
xlabel('tomato pulp feed rate (ton/h)')
ylabel('amounts of steam required (ton/h)')

% compute the variation of the steam economy with the tomato pulp
feed rate

for i=1:15
   e(i)=(FV(i,1)+FV(i,2)+FV(i,3)+FV(i,4))/S(i);
end

% plot the amounts of the steam required the at different tomato
pulp feed rates
figure
plot(FL((1:15),5),e(1:15), '-*')
xlabel('tomato pulp feed rate (ton/h)')
ylabel('steam economy (ton water evaporated/ton steam provided)')
ylim( [22 25])
```

When we run the code Figures E.4.26.7–E.4.26.10 will appear on the screen.

It also computes the amount of steam required when the feed rate of the tomato pulp fed to the cascade varies between 10 and 150 ton/h and computes the steam economy of the process.

iv. Lycopene degradation may be described with the following expression as

$$r = \frac{dc}{dt} = -kc. \tag{E.4.26.10}$$

We may assume that the temperature is constant at the *i*th effect than integrate Equation E.4.26.10 to obtain

$$c_{i+1} = c_i \exp\left(-k_i \tau_i\right), \tag{E.4.26.11}$$

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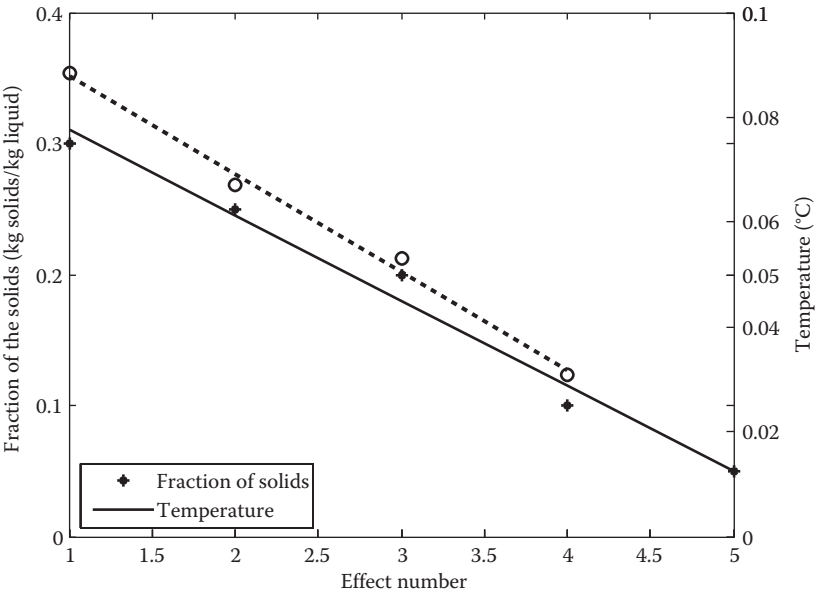


FIGURE E.4.26.7
Fraction of the solids and the boiling point elevation in each stage.

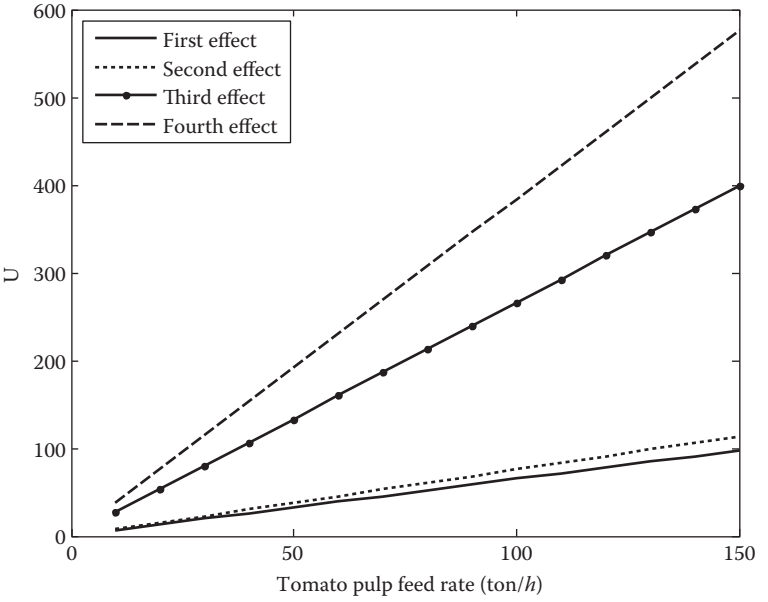


FIGURE E.4.26.8
Variation needed to be achieved in the apparent heat transfer coefficient U with the tomato pulp feed rate in order to maintain the fraction of the solids leaving each effect at a constant level.

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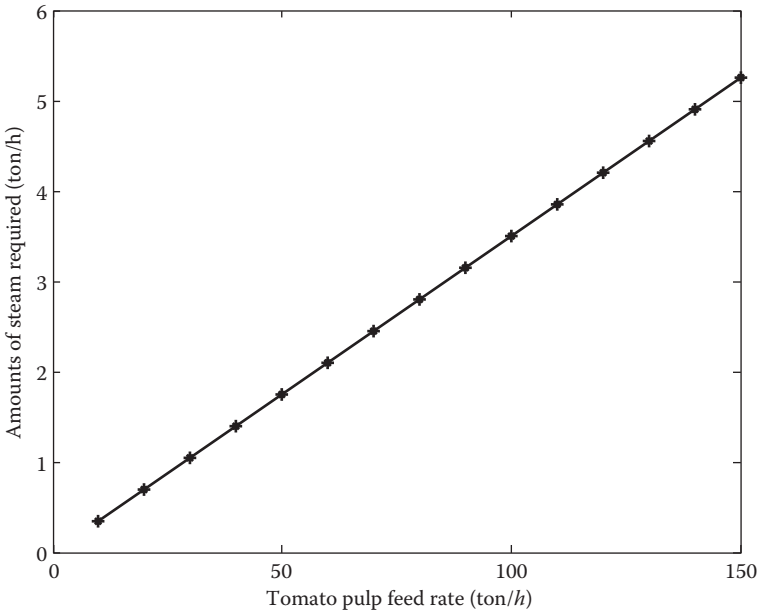


FIGURE E.4.26.9
Variation of the steam input rate to the first effect with the tomato pulp feed rate to the system.

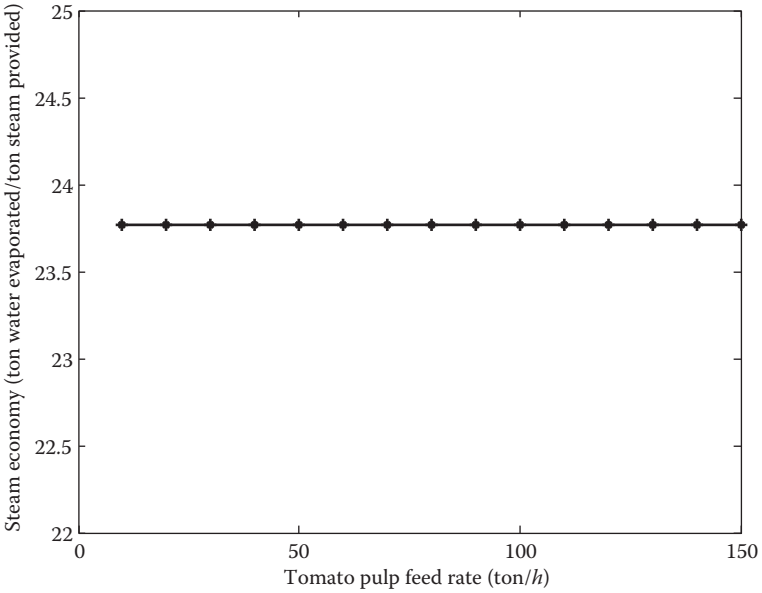


FIGURE E.4.26.10
Within the design constraint given in the problem statement, the steam economy of the process remains constant as the tomato pulp feed rate changes.

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MATLAB® CODE E.4.26.d

Command Window:

```
clear all
close all

xL=[0.30 0.25 0.20 0.10 0.05]; % fraction of the solids in the
liquid streams leaving each effect (externally imposed design
parameter)
T=[55.6 63.8 74.3 89.3]; % boiling temperature of the pure water at
the corresponding pressures
tau(5,1:4)=[0.15 0.20 0.31 0.75]; % residence time in each effect
when the tomato pulp feed rate is 50 ton/h (h)
EffectNumber=[1 2 3 4 5]; % effect number 5 refers to the feed
xc(5)=1; % initial fraction of the lycopene in the tomato pulp ehile
enetering into the system
FeedRate=[10:10:150]; % feed rate to the system (ton/h)

for j=1:length(FeedRate)
for  i=4:-1:1;
    tau(i,j)=60*tau(5)*(FeedRate(5)/FeedRate(j));
    k(i)=0.275271*exp(0.00241*xL(i))*exp(-2207/(T(i)+273.15));
   xc(i)=xc(i+1)*exp(-k(i)*tau(i,j))
end
xS(j)=xc(1); % fraction of the lycopene in the tomato pulp feed
surviving the process
end

% plot the amounts of the steam required the at different tomato
pulp feed rates
figure
plot(FeedRate,xS, '-*')
xlabel('tomato pulp feed rate (ton/h)')
ylabel('fraction of lycopene surviving the process')
```

When we run the code Figure E.4.26.11 will appear on the screen.

where τ_i is the average residence time in the ith effect. The rate constant k_i may be expressed as

$$k_i = 0.275271\exp(0.00241c_i)\exp\left(-\frac{2207}{T_i + 273.15}\right). \tag{E.4.26.12}$$

We will use MATLAB® code E.4.26.d to determine the lycopene retention in the final product.

4.4.2 Basic Computations for Filtration and Membrane Separation Processes

The particle size range of the filtration and membrane separation processes is shown in Figure 4.5. Particles within the ionic range (i.e., aqueous salts, sugars, etc.) are separated with *reverse osmosis*. *Ultrafiltration* is used within the molecular range (i.e., virus, albumin

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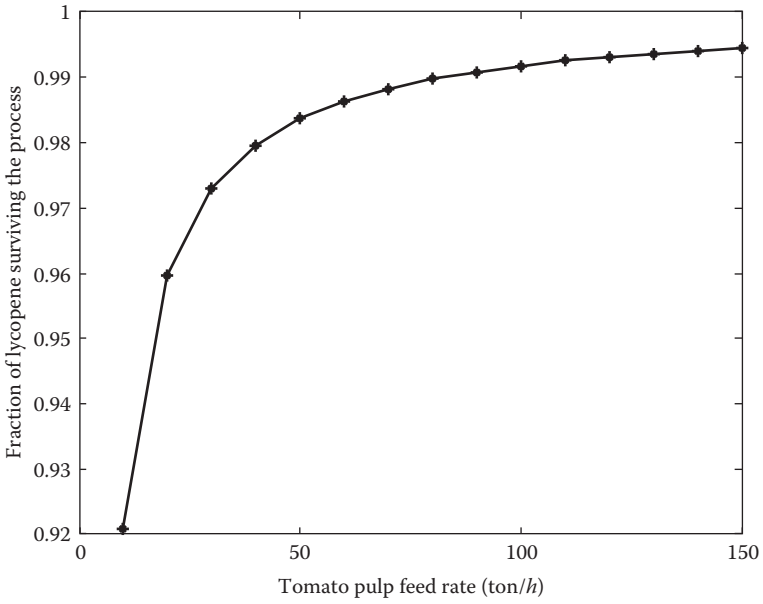


FIGURE E.4.26.11
Variation of the fraction of the lycopene of the pulp surviving the process with the tomato pulp feed rate.

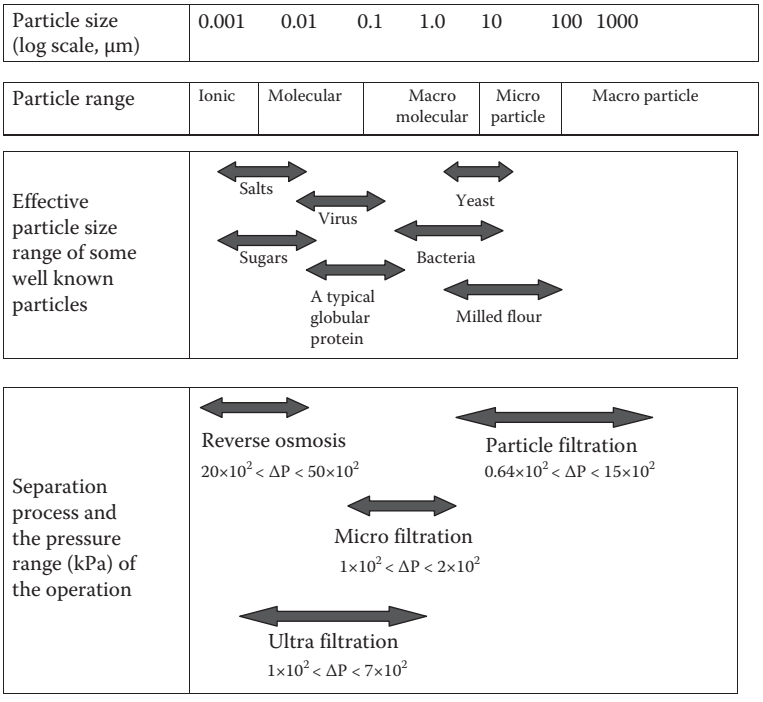


FIGURE 4.5
Size range of the particles involved in membrane separation and filtration processes.

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protein, etc.). *Microfiltration* is used to separate particles within the macromolecule range; and particle *filtration* techniques are employed for the micro- and macroparticles.

In a particle filtration process the solids are separated from a liquid by means of a medium that retains the solids, but allows the liquid. Accumulation of the particles on the medium clogs its holes and prevents the flow. *Filter aids* (i.e., inert particles of diatomaceous earth, cellulose, etc.) are used in filtration processes to keep these holes open. In a cake filtration process filtration actually occurs through the cake (Figure 4.6). The filter medium is precoated with a layer of filter aid before the beginning of filtration. The liquid food is also mixed with the filter aid and fed in to the filter. Filtration actually occurs through the cake, the food particles and the filter aid are retained in the filter, while the liquid passes through. Cake builds up continuously through the process, the food particles are dispersed among the filter aid particles, therefore clogging is prevented.

Sperry's equation is the most common model used to simulate filtration (Example 1.6):

$$\frac{dV}{dt} = \frac{A\Delta P}{\mu} \frac{1}{R_m + \alpha c V/A}. \tag{4.59}$$

The medium resistance R_m often varies with time. This behavior results when some of the solids penetrate the medium as it compresses under applied pressure. The specific cake resistance α is the most troublesome parameter and it changes with ΔP in most practical cakes due to the compressibility of the cake, this is often expressed as (Svarovsky 1985)

$$\alpha = \alpha_0 (\Delta P_c)^n, \tag{4.60}$$

where α_0 and n are constants, and ΔP_c is the pressure drop across the cake. Foods are usually highly complex systems. De LaGarza and Boulton (1984) modified Equation 4.59 to model wine filtrations (Example 1.6):

$$\frac{dV}{dt} = \frac{A\Delta P}{\mu} \frac{1}{R_m + \alpha c \left(V/A\right)^n}, \tag{4.61}$$

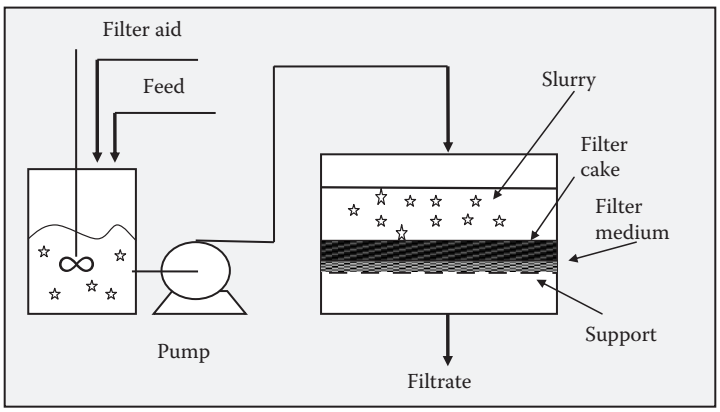


FIGURE 4.6
Schematic description of a cake filtration process.

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$$\frac{dV}{dt} = \frac{A\Delta P}{\mu} \frac{1}{R_m \exp(kV/A)}. \tag{4.62}$$

Equation 4.62 was also found appropriate to simulate apple and sour cherry juice filtrations (Bayindirli, Özilgen, and Ungan 1989).

Industrial filtration equipment is usually operated under constant pressure ΔP or with constant filtration rate dV/dt. In a constant pressure process Equation 4.59 may be rearranged as

$$\frac{dt}{dV} = K_1 V + B_1, \tag{4.63}$$

where $K_1 = \mu\alpha c/\Delta P A^2$ and $B_1 = \mu R_m \Delta P A$ or integrated to give

$$t = \frac{K_1}{2} V^2 + B_1 V. \tag{4.64}$$

In a constant rate process Equation 4.59 may be rearranged as

$$\Delta P = K_2 V + B_2, \tag{4.65}$$

where $K_2 = (\mu\alpha c/A^2)(dV/dt)$ and $B_2 = (\mu R_m/A)(dV/dt)$.

In a constant pressure process, if Equation 4.63 is valid, a plot of dt/dV versus V may be used to evaluate constants K_1 and B_1 from the slope and the intercept of Equation 4.63, respectively. A plot of ΔP versus V may be employed in a constant rate process to evaluate K_2 and B_2 as implied by Equation 4.65.

Example 4.27: Constant Pressure Filtration, Ultrafiltration, and Microfiltration Applications in Fruit Juice Processing

Green coconut water and watermelon juices are sterilized with cake and membrane filtration techniques (Figure E.4.27.1) in India to be consumed as a popular drink.

Reddy, Das, and Das (2005), while studying the filtration behavior of the green coconut water, found out that Equations 4.64 and 4.65 were very useful while analyzing their data. MATLAB® code E.4.27.a demonstrates the use of these equations in the filtration process modeling.

It was shown by Reddy, Das, and Das (2005) that Equations 4.64 and 4.65 were also very useful while analyzing the membrane filtration data. Constants of Equations 4.64 and 4.65 are $K = \mu\alpha c/\Delta P A^2$ and $B = \mu R_m \Delta P A$. In the processes where the filter cake is compressible, parameters α and R_m may change with pressure.

MATLAB code E.4.27.b demonstrates the effect of pressure on these constants.

Chhaya et al. (2008) described a process for sterilization of watermelon juice with microfiltration. Permeate flux v_m at any time of filtration is expressed as

$$v_m = \frac{\Delta P}{\mu\left[R_m + R_p(t)\right]}, \tag{E.4.27.1}$$

where ΔP is the cross membrane pressure, R_m and $R_p(t)$ are the membrane and fouling resistances, respectively. Parameter μ is the viscosity of the clarified juice. Combined resistance of reversible

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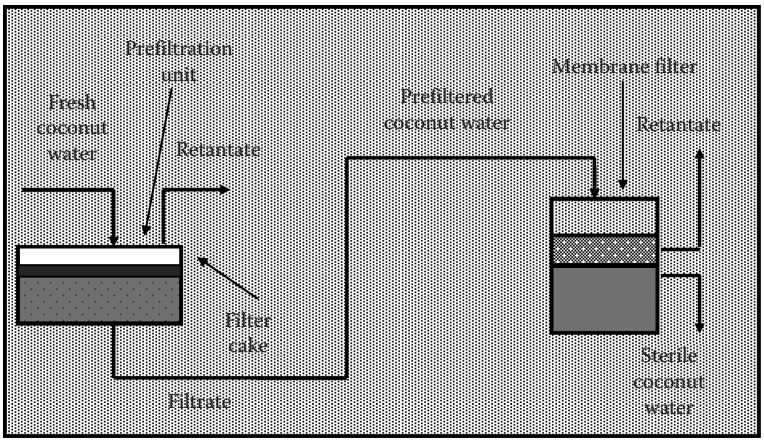


FIGURE E.4.27.1
A simple process flow chart for sterile coconut water production from fresh coconut water. Fresh coconut oil is prefiltered first to remove the course particles (retanatate). The filtrate is send to the membrane filter for sterilization, where microorganisms are expected to end up in the retantate. The watermelon juice sterilization process is similar to the membrane filtration described in the figure.

MATLAB® CODE E.4.27.a

Command Window:

```
clear all
close all
format compact

% enter the experimental data
Vdata1=[25 75 125 175]; % P=5.33 kPa, pre-filtration process
dtdVData1=[0.125 0.25 0.31 0.42]; % P=5.33 kPa, pre-filtration
process
Vdata2=[25 75 125 175]; % P= 16 kPa, pre-filtration process
dtdVData2=[0.075 0.14 0.2 0.26]; % P= 16 kPa, pre-filtration process
plot(Vdata1,dtdVData1, '^', Vdata2,dtdVData2, 's'); hold on
legend('P=5.33 kPa','P=16 kPa','Location','NorthWest')
grid on
xlabel('V (mL)')
ylabel('dt/dV (s/mL)')

% enter the model constants
Kp1=0.002; % P=5.33 kPa
B1=0.090; % P=5.33 kPa
Kp2=0.0013; % P=16 kPa
B2=0.043; % P= 16 kPa

% modeling
V=[25:200]; % model volumes

for i=1:length(V)
dtdV1(i)=Kp1*V(i)+B1;
dtdV2(i)=Kp2*V(i)+B2;
t1(i)=Kp1*(V(i).^2)/2+V(i)*B1; % compute the filtration times
t2(i)=Kp2*(V(i).^2)/2+V(i)*B2; % compute the filtration times
end
plot(V,dtdV1, ':', V,dtdV2, '-'); hold on

figure
plot(V,t1, ':', V,t2, '-'); hold on
grid on
```

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```
xlabel('V (mL)')
ylabel('t (min)')

% enter the experimental data
Vdata3=[0 50 100 150 200]; % P=5.33 kPa
tData3=[0 7 19 36 58]; % P=5.33 kPa
Vdata4=[0 50 100 150 200]; % P=16 kPa
tData4=[0 4 11 21 35]; % P=16 kPa
plot(Vdata3,tData3, 's', Vdata4,tData4, '^'); hold on
legend('P=5.33 kPa','P=16 kPa','Location','NorthWest')
```

When we run the code Figures E.4.27.2 and E.4.27.3 will appear on the screen.

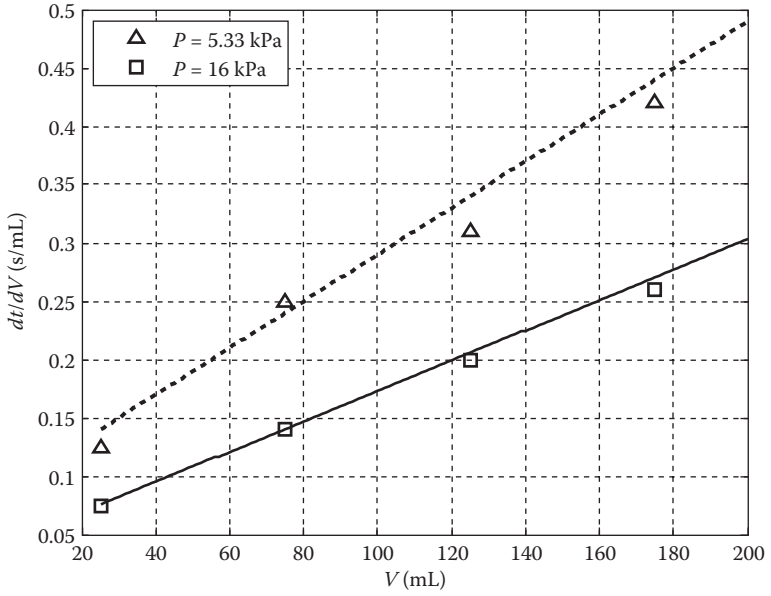


FIGURE E.4.27.2
Comparison of Equation 4.64 with the data obtained during filtration of the green coconut water. (Adapted from Reddy, K. V., Das, M., and Das, S. K., *Journal of Food Engineering*, 69, 381–85, 2005.)

fouling on the membrane surface and irreversible fouling inside the membrane pores contribute to $R_p(t)$, which may also be expressed as

$$R_p = R_{ps}\left[1-\exp(-\alpha t)\right]. \tag{E.4.27.2}$$

Equation E.4.27.2 may be rearranged as

$$\frac{R_p}{R_m} = \frac{R_{ps}}{R_m}\left[1-\exp\left(-\alpha t\right)\right]. \tag{E.4.27.3}$$

Equations E.4.27.1 and E.4.27.3 may be combined to obtain

$$v_m = \frac{\Delta P}{\mu R_m}\frac{1}{\left[1+\dfrac{R_{ps}}{R_m}\left[1-\exp(-\alpha t)\right]\right]}. \tag{E.4.27.4}$$

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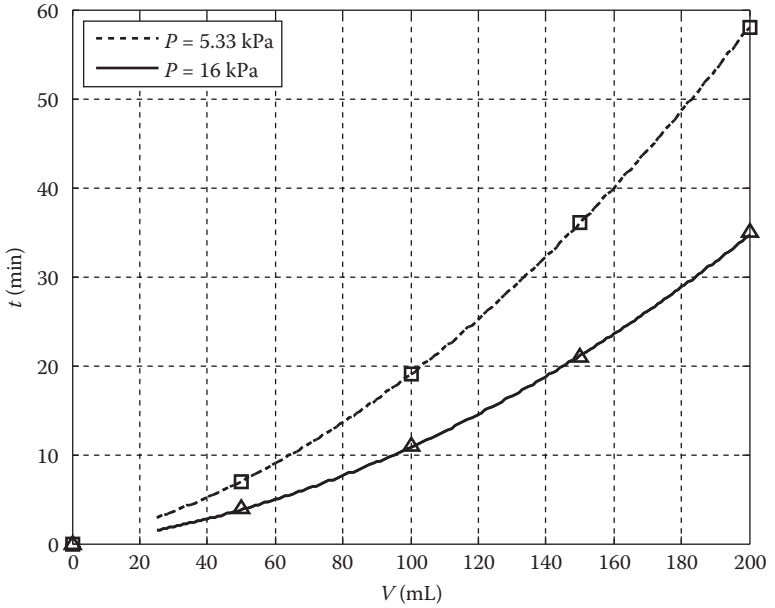


FIGURE E.4.27.3
Comparison of the model (Equation 4.65) and experimentally determined times for the collection of V (mL) of filtrate during constant pressure filtration of the green coconut water. (Adapted from Reddy, K. V., Das, M., and Das, S. K., *Journal of Food Engineering,* 69, 381–85, 2005.)

MATLAB® CODE E.4.27.b

Command Window:

```
clear all
close all
format compact

Pdata=[5.33 10.67 16.00]; % operating pressures (kPa)

% enter the prefilter parameters
RmData1=[ 3.497e9 4.740e9 5.042e9]; % (1/m)
alphaData1=[2.162e12  3.545e12 4.280e12]; % (m/kg)

% enter the membrane fitler parameters
RmData2=[ 1.979e10 2.829e10 3.076e10]; % (1/m)
alphaData2=[2.144e12  2.936e12 3.942e12]; % (m/kg)

% plot the data
plot(Pdata,RmData1, '^', Pdata, RmData2, 's'); hold on
legend('pre-filter','membrane filter','Location','NorthWest')
grid on
xlabel('P (kPa)')
ylabel('R_m(1/m)')
%  fit a polynomial empirical model (line) to the data
N=1;
PModel=4:1:20;
```

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```
c1= polyfit(Pdata,RmData1,N);
RmModel1=polyval(c1,Pdata);
c2 = polyfit(Pdata,RmData2,N);
RmModel2=polyval(c2,Pdata);
plot (Pdata,RmModel1,'-', Pdata,RmModel2,':'); hold on;

figure
plot(Pdata,log(alphaData1), '^', Pdata, log(alphaData2), 's'); hold
on
legend('pre-filter','membrane filter','Location','Best')
grid on
xlabel('P (kPa)')
ylabel('log(alpha)')
%  fit a polynomial empirical model (line) to the data
N=1;
c3= polyfit(Pdata,log(alphaData1),N);
logAlphaModel1=polyval(c3,Pdata);
c4 = polyfit(Pdata,log(alphaData2),N);
logAlphaModel2=polyval(c4,Pdata);
plot (Pdata,logAlphaModel1,'-', Pdata,logAlphaModel2,':'); hold on;
```

When we run the code Figure E.4.27.4 and Figure E.4.27.5 will appear on the screen.

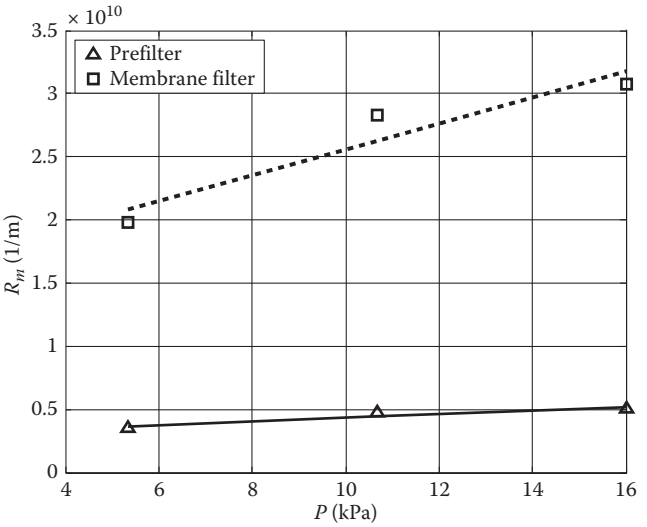


FIGURE E.4.27.4
Variation of filter medium (or membrane) resistance parameter R_m with pressure. (Adapted from Reddy, K. V., Das, M., and Das, S. K., *Journal of Food Engineering*, 69, 381–85, 2005.)

The term (R_{ps} / R_m) $[1 - \exp(-\alpha t)]$ increases with time and simulates the increased resistance to permeation with accumulation of the solids on the membrane. This concept was discussed with the analogy between cake filtration and ultrafiltration in Example 1.6. MATLAB® code E.4.27.c uses Equation E.4.27.3 to evaluate R_p/R_m and Equation E.4.27.4 to evaluate the permeation rates at $Re = 1.63 \times 10^5$.

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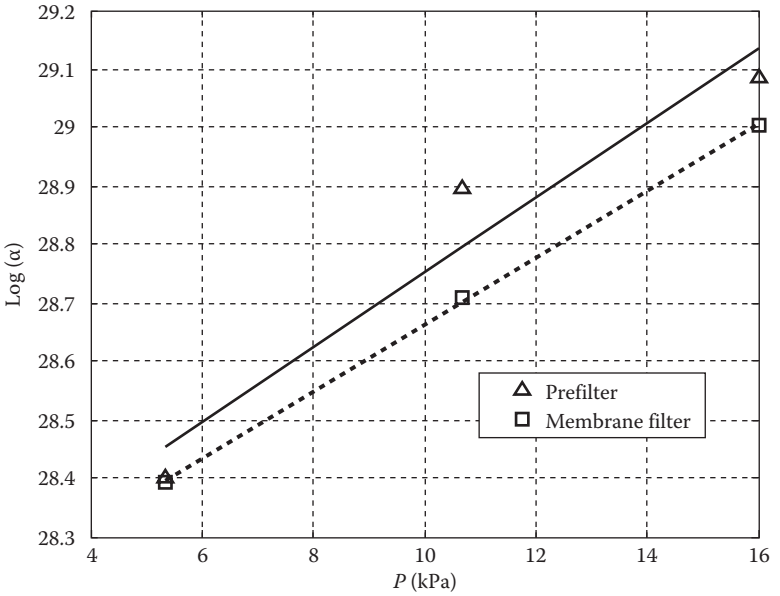


FIGURE E.4.27.5
Variation of the cake resistance parameter α with pressure. (Adapted from Reddy, K. V., Das, M., and Das, S. K., *Journal of Food Engineering*, 69, 381–85, 2005.)

MATLAB® CODE E.4.27.c

Command Window:

```
clear all
close all
format compact

% enter the data
tData1=[0.3 1.5 3.6 5.6 6.9 9.4 12.9 15.4 18.5 22.5 25.5];
RRdata1=[2 13.5 28 40 45.6 55 65 71 75.6 80 81]; % resistance ratio
Rp/Rm at P=136.5 kPa
tData2=[0.5 1.5 2.5 3.1 5.5 6.9 8.8 10.3 12.5 15 17.2 19.5 22 24.5
27.8];
RRdata2=[10 25 37.5 44 70 81 93.5 102 113 120 125 130 134 137 139];
% resistance ratio data Rp/Rm at P=276 kPa

tData1b=[1 3.5 5.4 6.3 8.8 12.5 15.5 18.8 22.6 27.5]; % P=136.5 kPa
Vdata1b=[64.8 30 22.5 20 16 12.5 11 10 8.9 8]; % P=136.5 kPa
tData2b=[2 3 5.5 7 8.5 10.5 12.5 15 19 22 24 27.5]; % P=276 kPa
Vdata2b=[71 48.5 41 26 20 18 17.5 17 16.5 16 15.5 15]; % P=276 kPa

% enter the model constants
K1=95; % K1=Rps/Rm when P=136.5 kPa
K2=150; % K2=Rps/Rm when P=276 kPa
alpha1=0.09; % when P=136.5 kPa
alpha2=0.11; % when P=136.5 kPa
```

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```
K3 = 810; % K3=(P/mu*Rm) when P=136.5 kPa
K4 =2000; % K4=(P/mu*Rm) when P=276 kPa

% modeling
for t = 1:31
    time(t) = t-1;
    RR1(t)=K1*(1-exp(-alpha1*(t-1))); % model resistance ratio Rp/Rm
at P=136.5 kPa
    RR2(t)=K2*(1-exp(-alpha2*(t-1))); % model resistance ratio Rp/Rm
at P=276 kPa
    Vm1(t) = K3 / (1+RR1(t));  % model permeate flux at P=136.5 kPa
    Vm2(t) = K4/ (1+RR2(t)); % model permeate flux at P=276 kPa
end

% plot the data and the model at  P=136.5 kPa
[AX,H1,H2] = plotyy(tData1, RRdata1, tData1b,log(Vdata1b)); hold on
set(H1,'LineStyle','*')
set(H2,'LineStyle','*')
ylim(AX(2), [2 5])
ylim(AX(1), [0 250])
[AX,H1,H2] = plotyy(time, RR1, time,log(Vm1)); hold on
ylim(AX(2), [2 5])
ylim(AX(1), [0 250])
xlabel('Time (min)')
ylabel('R_p/R_m')
set(get(AX(2),'ylabel'), 'string', 'log(Permeate Flux) '); % (L/
m^2h)
legend('P=136.5 kPa', 'P=276 kPa','Location','NorthEast')

% plot the data and the model at  P=276 kPa
[AX,H1,H2] = plotyy(tData2, RRdata2, tData2b,log(Vdata2b)); hold on
set(H1,'LineStyle','o')
set(H2,'LineStyle','o')
xlim([0 30])
ylim(AX(2), [2 5])
ylim(AX(1), [0 250])
xlabel('Time (min)')
ylabel('R_p/R_m')
[AX,H1,H2] = plotyy(time, RR2, time,log(Vm2)); hold on
ylim(AX(2), [2 5])
ylim(AX(1), [0 200])
set(H1,'LineStyle',':')
set(H2,'LineStyle',':')
```

When we run the code Figure E.4.27.6 will appear on the screen.

The rate of filtration of an incompressible liquid through a filter cake may be related with the permeability of the medium by using the Darcy's equation:

$$\frac{dV}{dt} = \frac{A\kappa\Delta P}{\mu H}, \tag{4.66}$$

where V is the volume of the fluid flowing through the medium, μ is the fluid viscosity, ΔP is the pressure drop across the medium, A and H are the cross-sectional area and the depth of the

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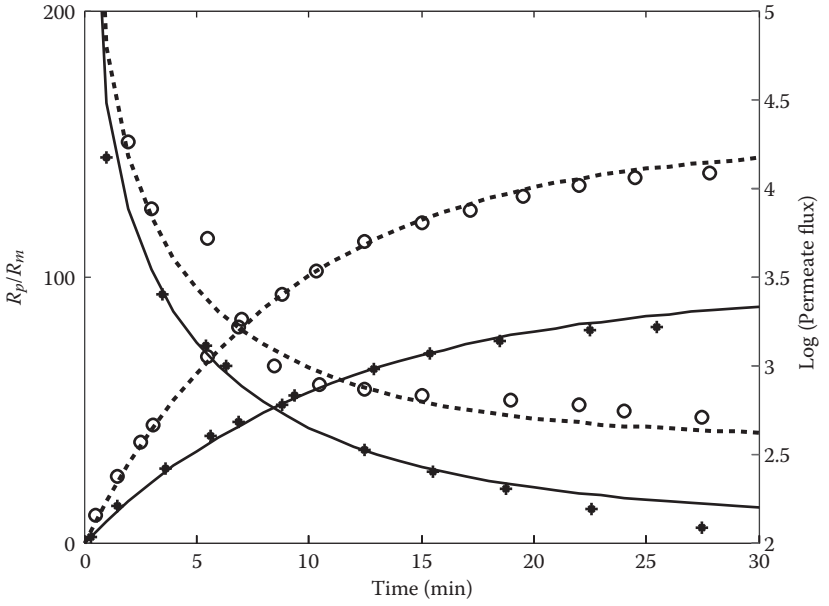


FIGURE E.4.27.6
Comparison of the membrane fouling resistance, Equation E.4.27.3, and permeation rate, Equation E.4.27.1. (Models with experimental data obtained from Chhaya, C., Pai, P., Majumdar, G. C., Dasgupta, S., and De, S., *Journal of Food Process Engineering*, 31, 768–82, 2008.) during sterilization of watermelon juice with microfiltration. Legends: *: $P = 136.5$ kPa, o: $P = 276$ kPa.

medium, respectively. Parameter κ is an empirically defined permeability of the medium related with the properties of the cake (Ingmanson 1953; Harvey, Bridger, and Tiller 1988). When the cake has uniform, straight, cylindrical voids, the permeability may be expressed as

$$\kappa = \frac{d_e^2 \varepsilon}{32}, \tag{4.67}$$

where d_e = (void volume)/(void cross-sectional area) is the diameter of the voids, and ε is the void fraction. For noncylindrical voids, κ may be defined as

$$\kappa = \frac{d_e^2 \varepsilon}{K^{\bullet\bullet}}, \tag{4.68}$$

where d_e = (void volume)/(solid surface area), and $K^{\bullet\bullet}$ is an empirical shape factor (also called the Kozeny constant). For the compressible mycelial microbial cakes, Oolman and Liu (1991) suggested that

$$\kappa = \frac{H}{H_0} \frac{(\varepsilon_0 - \beta)^3 d_h^2}{(1-\beta)^2 16 K^{\bullet\bullet} (1-\varepsilon_0)^2}, \tag{4.69}$$

where $\beta = \alpha(\Delta P/g\rho_c H)^n$, α = constant, ρ_c = grams of dry hyphae/cm^3 cake, g = gravitational acceleration, n = positive constant, ε_0 = void fraction of a developed cake when ΔP equals zero, H_0 = height of a developed cake when ΔP equals zero and d_h = diameter of hyphae. Equations 4.66 through 4.69 relate the filtration rates to the cake characteristics, therefore requiring a more detailed characterization of the cake then with those of Equations 4.59 through 4.62.

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When pure solvent and a solution (solvent + solute) are separated with a solute impermeable membrane and no external pressure is applied ($\Delta P = 0$), solvent tends to diffuse through the membrane toward the solution side to equalize the solvent chemical potential on both sides (Figure 4.7). When the solution is dilute and consists of a single solute the osmotic pressure (π) may be calculated as

$$\pi = cRT, \tag{4.70}$$

where c = concentration of the solute, R = gas constant, and T = absolute temperature. In the concentrated solutions of a single solute, the osmotic pressure may be calculated as

$$\pi = A_1 c + A_2 c^2 + A_3 c^3 + \ldots, \tag{4.71}$$

where A_1, A_2, and A_3 are constants. When there is more than one solute in a dilute solution, the osmotic pressure may be calculated as

$$\pi = RT \sum_{i=1}^{n} c_i, \tag{4.72}$$

where c_i = concentration of each solute. If we should apply pressure ΔP to the solute side, osmosis prevails as long as $\pi > \Delta P$. Solvent flux stops when $\pi = \Delta P$. If we should increase ΔP such that $\Delta P > \pi$, the solvent flux is reversed and became toward the pure solvent side. This is called reverse osmosis (RO). Ultrafiltration (UF) and microfiltration (MF) are essentially similar to the reverse osmosis, but the particle size range of the processes is different.

The rejection coefficient used to describe the efficiency of a membrane system for the separation of a specified solute from a well-defined solution and defined as

$$R = \frac{\begin{pmatrix}\text{solute concentration}\\ \text{at the high pressure}\\ \text{side of the membrane}\end{pmatrix} - \begin{pmatrix}\text{solute concentration}\\ \text{at the low pressure}\\ \text{side of the membrane}\end{pmatrix}}{\begin{pmatrix}\text{solute concentration}\\ \text{at the high pressure}\\ \text{side of the membrane}\end{pmatrix}}. \tag{4.73}$$

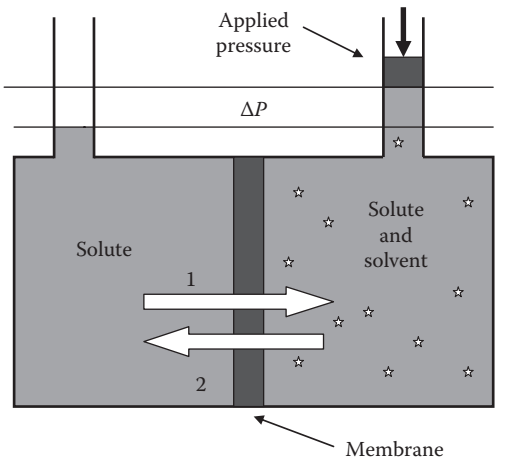


FIGURE 4.7
Solvent flux in osmosis and reverse osmosis processes. The arrow with number 1 indicates the direction of solvent transport in reverse osmosis; the arrow with number 2 indicates the direction of solvent transport in osmosis.

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A rejection coefficient of $R = 1$ implies a perfect membrane and $R = 0$ describes a nonfunctional membrane.

There are different mechanisms suggested for transport through membranes. Since the reverse osmosis membranes are made from different materials and the physicochemical parameters are unique to each solution-membrane system, it is reasonable to assume various rejection and transport mechanisms. According to the *sieve mechanism* concept, a semipermeable membrane has pores intermediate in size between solvent and solute molecules. Separation occurs because solute molecules are blocked out of the pores, while the smaller molecules are allowed to enter. The sieve mechanism may account for removal of large molecules in *UF*; however, the molecules separated in *RO* are approximately the same size, therefore purely steric explanation for membrane rejection is not possible (Cheryan 1992).

The *hydrogen-bonding mechanism* was developed specifically for cellulose acetate membranes. Permeation is suggested to occur as the molecules migrate through the membrane from one hydrogen-bond site to the other. Water molecules also absorbed on the membrane surface by making hydrogen-bonds, and prevent solute ions from entering. Solute molecules may move through the membrane by displacing the solvent molecules from the absorption sites. Since displacement requires large amounts of energy, relatively few solute molecules are absorbed by the membrane (Cheryan 1992).

The *solution-diffusion mechanism* attributes the solute rejection to large differences in the solubility and diffusivity of the solute and the solvent materials in the membrane material. According to the *preferential sorption-capillary flow mechanism*, partial sorption on the membrane surface is achieved with repulsive or attractive force gradients at the membrane surface. The solvent and the solute molecules move through the membrane pores with the kinetic effects governed by both potential force gradients and steric effects associated with the structure and size of the solute and solvent molecules relative to the membrane pores. A membrane transport model is needed to relate the solvent or solute fluxes to the operating conditions or the other measurable properties of the system. An extensive review of the membrane transport models has been presented by Cheryan (1992). Some of these models that are suitable for practical calculations are summarized in Table 4.1.

The Kadem–Katchalsky and Pusch models are based on the principles of irreversible thermodynamics (Kadem and Katchalsky 1958; Pusch 1977). The solution-diffusion model assumes that the membrane is a nonporous diffusive barrier in which all components dissolve in accordance with phase equilibrium considerations and diffuse through by the same mechanism that govern diffusion through liquids and solids (Loeb and Longsdale 1972). Pore flow model considers the flux through the membrane as viscous flow through a highly porous membrane (Merten 1966; Aiba, Humphrey and Millis 1973). Separation of the solute and solvent are assumed to occur because the solid concentration in the pore fluid is not the same as that in the feed solution.

After assuming chemical equilibria at the solution-membrane interfaces, solute concentration in the pore fluid at each interface is related to the solute concentration in the permeate and feed solutions through equilibrium or partition coefficients (Cheryan 1992). A pore flow model includes a tortuosity factor (τ), which accounts for the twisting of the pores and an increase in the effective pore length. Solute flux for this model is the sum of the solute flux due to convective or bulk movement within the pores and diffusion of solute through the membrane pores (Cheryan 1992). A finely porous model is developed for the reverse osmosis membranes whose transport properties are intermediate between those of the solution-diffusion and the pore flow models (Merten 1966). The finely porous model is a frictional transport model. The frictional transport models assume that the thermodynamic driving forces for transport of the particles across the membrane are balanced by the frictional forces between the particle and all others in the surrounding medium. There are also other models published in the literature that use a combination of the models listed in Table 4.1. The detailed discussion of these models are beyond the scope of the text and an interested reader is recommended to refer to Cheryan (1992).

Constants of the models given in Table 4.1 varies with the kind of membrane, composition, and pH of the solution and the operating conditions of the membranes. Fouling of the

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TABLE 4.1

Models for Membrane Transport

Kadem and Katchalsky's model	$J_{solvent} = L_{solvent}(\Delta P - \sigma\Delta\pi)$	(4.74)
	$J_{solute} = L_{solute}\Delta\pi + (1-\sigma)\, J_{solvent} C_{ln}$	(4.75)
Pusch's model	$J_{solvent} = L_{solvent}(\Delta P - \sigma\Delta\pi)$	(4.76)
	$J_{solute} = \left[\frac{L_{osmotic}}{L_{solvent}} - \sigma^2\right] L_{solvent}\bar{c}\Delta\pi + J_{solvent}(1-\sigma)\bar{c}$	(4.77)
	$R_{max} = \sigma$	(4.78)
	$R = \frac{R_{max} J_{solvent}}{J_{solvent} + \left[\frac{L_{osmotic}}{L_{solvent}} - R_{max}^2\right] L_{solvent}\pi_{high}}$	(4.79)
Solution-diffusion model	$J_{solvent} = A(\Delta P - \Delta\pi)$	(4.80)
	$J_{solute} = B\Delta c$	(4.81)
	where	
	$A = -\frac{D_{solvent.M} c_{solvent.M} \bar{v}_{solvent}}{RT}$	(4.82)
	$B = -\frac{D_{solute.M} K_{solute}}{l}$	(4.83)
	$R_{max} = 1$	(4.84)
	$R = \frac{A(\Delta P - \Delta\pi)}{A(\Delta P - \Delta\pi) + Bc_{solvent/high}}$	(4.85)
Pore flow model	$J_{solvent} = \varepsilon v_D$	(4.86)
	$J_{solute} = \frac{v}{\varepsilon}\frac{K_{low}c_{low} - K_{high}c_{high}\exp[v\tau l/\varepsilon D_{solute/solvent}]}{1-\exp[v\tau l/\varepsilon D_{solute/solvent}]}$	(4.87)
	where	
	$v_p = \frac{r^2 n}{8\mu}\frac{\Delta P}{\tau l}$	(4.88)
	$R_{max} = 1 - \frac{K_{high}}{\varepsilon}$	(4.89)
	$R = 1 - \frac{K_{high}\exp[v\tau l/\varepsilon D_{solute/solvent}]}{K_{low} - \varepsilon + \varepsilon\exp[v\tau l/\varepsilon D_{solute/solvent}]}$	(4.90)
Finely porous model	$J_{solvent} = \varepsilon v$	(4.91)
	$J_{solute} = \frac{v}{\varepsilon b}\frac{K_{low}c_{low} - K_{high}c_{high}\exp[(v\tau l/\varepsilon)(f_{solute/solvent}/R_gT)]}{1-\exp[(v\tau l/\varepsilon)(f_{solute/solvent}/R_gT)]}$	(4.92)
	where	
	$v = \frac{H}{\varepsilon}\left[\frac{1}{1+(Hf_{solute/membrane}/MW\varepsilon)c_{low}}\right]\frac{\Delta P}{\tau l}$	(4.93)
	$b = 1 + (f_{solute/membrane}/f_{solute/solvent})$	(4.94)

(*Continued*)

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TABLE 4.1 (CONTINUED)

Models for Membrane Transport

$$R_{max} = 1 - \frac{K_{high}}{\varepsilon} \tag{4.95}$$

$$R = 1 - \frac{K_{high} \exp\left[\left(v\,\tau\, l/\varepsilon\right)\left(f_{solute/solvent} / R_g T\right)\right]}{K_{low} - b\varepsilon + b\varepsilon \exp\left[\left(v\,\tau\, l/\varepsilon\right)\left(f_{solute/solvent} / R_g T\right)\right]} \tag{4.96}$$

Source: Cheryan, M., *Handbook of Food Engineering*, Marcel Dekker, Inc., New York, 1992.

where

b = friction factor

Δc = solute concentration difference across the membrane

c_{ln} = log mean solute concentration difference across the membrane

$\bar{c} = \Delta\pi / RT\Delta\ln(a)$ (where $\Delta\ln(a)$ is the difference of the natural logarithms of the solute activity on both sides of the membrane)

c_{low} = solute concentration at the low pressure side solution/membrane interface

c_{high} = solute concentration at the high pressure side solution/membrane interface

$c_{solvent/high}$ = solvent concentration at the high pressure side solution/membrane interface

$c_{solvent.M}$ = concentration of the solvent in the membrane

$D_{solute/solvent}$ = diffusivity of solute in solvent

$D_{solvent.M}$ = diffusivity of solvent in the membrane

$D_{solute.M}$ = diffusivity of solute in the membrane

$f_{solute/membrane}$ = friction coefficient between the solute and membrane

$f_{solvent/solvent}$ = friction coefficient between the solute and solvent

$H = \varepsilon r^2 / 8\mu$ = hydraulic permeability of the membrane

$J_{solvent}$ = solvent flux through the membrane

J_{solute} = solute flux through the membrane

K_{high} = solute distribution coefficient at the high pressure side of the membrane

K_{low} = solute distribution coefficient at the low pressure side of the membrane

K_{solute} = generalized solute distribution coefficient

l = thickness of the membrane

$L_{solvent}$ = hydrodynamic (solvent) permeability coefficient

L_{solute} = solute permeability coefficient

$L_{osmotic}$ = osmotic permeability coefficient

MW = molecular weight of the solute

n = number of pores per unit membrane area

r = pore radius

R_{max} = maximum attainable value of the rejection coefficient

$\bar{v}_{solvent}$ = average transverse velocity of the solvent

ΔP = pressure difference across the membrane

R_g = gas constant

T = absolute temperature

v_p = center-of-mass pore fluid velocity

ε = fractional pore area

μ = viscosity

π_{high} = osmotic pressure on the high pressure side of the membrane

$\Delta\pi$ = osmotic pressure difference across the membrane

σ = reflection coefficient

τ = tortuosity factor

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membranes is the major problem in membrane separation processes, which may also change the efficiency of the separation processes and the value of the model constants. In some processes solute molecules may tend to accumulate on the surface of the membrane after preferential transport of the solvent molecules, then a solute concentration gradient is established between the bulk solution and the solution-membrane interface. This is called *concentration polarization*, and increases the effective solute concentration exposed to the membrane (Figure 4.8). Higher effective solute concentration and subsequently a higher osmotic pressure difference is experienced between the both sides of the membrane as a result of concentration polarization, then the efficiency of separation process may decrease. Concentration polarization may be minimized by supplying liquid flow parallel to the membranes, which removes the accumulating solute molecules.

Most of the membrane separation processes are isothermal, but in osmotic distillation water evaporates on the feed side interface of the membrane, vapor diffuses through the membrane and condenses at the other side (referred to as permeate site). The phase change phenomena causes a temperature drop at the feed side and a temperature increase at the permeate side of the membrane (Figure 4.9). This is referred to as "temperature polarization" in the literature (Bui, Nguyen, and Joachim 2005).

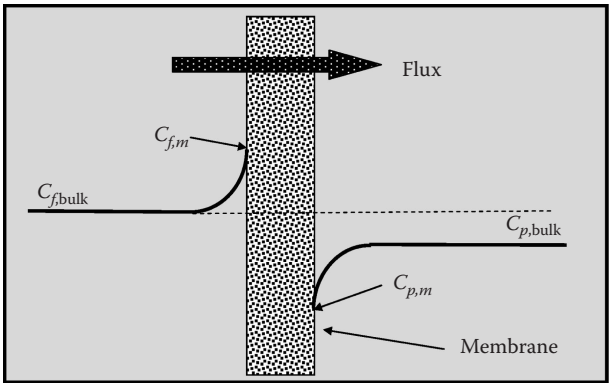


FIGURE 4.8
Concentration polarization in osmotic distillation.

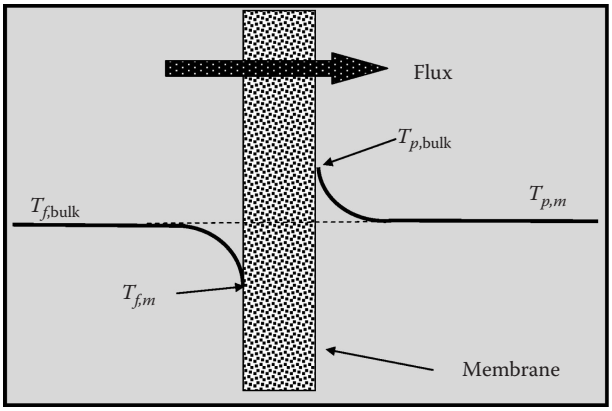


FIGURE 4.9
Temperature polarization in osmotic distillation.

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Example 4.28: Mathematical Modeling of Osmotic Concentration of Foods

In an osmotic separation process (Figure E.4.28.1) flux, F, may be expressed as

$$F = \frac{\Delta\pi - \Delta P}{R_{\text{total}}}. \tag{E.4.28.1}$$

Where $\Delta\pi$ and ΔP are osmotic and hydrolic pressure differences across the membrane, respectively, and R_{total} is the total mass transfer resistance. Dova, Petros, and Lazarides (2007) suggested that there were two boundary layers adjacent to the membrane: The osmotic layer on the osmotic liquid side and the feed layer on the feed side. The total resistance may be analyzed in three terms:

$$R_{\text{total}} = R_m + R_o + R_f. \tag{E.4.28.2}$$

Where R_m = membrane resistance, R_o = resistance on the side of the osmotic layer, R_f = resistance on the side of the feed layer.

Membrane resistance R_m consists of two components:

$$R_m = \frac{1}{A} + R_b. \tag{E.4.28.3}$$

Where $1/A$ is the resistance of the top ultra-thin, selective layer (A is the osmotic coefficient) and R_b is the resistance of the backing material. Membrane resistance R_m depends on the void fraction, tortuosity, thickness of the ultra-thin selective layer, and diffusivity of water in the osmotic medium solution (Dova, Petros, and Lazarides 2007).

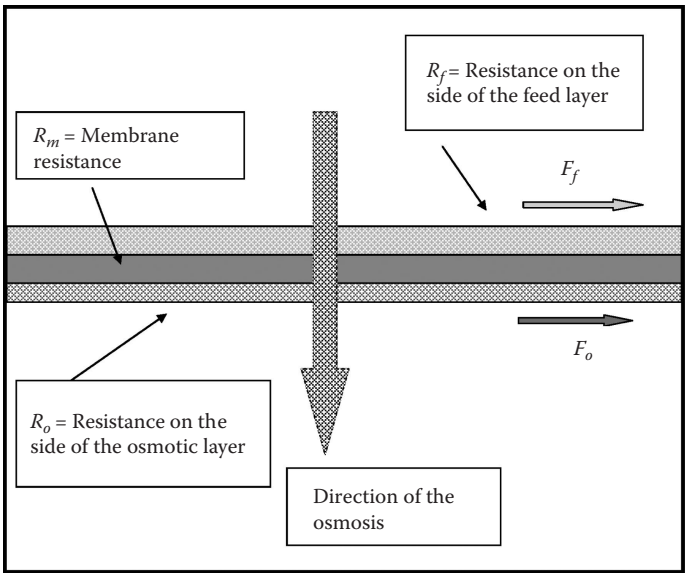


FIGURE E.4.28.1
Schematic description of the resistances to osmosis.

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Parameters R_o and R_f are indeed the resistances of the boundary layers and tend to increase with the fluid velocities (or flow rates). Equation E.4.28.2 may be rewritten as (Dova, Petros, and Lazarides 2007)

$$R_{\text{total}} = \left(k_1 \frac{\mu_o^{a1}}{F_o^{b1}} + k_2 \frac{\mu_o^{a2}}{F_o^{b2}} \right)_o + \frac{1}{A} + \left(k_3 \frac{\mu_f^{a3}}{F_f^{b3}} + k_4 \frac{\mu_f^{a4}}{F_f^{b4}} \right)_f . \quad \text{(E.4.28.4)}$$

Where subscripts *o* and *f* refer to the osmotic and feed side boundary layers, respectively; *F* is the flow rate and μ is the viscosity in the corresponding boundary layer. Parameters *a*1, *a*2, *a*3, *a*4, *b*1, *b*2, *b*3, and *b*4 are constants. We also have

$k_1 \frac{\mu_o^{a1}}{F_o^{b1}}$	boundary layer resistance on the osmotic side
$k_2 \frac{\mu_o^{a2}}{F_o^{b2}}$	impact of the osmotic side on compression of the membrane backing material
$k_3 \frac{\mu_f^{a3}}{F_f^{b3}}$	boundary layer resistance on the feed side
$k_4 \frac{\mu_f^{a4}}{F_f^{b4}}$	impact of the feed side on compression of the membrane backing material

After combining Equations E.4.28.1 and E.4.28.4 the flux may be expressed as

$$F = \frac{\Delta\pi - \Delta P}{B_1 \mu_1^{B2} F_1^{B3} + \frac{1}{A} + B_4 \mu_2^{B5} F_2^{B6}}, \quad \text{(E.4.28.5)}$$

where $B_1, \ldots B_6$ are constants. MATLAB® code E.4.28 simulates the flux as a function of F_1 and F_2.

MATLAB® CODE E.4.28

Command Window:

```
clear all
close all

% constants of the model
B1=3.14e5;
B2=1.1;
B3=0.7;
B4=3.79e9;
B5=2.48;
B6=0.317;
A=2.9; %  (m2)

% physical properties
mu1=1.2e3; % viscosity of the osmotic medium (Pas)
mu2=0.97e3; % viscosity of the feed (Pas)
deltaP=1; % atm
deltaPi=250; % atm

% feed rates
```

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```
F1=[0.1:0.05:0.6]; % flow rate of the osmotic medium (kg/s)
F2=[0.1:0.05:0.6]; % flow rate of the feed (kg/s)

for i=1:length(F1)
for j=1:length(F2)

F(i,j)=(deltaPi-deltaP)/((B1*(mu1^B2)*(F1(i)^B3))+(1/A)+
(B4*(mu2^B5)*(F2(i)^B6))); % flux

end
end

surf(F1,F2,F);
colormap gray

ylabel('F1')
xlabel('F2')
zlabel('F')
```

When we run the code Figure 4.28.2 will appear on the screen.

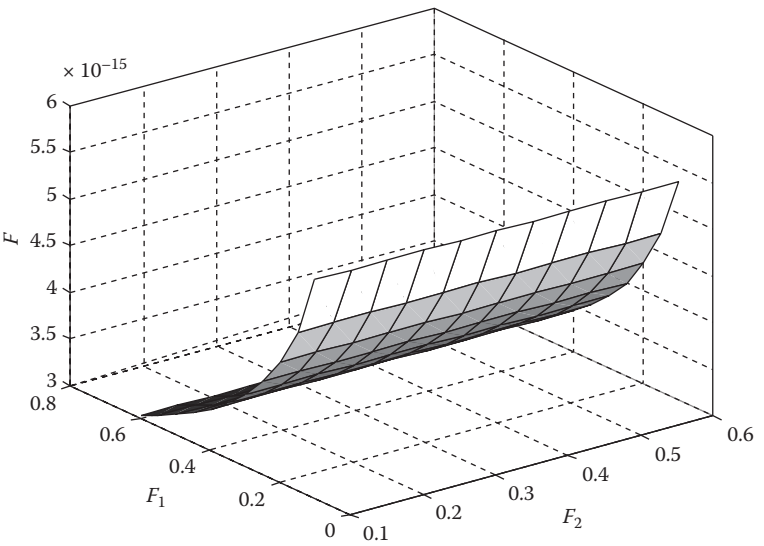


FIGURE E.4.28.2
Schematic description of the variation of the permeation rate with F_1 and F_2. (Adapted from Dova, M. I., Petros, K. B., and Lazarides, H. N., *Journal of Food Engineering*, 78, 431–37, 2007.)

Example 4.29: Mass Transfer in Mixed Solute Osmotic Dehydration of Apple Rings

In the osmotic dehydration process, cell membranes function like the membranes employed in the conventional osmotic membrane separation processes. In conventional drying processes, liquid water in the foods undergo a phase and evaporate. In an osmotic drying process, water is transported from the fruit into the concentrated solute phase without phase change. Fruits and

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vegetables are subjected to osmotic dehydration usually prior to air drying, freeze drying, or freezing. The most commonly used osmotic agents are sucrose for fruits and sodium chloride for vegetables. Other osmotic agents such as lactose, maltodextrin, ethanol, glucose, glycerine, and corn syrups have also been used. Osmotic drying is a multicomponent mass transfer process, where water is removed from the fruits and vegetables and osmotic agents are taken up (Biswal and Bozorgmehr 1992). Mass flux N was previously expressed empirically as

$$N = k_c\left(c_i - c_\infty\right). \tag{2.43e}$$

It was shown in Example 2.16 that when an unsteady state concentration profile occurs near the interface the mass transfer coefficient may be expressed as $k_c = \sqrt{D/\pi t}$. The total variation of any substrate in the apple slices may be described as

$$V\frac{dc}{dt} = A\sqrt{\frac{D}{\pi t}}\left(c_i - c_\infty\right), \tag{E.4.29.1}$$

where A is the mass transfer area and V is the volume of the fruit slices. When A, c_i, c_∞, D, and V do not change much, Equation E.4.29.1 may be rearranged as

$$\frac{dc}{dt} = \left\{\frac{A\left(c_i - c_\infty\right)}{V}\sqrt{\frac{D}{\pi}}\right\}\frac{1}{\sqrt{t}}, \tag{E.4.29.2}$$

when the term $\left\{\left[A\left(c_i - c_\infty\right)/V\right]\sqrt{D/\pi}\right\}$ is constant. Equation E.4.29.2 may be rearranged and integrated as

$$c = c_0 + \kappa\sqrt{t}, \tag{E.4.29.3}$$

where $\kappa = \left\{\left[A(c_i - c_\infty)/2V\right]\sqrt{D/\pi}\right\}$.

The moisture loss and solutes uptake by the apple rings are simulated with MATLAB® codes E.4.29.a and E.4.29.b.

MATLAB® CODE E.4.29.a

Command Window:

```
clear all
close all
format compact

% MODELING THE MOISTURE LOSS BY THE APPLE RINGS

% moisture loss data at 35 oC
cDataM1= [0 0.32 0.46 0.56 0.59]; % with (10 % NaCl)/(40 % sucrose)
ratio
cDataM2= [0 0.15 0.20 0.24 0.30]; % with (0 % NaCl)/(30 % sucrose)
ratio
tDataM= [0 7.5 11 13.5 16]; % sqrt(min)

% plot the data
```

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```
plot(tDataM, cDataM1, 'p'); hold on;
plot(tDataM, cDataM2, 'd'); hold on;
ylabel('Moisture Loss')
xlabel('sqrt(TIME) (sqrt(min))')
legend('at 35 oC with (10 % NaCl)/(40 % sucrose)', 'at 35 oC with (0
% NaCl)/(30 % sucrose)','Location','NorthWest')

% modeling
N=1;
X= tDataM;
Y= cDataM1;
[A3 B3 S R]=LineFitting(X,Y,N);
fprintf('\n At 20 oC with (10 %% NaCl)/(50 %% sucrose) the model
is')
c0=A3;
Kappa=B3;
StandardError=S;
CorrelationCoefficient=R;
fprintf('\n c= %3.2f+%3.2f*sqrt(t) with r= %3.2f Se= %3.2f
\n',c0,Kappa, CorrelationCoefficient, StandardError)
% plot the model
cModel=c0+Kappa.*tDataM;
plot(tDataM, cModel, '-'); hold on;

N=1;
X= tDataM;
Y= cDataM2;
[A4 B4 S R]=LineFitting(X,Y,N);
fprintf('\n At 20 oC with (0%% NaCl)/(30%% sucrose) the model is')
c0=A4;
Kappa=B4;
StandardError=S;
CorrelationCoefficient=R;
fprintf('\n c= %3.2f+%3.2f*sqrt(t) with r= %3.2f Se= %3.2f
\n',c0,Kappa, CorrelationCoefficient, StandardError)
% plot the model
cModel=c0+Kappa.*tDataM;
plot(tDataM, cModel, '-'); hold on;
```

When we run the code the following lines and Figure E.4.29.1 will appear on the screen.

```
At 20 oC with (10 % NaCl)/(50 % sucrose) the model is
 c= 0.02+0.04*sqrt(t) with r= 1.00 Se= 0.43

 At 20 oC with (0% NaCl)/(30% sucrose) the model is
 c= 0.00+0.02*sqrt(t) with r= 1.00 Se= 0.20
```

Example 4.30: Mass Transfer Models for the Membrane Distillation Process

The membrane distillation process may be employed for separating water from aqueous solutions. The feed and the permeate side streams may be pumped in a cocurrent or countercurrent manner through different sides of the membrane. The difference in the water vapor pressures of both sides is the driving force for the water vapor transport. A schematic description of a membrane distillation process is given in Figure E.4.30.1.

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MATLAB® CODE E.4.29.b

Command Window:

```
clear all
close all
format compact

% MODELING THE SOLUTES UPTAKE BY THE APPLE RINGS

% NaCl + sucrose uptake data at 20 oC
cDataS1= [0 0.5 0.8 1.0 1.3]; % with (10 %NaCl)/(40% sucrose)
cDataS2= [0 0.1 0.2 0.22 0.35]; % with (2.5% NaCl)/(47.5% sucrose)
tDataS= [0 7.5 11 13 15.5]; % sqrt(min)

figure
% plot the data
plot(tDataS, cDataS1, 'p'); hold on;
plot(tDataS, cDataS2, 'd'); hold on;
ylabel('(Moles of NaCl + sucrose)/(kg water)')
xlabel('sqrt(TIME) (sqrt(min))')
legend('at 20 oC with (10% NaCl)/(40 % sucrose)', 'at 20 oC with
(2.5% NaCl)/(47.5% sucrose)','Location','NorthWest')

% modeling
N=1;
X= tDataS;
Y= cDataS1;
[A3 B3 S R]=LineFitting(X,Y,N);
fprintf('\n At 20 oC with (10%% NaCl)/(40%% sucrose) the model is')
c0=A3;
Kappa=B3;
StandardError=S;
CorrelationCoefficient=R;
fprintf('\n c= %3.2f+%3.2f*sqrt(t) with r= %3.2f Se= %3.2f
\n',c0,Kappa, CorrelationCoefficient, StandardError)
% plot the model
cModel=c0+Kappa.*tDataS;
plot(tDataS, cModel, '-'); hold on;

N=1;
X= tDataS;
Y= cDataS2;
[A4 B4 S R]=LineFitting(X,Y,N);
fprintf('\n At 20 oC with (2.5%% NaCl)/(47.5%% sucrose) the model
is')
c0=A4;
Kappa=B4;
StandardError=S;
CorrelationCoefficient=R;
fprintf('\n c= %3.2f+%3.2f*sqrt(t) with r= %3.2f Se= %3.2f
\n',c0,Kappa, CorrelationCoefficient, StandardError)
% plot the model
cModel=c0+Kappa.*tDataS;
plot(tDataS, cModel, '-'); hold on;
```

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When we run the code the following lines and Figure E.4.29.2 will appear on the screen:

```
At 20 oC with (10% NaCl)/(40% sucrose) the model is
 c= -0.05+0.08*sqrt(t) with r= 1.00 Se= 0.89

 At 20 oC with (2.5% NaCl)/(47.5% sucrose) the model is
 c= -0.02+0.02*sqrt(t) with r= 1.00 Se= 0.23
```

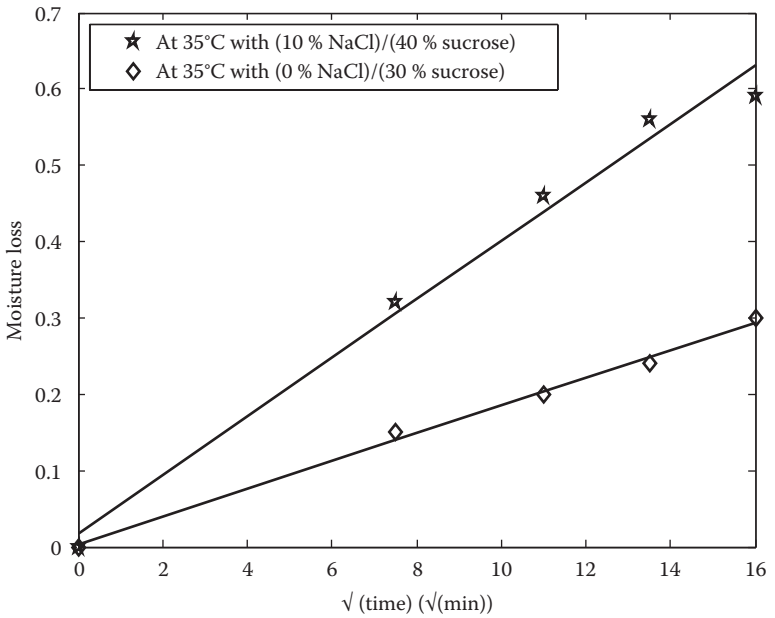


FIGURE E.4.29.1
Comparison of Equation E.4.29.3 with the experimental data. Moisture loss was defined as $[c_0 - c(t)]/c_0$. Total solutes dissolved in the osmotic solution was 50%. (Adapted from Biswal, R. N., and Bozorgmehr, K., *Transactions of the ASAE*, 35, 257–62, 1992.)

In a membrane distillation process the flux is modeled as

$$J = K\Delta P_w. \tag{E.4.30.1}$$

Where K is the overall transport coefficient, $\Delta P_w = P_{w,1} - P_{w,2}$ is the water vapor pressure difference across the membrane. The overall transport coefficient K may be expressed as

$$\frac{1}{K} = \frac{1}{K_f} + \frac{1}{K_m} + \frac{1}{K_p}, \tag{E.4.30.2}$$

where $1/K_f$, $1/K_m$, and $1/K_s$ are the transport resistances of the feed, boundary layer, membrane, and the permeate boundary layer, respectively. When we have a shell and tube heat exchanger

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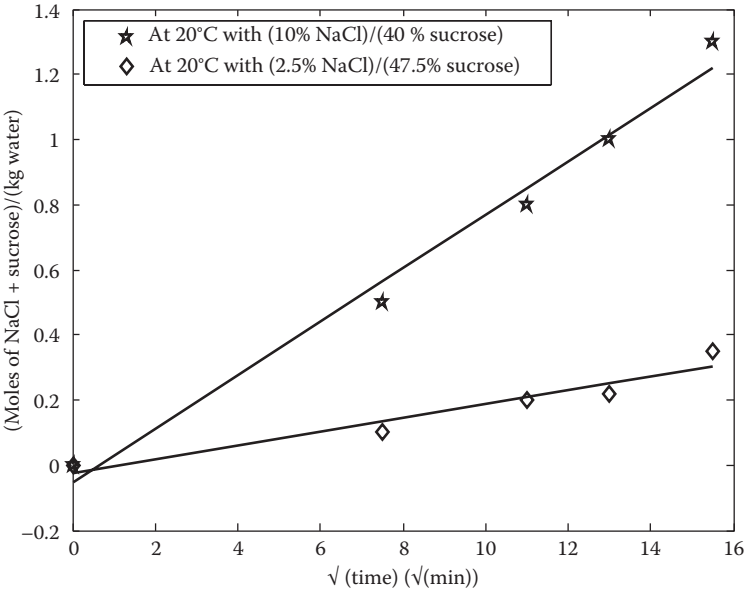


FIGURE E.4.29.2
Comparison of Equation E.4.29.3 with the experimental data. Moles of (NaCl + sucrose)/kg of water is the total molality of the solutes uptake by apple rings. The total of the solutes dissolved in the osmotic solution was 50%. (Adapted from Biswal, R. N., and Bozorgmehr, K., *Transactions of the ASAE*, 35, 257–62, 1992.)

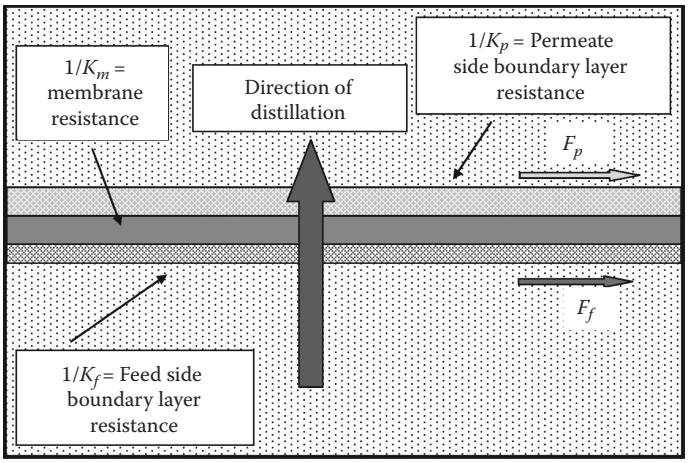


FIGURE E.4.30.1
Schematic description of the resistances to membrane distillation.

like the membrane system, the vapor transport through the membrane is modeled with an ordinary diffusion model, K_m may be expressed as

$$K_m = K_{m,\text{diffusion}} = \left(\frac{\varepsilon D_{w,\text{air}}}{\tau}\right)\left(\frac{MW}{RTy_{\ln f_i}\ln\left(r_o/r_i\right)}\right), \tag{E.4.30.3}$$

where ε and τ are membrane porosity and tortuosity, respectively; $D_{w,\text{air}}$ is the diffusivity of water vapor through stagnant air, MW is the molecular weight of water, R is the gas constant, T is

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temperature; r_i and r_o are the inside and outside diameter of the fibers. When a fluid flows in a pipe, its pressure drops as predicted by the Hagen–Poiseuille equation. Equation E.4.30.3 may be corrected for this effect as

$$\frac{1}{K_m} = \frac{1}{K_{m,\text{diffusion}}} + \frac{1}{a(1-b) + ab(P_m/P_{ref})}, \tag{E.4.30.4}$$

where a is the membrane permeation constant evaluated at reference pressure P_{ref}, b is a constant introducing the contribution of the pressure drop along the tube.

Mass transfer coefficients on either side of the membrane may be calculated from the empirical equations of the following form:

$$\text{Sh} = \alpha \text{Re}^{\beta} \text{Sc}^{\chi}, \tag{E.4.30.5}$$

where α, β, and χ are constants, $\text{Sh} = kd/D_w$ = Sherwood number, $\text{Re} = vd\rho/\mu$ = Reynolds number, and $\text{Sc} = \mu/\rho D_w$, d = diameter of the tube, D_w = diffusivity of water, μ = viscosity of the fluid, ρ = density of the fluid. It should be noticed that these dimensionless numbers are evaluated with the physical properties (ρ, μ, D_w) and constants (d, k, v) related to the site that Equation E.4.30.5 is related with. The mass transfer coefficient k of each side is substituted for K_p or K_f after making appropriate conversions to make all the resistances have the same units. A review of the empirical equations of the type described by Equation E.4.30.5 are given by Bui, Nguyen, and Joachim (2005) for osmotic distillation in a hollow fiber module.

Concentration polarization reduces the mass transfer rate through the membrane, then the rate of flux becomes:

$$J = K\Delta P_{w,m} = \Theta K \Delta P_{w,b}, \tag{E.4.30.6}$$

where $\Delta P_{w,m}$ is the water vapor pressure differences across the membrane when there is no concentration polarization. Concentration polarization reduces $\Delta P_{w,m}$ to $\Delta P_{w,b}$, which is the actual mass transfer driving force when there is concentration polarization. These two driving forces are related as

$$P_{w,m} = \Theta \Delta P_{w,b}, \tag{E.4.30.7}$$

where $\Theta < 1$ and represents the fraction of $\Delta P_{w,m}$ that is available for mass transfer when there is concentration polarization.

Numerous resistances are involved in the membrane separation processes as described by Equations E.4.30.1 through E.4.30.7. Some of the physical properties involved in these equations are either difficult or impossible to predict accurately. Equation E.4.30.1 is an easy and useful model for practical purposes. MATLAB® code E.4.30 exemplifies the use of Equation E.4.30.1 in a membrane distillation process.

MATLAB® CODE E.4.30

Command Window:

```
clear all
close all
format compact
```

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```
% enter the data
deltaPdata=[500 900 1200 1850 2700 3850 5200 6700]; %  water vapor
pressure difference between the feed and permeate sides (Pa)
fData=[4 6 10 15 20 28 38 48]; % flux data (L/h m2)

%  plot the data
plot(deltaPdata, fData, 'o'); hold on
ylabel(' Flux (L/hm^2)')
xlabel('water vapor pressure difference (Pa)')

%  fit a polynomial empirical model to the data
N=1; % degree of the fitted polynomial determine N
c = polyfit(deltaPdata, fData,N);  % best fitting line to the data
fluxModel=polyval(c,deltaPdata);
plot(deltaPdata, fluxModel, '-'); hold on
legend('data','model','Location','SouthEast')
grid on

K= c(1)  % constant of the model
```

When we run the code the following lines and Figure E.4.30.2 will appear on the screen:

```
K =
    0.0071
```

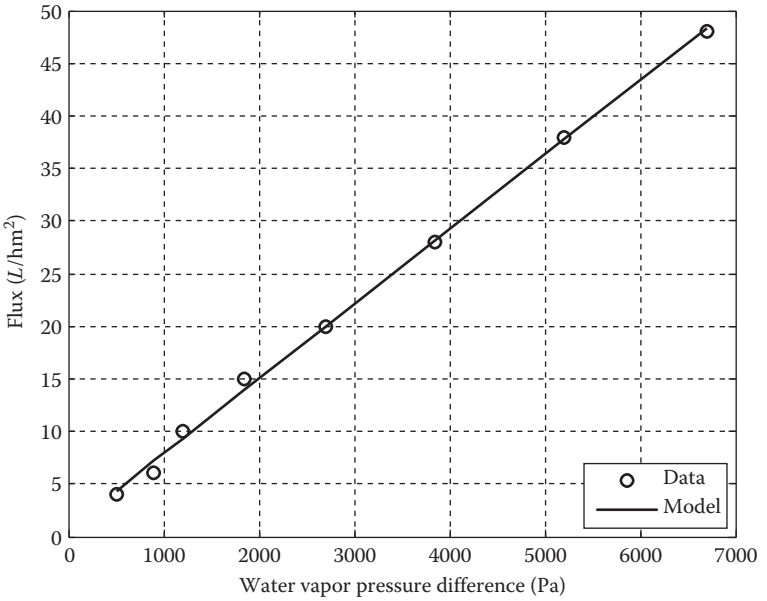


FIGURE E.4.30.2
Comparison of Equation E.4.30.1 with the data obtained during recovery of volatile aroma compounds from black currant juice by vacuum membrane distillation, $K = 7.1 \times 10^{-5}$ m/Pa h. (Adapted from Bagger-Jorgensen, R., Meyer, A. S., Varming, C., and Johson, G., *Journal of Food Engineering*, 64, 23–31, 2004.)

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4.4.3 Basic Computations for Extraction Processes

In a liquid/solid extraction process the food solids are brought in to contact with a liquid solvent. The solvent dissolves the solute in the solid phase, then two phases are separated. The liquid/solid extraction process is also referred to as leaching. Solid/liquid extraction may be employed to remove or separate some components from the food materials (i.e., crystal sugar production from sugar cane), or it may occur unintentionally in other processes (i.e., blanching). The biological materials have cellular structure and their soluble constituents are usually inside the cell walls, which may make the extraction process difficult. Grinding or drying the raw food materials may help to improve the extraction process by breaking the cell walls.

Extraction is a stage contacting process. *Stage* is a unit of equipment, in which two or more phases are brought into contact for a predetermined period, then separated from each other. When these phases are contacted for a long period to attain thermodynamic equilibrium, the stage is referred to as an *equilibrium stage*. Theoretical or ideal stage are the other names for an equilibrium stage.

Example 4.31: Extraction of Sugar From Beets

The extraction of beet sugar may be resolved in two steps (Yang and Brier 1958): (1) Diffusion of sugar beet solution through the permeable membrane of beet cells toward the interface between the beets and the extracting solution, (2) mass transfer of sugar through a liquid film at the interface into the extracting solution. Diffusion of sugar inside the beet may be modeled with the equation of continuity after simplifying Equation 2.12 as

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}, \tag{E.4.31.1}$$

where c is the sugar concentration in the beet, D is the diffusion coefficient of sugar, t is time, and z is the distance of diffusion within the solid slab extracted. When we consider a slab of finite thickness $2L$, the following initial and the boundary values exist:

$$\text{IC: } c = c_0 \text{ for } -L \le z \le L \text{ at } t = 0, \tag{E.4.31.2}$$

$$\text{BC: } c = c^* \text{ at } z = -L \text{ and } z = L, \tag{E.4.31.3}$$

where c^* is the sugar concentration of the beets in equilibrium with c_b (i.e., sugar concentration in bulk liquid). The solution of Equation E.4.31.1 with the given IC and BC is

$$\frac{\bar{c} - c^*}{c_0 - c^*} = \frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left[\frac{-D(2m+1)^2\pi^2 t}{L^2}\right]. \tag{E.4.31.4}$$

Mass transfer through the liquid film at the solid/liquid interface may be expressed as

$$-\frac{d\bar{c}}{dt} = kA(c^* - c_b), \tag{E.4.31.5}$$

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where k is the mass transfer coefficient per unit mass transfer area, and A is the total mass transfer area. Yang and Brier (1958) calculated kA in the experiments performed with the different liquid phase flow rates and temperatures. The variation of parameter kA with time was found not to be affected by the experimental conditions implying that the resistance of the liquid film around the beet slices were negligible in comparison with that of the internal mass transfer. MATLAB® code E.4.31 simulates a variation of the dimensionless average beet sugar contents with time.

MATLAB® CODE E.4.31

Command Window:

```
clear all
close all
format compact

 % enter the experimental data
tData=[10 20 30 40 50 60]; % experimental data (time, min)
cData65=[0.4 0.21 0.13 0.07 0.05 0.037];  % experimental data at 65
oC (dimensionless concentration)
cData80=[0.3 0.16 0.08 0.05 0.035 0.026];  % experimental data at 65
oC (dimensionless concentration)

% plot the experimental data
semilogy(tData,cData65, '*'); hold on
semilogy(tData,cData80, 'o'); hold on
legend('T=65 oC','T=80 oC','Location','SouthWest')
grid on
xlabel('Time (min)')
ylabel('(c-c*)/(c0-c*)')

% enter the model constants
D0=[1.87 2.38]; % at T=65 oC and T=80 oC, respectively
alpha=[0.009 0.015];
 L=16;

% model
for k=1:2
    t(1)=0;
  for i=1:7
      D(k)=D0(k)-alpha(k)*t(i);
       sum=0;
           for m=0:1000
             sum=sum+1/(2*m+1)^2*exp(-D(k)*((2*m+1)^2)*(pi^2*t(i)/
L^2));
           end
             c(i)=sum*8/pi^2;
         if k ==1
           % plot the model (T=65 oC)
           semilogy(t,c, '-'); hold on
         end
         if i<=6
         t(i+1)=t(i)+10;
         end
 end
```

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```
end
if k ==2
% plot the model (T=80 oC)
semilogy(t,c, ':'); hold on
end
```

When we run the code Figure E.4.31 will appear on the screen.

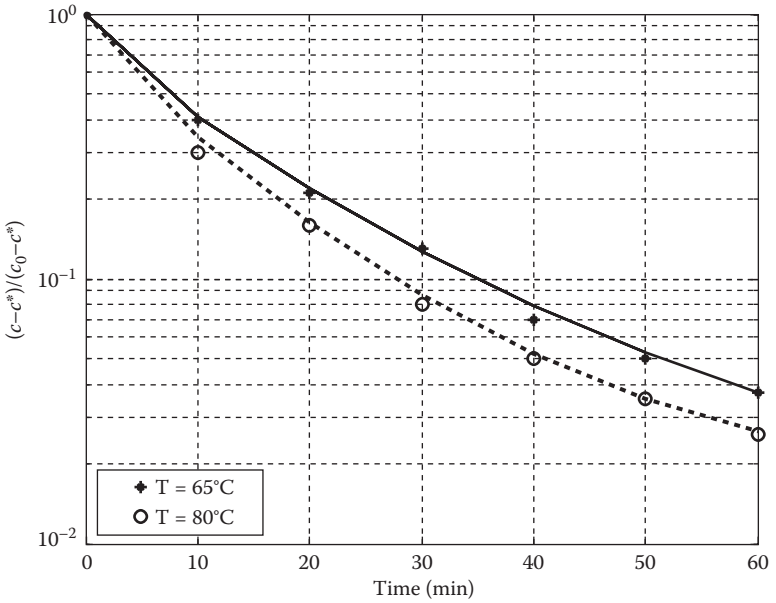


FIGURE E.4.31
Variation of the dimensionless average beet sugar contents with time. Experimental data obtained during extraction of 1 kg of beets with 1 kg of water. (Adapted from Yang, H. H., and Brier, J. C., *AIChE Journal*, 4, 453–59, 1958.) Variation of the diffusivity with time may be attributed to the deterioration of the sugar beet tissue.

Example 4.32: Countercurrent Desalting of Pickles

Salt stock pickles have about 15%–18% salt. They need to be extracted with water to reduce the salt content to about 4%. When the pickles are flushed with successive washing with fresh water "weak brine" with 2–3% salt is produced. The recovery of salt from such a low concentration solution is prohibitively expensive; on the other hand the weak brine is difficult to dispose of because of the environmental considerations. With countercurrent extraction, however, the salt stock and water are countercurrently contacted in successive tanks, resulting in a proportionally lower volume of high concentration spent brine with 13%–14% salt, from which it may be economically feasible to recover salt, or it would be easier to dispose of the smaller volumes of the spent brine. A schematic drawing of a countercurrent desalting process is shown in Figure E.4.32.1 (Bomben et al. 1994).

When the viscosity and density changes, the salt solutions are not large enough to affect the calculations, and flow rates of the overflow and underflow streams are not the same and the

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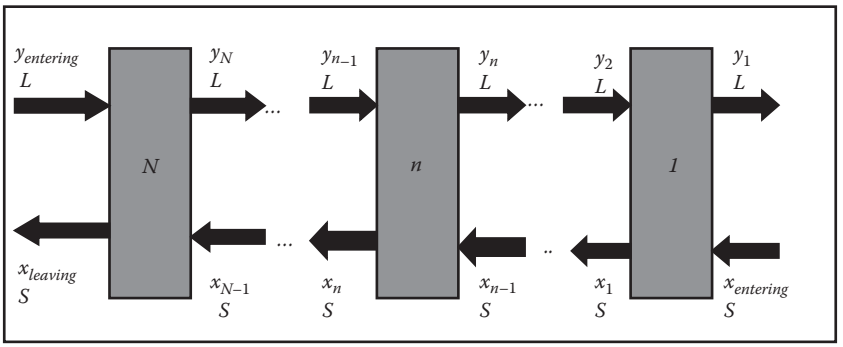


FIGURE E.4.32.1
A schematic drawing of a countercurrent desalting process. It should be noticed that in a stagewise contacting process a stream is subscripted with the number of the stage that it is coming from.

number of the theoretical stages required to achieve a required separation may be calculated as (Bomben et al. 1994)

$$N_{\text{theoretical}} = \frac{\log\left(\dfrac{y_{\text{entering}} - x_{\text{leaving}}}{y_{\text{leaving}} - x_{\text{entering}}}\right)}{\log\left(\dfrac{y_{\text{entering}} - y_{\text{leaving}}}{y_{\text{entering}} - x_{\text{entering}}}\right)}, \tag{E.4.32.1}$$

where x and y indicates the salt concentration in the underflow and overflow, respectively; the subscripts indicate whether the concentrations are pertinent to leaving or entering streams. In a solid/liquid extraction process, the solid phase is referred to as underflow and the liquid phase is referred to as overflow by convention. In a special case when the rates of overflow and underflow are the same, a simpler equation is substituted for Equation E.4.32.1:

$$N_{\text{theoretical}} = \frac{y_{\text{entering}} - y_{\text{leaving}}}{y_{\text{entering}} - x_{\text{leaving}}} = \frac{x_{\text{leaving}} - x_{\text{entering}}}{y_{\text{entering}} - x_{\text{leaving}}}. \tag{E.4.32.2}$$

The overall salt balance around the entire process leads to

$$x_{\text{leaving}} = x_{\text{entering}} - \frac{L}{S}\left(y_{\text{leaving}} - y_{\text{entering}}\right), \tag{E.4.32.3}$$

where L and S are the flow rates of the overflow and underflow streams, respectively.

The salt stock pickles are long, circular cylinders with an equivalent radius:

$$R = \sqrt{\frac{m}{\rho\pi l}} \tag{E.4.32.4}$$

where l, μ, and π are the length, mass, and density of the salt stock pickle, respectively. When the contacting vessel is well mixed, the rate limiting step is a diffusion of salt in the pickles and diffusivity is a constant, the extraction process may be simulated with the equation of continuity in the cylindrical coordinate system as

$$\frac{\partial c}{\partial t} = D\left[\frac{1}{r}\frac{\partial}{\partial r}\left(r\frac{\partial c}{\partial r}\right)\right], \tag{E.4.32.5}$$

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where c is the salt concentration in the pickles. The solution to Equation E.4.32.5 may be expressed as

$$\frac{M(t)}{M_\infty} = 1 - \sum_{n=1}^{\infty} \frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2\lambda^2} \exp\left(-\frac{D^2\lambda_n^2 t}{R}\right), \tag{E.4.32.6}$$

where $M(t)$ and M_∞ are the amounts of salt having left the salt stock after time t and at equilibrium, respectively; α is the ratio of the rate of overflow to underflow (L/S) and λ_n is the nonzero roots of

$$\alpha\lambda_n J_0(\lambda_n) + 2J_1(\lambda_n) = 0. \tag{E.4.32.7}$$

The right-hand side of Equation E.4.32.6 is almost equal to the Murphree stage efficiency η for a solid/liquid extraction process:

$$\eta = \frac{M(t)}{M_\infty}, \tag{E.4.32.8}$$

where the Murphree stage efficiency η is defined as the ratio of the number of the theoretical stages ($N_{\text{theoretical}}$) to those of the actual stages (N_{actual}):

$$\eta = \frac{N_{\text{theoretical}}}{N_{\text{actual}}}. \tag{E.4.32.9}$$

The variation of $M(t) / M_\infty$ with $\sqrt{Dt/R^2}$ simulated with MATLAB® code E.4.32.

MATLAB® CODE E.4.32

Command Window:

```
clear all
close all
format compact

% enter the data
Texp = [0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1.0];
MMexp1 = [0 0.78 0.92 0.97 0.98 0.99 1.0 1.0 1.0 1.0 1.0];
MMexp2 = [0 0.22 0.50 0.68 0.80 0.89 0.96 0.98 0.99 1.0 1.0];

%  plot the data
plot(Texp, MMexp1, '*'); hold on;
plot(Texp, MMexp2, 'o'); hold on;
legend('90 % of the solute has been uptaken by the cylinder at the
end', '30 % of the solute has been uptaken by the cylinder at the
end','Location','SouthEast')
grid on
ylabel('M(t)/Minfinity')
xlabel('sqrt(D*t/R^2)')

% determine the non zero roots:
alpha = [0.1 2.5];
```

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```
for q = 1:2

n = 0; m = 0;

for L = 0.005:0.001:1000
    G = alpha(q) * L * besselj(0,L) + 2 * bessel(1,L);
    if abs(G) <= 0.005;
        n = n + 1;
        R(q,n) = L;
    end
end

j = 1; Lr(q,j) = R(q,j);

for l = 2:n
    if R(q,l) > (R(q,(l-1)) + 1)
        j = j + 1;
        Lr(q,j) = R(q,l);
    end
end
%  model
y = 0;

for DRt = 0:0.001:1
    sum = 0;
    for i = 1:j
        sum = sum + ((4 * alpha(q) * (1 + alpha(q))) / (4 + (4 *
alpha(q)) + ((alpha(q)^2) * (Lr(q,i)^2)))) * exp(- DRt *
(Lr(q,i)^2));
    end
    y = y + 1;
    MM(q,y) = (1 - sum);
    T(q,y) = (DRt)^0.5;
end

%  plot the model
plot(T(q,:),MM(q,:)); hold on;
end
```

When we run the code Figure E.4.32.2 will appear on the screen.

Bomben et al. (1994) determined the diffusion coefficient D after comparing the experimentally determined values of $M(t) / M_\infty$ with Equation E.4.32.6. They chose the experimental conditions such that $S = L$, then after combining Equations E.4.32.2, E.4.32.3, and E.4.32.9 they obtained

$$y_{\text{leaving}} = \frac{y_{\text{entering}} + \eta N_{\text{actual}} x_{\text{entering}}}{1 + \eta N_{\text{actual}}}. \tag{E.4.32.10}$$

In a six stage experimental procedure ($N_{\text{actual}} = 6$), when contacting time of each stage was 8 hours at 49°C, with $L/S = 1$, $x_{\text{entering}} = 16.7\%$ NaCl and $y_{\text{entering}} = 0\%$ NaCl they calculated $y_{\text{leaving}} = 14.3\%$ NaCl, corresponding to $x_{\text{leaving}} = 2.5\%$ NaCl. The experimental results under these conditions were $y_{\text{leaving}} = 13.2$–$13.6\%$ NaCl and $x_{\text{leaving}} = 2.0$–2.8% NaCl, implying good agreement between the model and the data.

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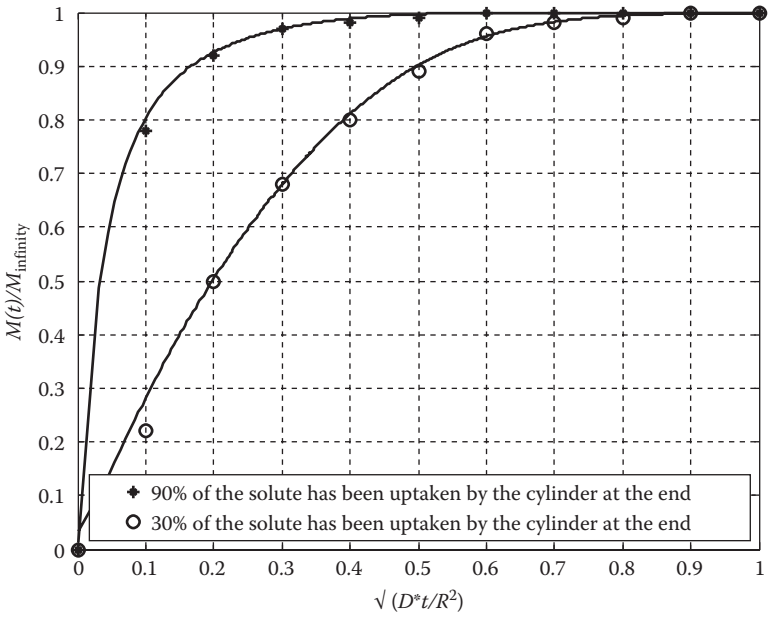


FIGURE E.4.32.2

Variation of $M(t)/M_{\infty}$ with $\sqrt{Dt/R^2}$. The points shown with the markers have been adapted from Crank, J. *Mathematics of Diffusion*, University Press, Oxford, 1956. Equation E.4.32.6 describes solute uptake by a cylinder submerged in a well-mixed batch of solute. Parameter α is the volumetric ratio of the cylinder to that of the liquid phase; $M(t)$ is the total amount of the solute uptaken by the cylinder until time t, and parameter M_{∞} is the total amount of the solute uptaken by the cylinder when an equilibrium is reached. The curves refer to the cases that either 30 or 90% of the solute available in the batch were uptaken by the cylinder when an equilibrium is reached. Equation E.4.32.6 was assumed representing the phenomena; also when mass transfer is from the cylinder to liquid phase.

There are also well-established graphical solution procedures for the stagewise contacting problems; an interested reader is recommended to refer to Treybal (1980), Geankoplis and Toliver (2003), and McCabe, Smith, and Harriot (2005) for the details.

Example 4.33: Chart Solution to Unsteady State Leaching Problems With External Mass Transfer Resistance

a. MATLAB® codes, which were used to produce Heisler Charts (Example 2.14) may also be employed in mass transfer studies. MATLAB® code E.4.33 estimates the dimensionless concentration at the center plane of an infinite slab, centerline of an infinite cylinder, or at the center of a sphere when resistance to external mass transfer is negligible when compared to that of the internal mass transfer (i.e., Bi → ∞). In numerical applications this condition is achieved at reasonably high values of the Biot number.

Figure E.4.33 may be used in unsteady leaching problems when the external mass transfer resistance is negligible and the diffusion rate of the solvent into the solid particle is the rate limiting step. Where unaccomplished average concentration fraction $E(t)$ is defined as (Treybal 1980)

$$E(t) = \frac{c_1 - c_{av}(t)}{c_1 - c_0}, \tag{E.4.33.1}$$

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MATLAB® CODE E.4.33

Command Window:

```
clear all
close all
format compact

%  YOU MAY NEED TO REFER TO THE MATLAB CODE OF EXAMPLE 2.14 TO
UNDERSTAND THIS CODE

% infinite slab
Bi = 100; Dt = 2;

G = 0; j = 0; j2 = 0; j3 = 0;
for i= 1:50000
    r = i / 1000;
    k(i) = r / cot(r);
    if (Bi - Dt) <= k(i)
        if k(i) <= (Bi + Dt)
            j = j + 1;
            G(j) = r;
        end
    end

% infinite cylinder
    k2(i) = r * bessel(1,r)/bessel(0,r);
    if (Bi - Dt) <= k2(i)
        if k2(i) <= (Bi + Dt)
            j2 = j2 + 1;
            G2(j2) = r;
        end
    end

% sphere
k3(i) = 1- r*cot(r);
    if (Bi - Dt) <= k3(i)
        if k3(i) <= (Bi + Dt)
            j3 = j3 + 1;
            G3(j3) = r;
        end
    end
    t(i) = r;
end

% infinite slab
n = 1;
R(n) = G(1);
for l = 2:j
    if G(l) > (1.2*G(l-1))
        n = n + 1;
        R(n) = G(l);
    end
end
```

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```
% infinite cylinder
n = 1;
R2(n) = G2(1);
for l = 2:j2
    if G2(l) > (1.2*G2(l-1))
        n = n + 1;
        R2(n) = G2(l);
    end
end

% sphere
n = 1;
R3(n) = G3(1);
for l = 2:j3
    if G3(l) > (1.2*G3(l-1))
        n = n + 1;
        R3(n) = G3(l);
    end
end

%  SERIES SOLUTIONS
e = 0;
for Fo = 0.01:0.01:0.7
    sum1 = 0; sum2 = 0; sum3 = 0;
    for i = 1:4

% infinite slab
        sum1 = sum1 + 2 * exp(-(R(i)^2) * (Fo)) * (sin(R(i)) / (R(i)
+ sin(R(i)) * cos(R(i))));

% infinite cylinder
        sum2 = sum2 + 2 * (1/R2(i)) * exp(-R2(i)^2 * Fo) *
bessel(1,R2(i)) / ((bessel(0,R2(i)))^2 + (bessel(1,R2(i)))^2);

% sphere
        sum3 = sum3 + 2 * exp(-(R3(i)^2) * (Fo)) * (sin(R3(i))
- R3(i) * cos(R3(i))) / (R3(i) - sin(R3(i)) * cos(R3(i)));
    end
    e = e + 1;

% sum of the serries for slab, cylinder and sphere
    Q1(e) = sum1; Q2(e) = sum2; Q3(e) = sum3;
    f(e) = Fo;
end

% PLOT THE FIGURE
semilogy(f,Q1,'-'); hold on;
semilogy(f,Q2, ':'); hold on;
semilogy(f,Q3, '-.'); hold on;

%  insert legend and define its location
```

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```
legend( 'infinite slab', 'infinite cylinder', 'sphere',
'Location','SouthWest')

xlabel('Fourier Number')
ylabel('(c1-c_a_v(t))/(c1-c0)')
```

When we run the code Figure E.4.33 will appear on the screen.

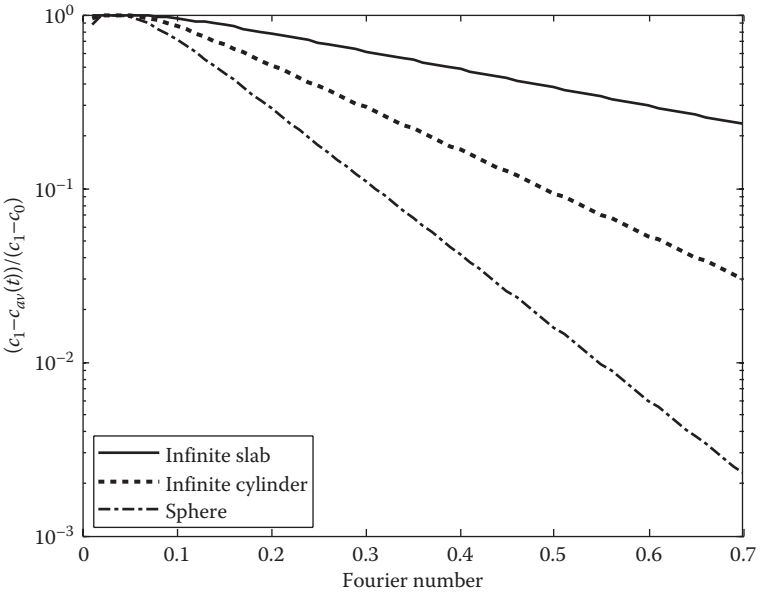


FIGURE E.4.33
Variation of the fraction of the unaccomplished average concentration with Fourier number during unsteady-state diffusion with negligible surface resistance.

where c_1 = solute concentration in the medium, $c_{av}(t)$ = average solute concentration in the solid at time t, c_0 = initial solute concentration in the solid. Fourier number, Fo_d, based on the characteristic dimension d is defined as

$$\text{Fo}_d = \frac{D_{eff}t}{d^2}, \tag{E.4.33.2}$$

where D_{eff} is the effective diffusivity and t is time. The following relations for E are used in different geometries:

Infinite slab with dimensions $a \times b \times c$ ($b \to \infty$, $c \to \infty$)	$E(t) = E_a(t)$
Infinite slab with dimensions $a \times b \times c$ ($c \to \infty$)	$E(t) = E_a(t)E_b(t)$
Slab with dimensions $a \times b \times c$	$E(t) = E_a(t)E_b(t)E_c(t)$
Cylinder (radius = a, height = $2c$)	$E(t) = E_r(t)E_c(t)$
Sphere (radius = a)	$E(t) = E_s(t)$

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b. Olives (may be assumed cylinders with radius $r = 0.7$ cm and height $2c = 2.5$ cm) loses 80% of their initial salt content when leached in water for 24 hours. Calculate the time needed to remove 65% of the initial salt.

Solution: The dimensionless numbers based on the characteristic dimensions are

$$\mathrm{Fo}_r = \frac{D_{eff}t}{r^2} = 49D_{eff} \tag{E.4.33.3}$$

and

$$\mathrm{Fo}_c = \frac{D_{eff}t}{c^2} = 15.4D_{eff}. \tag{E.4.33.4}$$

We will make a trial and error solution to find out D_{eff} is required to remove 80% of the salt in 24 hours. When $D_{eff} = 0.034$ cm^2/h, we will calculate from Equations E.4.33.3 and E.4.33.4 $\mathrm{Fo}_r = 0.166$ and $\mathrm{Fo}_c = 0.52$. Unaccomplished concentration profiles $E_r(t)$ and $E_c(t)$ corresponding to these Fourier numbers will be read from the chart as: $E_r(t) = 0.28$ and $E_c(t) = 0.75$. The overall unaccomplished average concentration fraction is

$$E(t) = E_r(t)E_c(t). \tag{E.4.33.5}$$

After substituting the numbers in Equation E.4.33.5, we will find $E(t) = 0.21 \cong 0.220$, confirming that the fraction of the salt removed is $1 - 0.21 = 79\% \cong 80\%$.

We will substitute $D_{eff} = 0.0034$ cm^2/h in the Fourier numbers:

$$\mathrm{Fo}_r = \frac{D_{eff}t}{r^2} = 0.007t \tag{E.4.33.6}$$

and

$$\mathrm{Fo}_c = \frac{D_{eff}t}{c^2} = 0.0022t. \tag{E.4.33.7}$$

We will perform another set of trial and error calculations. When $t = 15$ hours, we will calculate from Equations E.4.33.6 and E.4.33.7 $\mathrm{Fo}_r = 0.105$ and $\mathrm{Fo}_c = 0.033$. Unaccomplished concentration fractions E_r and E_c corresponding to these dimensionless numbers will be read from the chart as $E_r(t) = 0.395$ and $E_c(t) = 0.87$. After substituting the numbers in Equation E.4.33.5 we will find $E(t) = 0.344$, confirming that the fraction of the salt removed is $1 - 0.344 = 65.6\% \cong 65\%$.

Figure E.4.33 may also be used in unsteady state conduction heating problems when the external heat transfer resistance is negligible after substituting α = (thermal diffusivity) α D_{eff} in Equation E.4.33.2:

$$\mathrm{Fo}_d = \frac{\alpha\tau}{d^2}, \tag{E.4.33.8}$$

where Fo_d is the Fourier number with $E(t) = (T_1 - T_{av}(t))/(T_1 - T_0)$, where T_1 = temperature of the medium, $T_{av}(t)$ = average temperature of the solid at time t and T_0 = initial temperature of the solid.

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Example 4.34: Assessment of the External Mass Transfer Resistance During Extraction of the Polyphenols From Grape Pomace

In Examples 4.16 and 4.17 the same partial diffential equation was used with two different sets of boundary conditions to simulate mass transport within a solid matrix:

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial z^2}. \qquad \text{(E.4.13.1) and (E.4.14.1)}$$

In Example 4.13, the external mass transfer coefficient between the surface of the cookie and the external medium was so high that the external resistance to mass transfer was neglected. In Example 4.14 surface mass transfer coefficient was a finite number, external mass transfer resistance was not neglected so the following bounday condition was employed while solving the partial differential equation:

$$-D\left[\frac{\partial c(z,t)}{\partial (z)}\right]_{z=0} = h\left(c(z,t)_{z=L} - c_\infty\right) \quad \text{(BC)}. \qquad \text{(E.4.14.3)}$$

The solutions to Equations E.4.13.1 and E.4.14.1, with the appropriate BC and ICs, are discussed in detail in these examples. Guerrero, Torres, and Nunez (2008), while studying extraction of the polyphenols from spherical grape pomace particles, assumed negligible external mass transfer resistance and used the following equation to model the variation of the average polyphenols concentration in the particles with time:

$$Y(t) = \frac{c - c_e}{c_0 - c_e} = \frac{4R}{\pi}\sum_{n=1}^{\infty}\frac{1-(-1)^n}{\pi n}\exp\left(-\frac{n^2\pi^2}{R^2}D_{eff}t\right). \qquad \text{(E.4.34.1)}$$

In packed bed operations, the relation between the Sherwood (Sh), Reynold's (Re) and the Schmidt (Sc) numbers is given as

$$\text{Sh} = \frac{1.09}{\varepsilon}\text{Re}^{2/3}\,\text{Sc}^{1/3}, \qquad \text{(E.4.34.2)}$$

where $\text{Sc} = \mu/(\rho D_{AB})$, $\text{Re} = (d_p v\rho)/(\mu)$ and $\text{Sh} = (kR)/D_{eff}$, ε = porosity of the grape pomace bed, μ = viscosity of the solvent, ρ = density of the solvent, d_p = particle diameter, R = particle radius, D_{AB} = binary diffusion coefficients of polyphenols in solvent, D_{eff} = effective diffusion coefficient of polyphenols in solvent while diffusing in the pomace particles, and v = solvent velocity. The Sherwood number is the ratio of the numerical values of the internal to external mass transfer resistances. MATLAB® code E.4.34 first determines the effective diffusion coefficient D_{eff} during the extraction of the polyphenols from grape pomace, then assesses the validity of the negligible external mass transfer resistance assumption.

MATLAB® CODE E.4.34

Command Window:

```
clear all
close all
format compact

%OF THE MODEL & COMPUTATION OF THE EFFECTIVE DIFFUSIVITIES
```

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```
% enter the data
R=2.5e-4; % particle radius (m)
% Deff=effective internal diffusion coefficient of the solute in the
solid phase (m^2/s)
D040=1.33e-11; a40=8e-13; % constants of the effective diffusivity
at T=40 oC and 2 mL/s solvent flow rate
D050=2.11e-11; a50=38e-13; % constants of the effective diffusivity
at T=40 oC and 2 mL/s solvent flow rate
y1=[0 -0.20 -0.4 -0.5 -0.65 -0.8 -1.0 -1.2 -1.3 -1.4];
y2=[0 -0.25 -0.75 -1.25 -1.75 -2.25 -2.8 -3.5];
tData1=[0 10 20 30 40 50 60 70 80 90];
tData2=[0 10 20 30 40 50 60 70];

% plot the data
plot(tData1,y1, 'x', tData2,y2, 'o') ; hold on
xlabel('Time (min)')
ylabel('ln(y)')
legend('T=40 ^o C, solvent flow rate = 2 mL/min','T=50 ^o C, solvent
flow rate = 4 mL/min' ,'Location','Best')

% modeling the data obtaiened at T=40 oC with solvent flow rate of 2
mL/min
tIncrement=1; % time increment (min)
for k=1:90
t(k)= tIncrement*(k-1);% times (min)
Deff=D040+a40*t(k);
for n=1:10
    s(n)=((1-(-1)^n)/(n*pi))*exp(-((n*pi/R)^2)*Deff*t(k));
end
lnY(k)=log(sum(s));
end
plot(t,lnY); hold on % plot the model

% modeling the data obtaiened at T=50 oC with solvent flow rate of 4
mL/min
tIncrement=1; % time increment (min)
for k=1:70
t50(k)= tIncrement*(k-1);% times (min)
Deff=D050+a50*t(k);
for n=1:10
    s(n)=((1-(-1)^n)/(n*pi))*exp(-((n*pi/R)^2)*Deff*t50(k));
end
lnY50(k)=log(sum(s));
end
plot(t50,lnY50); hold on % plot the model

% COMPUTATION OF THE EXTERNAL MASS TRANSFER COEFFICIENT

% enter the physical parameters
R=0.004; % average particle diameter (m)
epsilon=0.49; % void fraction of the bed

% compute the external mass transfer coefficient
Re40=0.297; % Reynolds number ar T=40 oC with 2 mL/s flow rate
(Reynold's number Re = 2R*v*rho/mu)
Re50=0.69; % Reynolds number ar T=50 oC with 4 mL/s flow rate
```

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```
Sc40= 309; % Schmidt's number at T=40 oC with 2 mL/s flow rate
(Sc=mu/(rho*Diff)
Sc50= 228; % Schmidt's number at T=50 oC with 4 mL/s flow rate

for k=1:10:50
    t(k)= tIncrement*(k-1);
    Deff50(k)=D050+a50*t(k);
end

DeffAvg50=mean(Deff50);

for k=1:10:90
    t(k)= tIncrement*(k-1);
    Deff40(k)=D040+a50*t(k);
end

DeffAvg40=mean(Deff40);

Sh50=(1.09/epsilon)*(Re50^(2/3))*(Sc50^(1/3))  % Sherwood number
Sh40=(1.09/epsilon)*(Re40^(2/3))*(Sc40^(1/3))  % Sherwood number
```

When we run the code the following lines and Figure E.4.34 will appear on the screen:

```
Sh50 =
   10.6115
Sh40 =
    6.6945
```

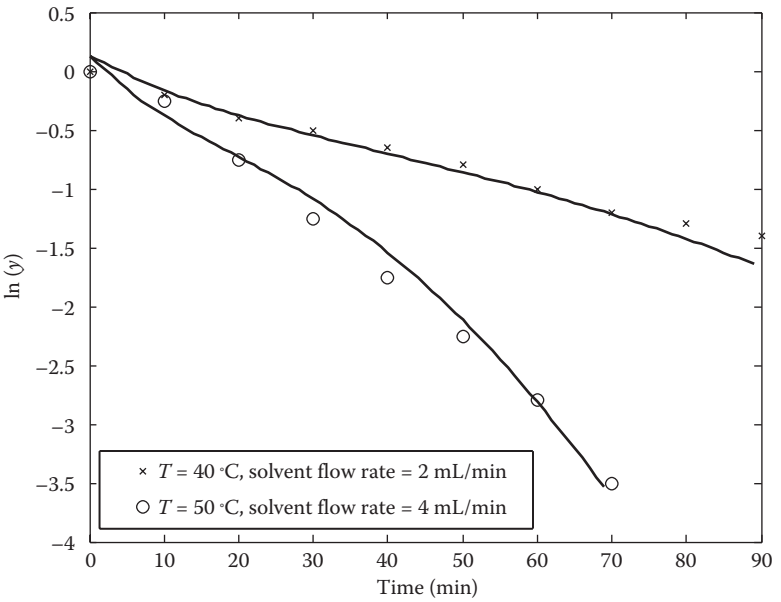


FIGURE E.4.34
Comparison of the data with the model. (Adapted from Guerrero, M. S., Torres, J. S., and Nunez, M. J., *Bioresource Technology,* 1311–18, 2008.)

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It was found that Sh = 10.6 at 50°C with 4 ml/s flow rate and Sh = 6.7 at 40°C with 2 ml/s flow rate, implying that the ratio of the internal to external mass transfer resistances were 10.6 and 6.7 in each case. This result confirms the validity of the negligible external mass transfer resistance.

Example 4.35: Mathematical Modeling of Blanching Potatoes

Blanching is a major step in the production of potato products. During blanching of potato slices glucose, potassium, magnesium, phosphorus, and other potato constituents are extracted. A schematic drawing of a continuous blancher is depicted in Figure E.4.35.1.

The solute balance around a continuous blancher requires:

$$\begin{pmatrix}\text{input rate of}\\ \text{the solute}\\ \text{into the}\\ \text{blancher}\end{pmatrix}-\begin{pmatrix}\text{output rate of}\\ \text{the solute}\\ \text{from the}\\ \text{blancher}\end{pmatrix}=\begin{pmatrix}\text{accumulation}\\ \text{rate of the}\\ \text{solute in the}\\ \text{blancher}\end{pmatrix}. \tag{E.4.35.1}$$

Equation E.4.35.1 may be written in mathematical terms as (Kozempel, Sullivan, and Craig 1981)

$$\left[(W_{ps}x)c_{\text{in}}+W_w s_{\text{in}}\right]-\left[(W_{ps}x)c_{\text{out}}+W_w s_{\text{out}}\right]=V\rho\frac{ds}{dt}+\frac{W_{ps}x\tau}{2}\frac{d(c_{\text{in}}+c_{\text{out}})}{dt}, \tag{E.4.35.2}$$

where W_{ps} is the input rate of the dry potato solids into the blancher, x is the moisture content of the potatoes, expressed in kg water/dry potato solids, and c_{in} is the solute concentration (i.e., potassium) in the water contents of the potato; W_w is flow rate of water into the blancher and s_{in} is the solute concentration in the input water. The output concentrations of the same streams were denoted as c_{out} and s_{out}. Volume and density of the blanching water in the precooker were V and ρ, respectively. Residence time of the potatoes in the blancher is τ. The term $(c_{\text{in}}+c_{\text{out}})/2$ is the average solute concentration in water in the potatoes.

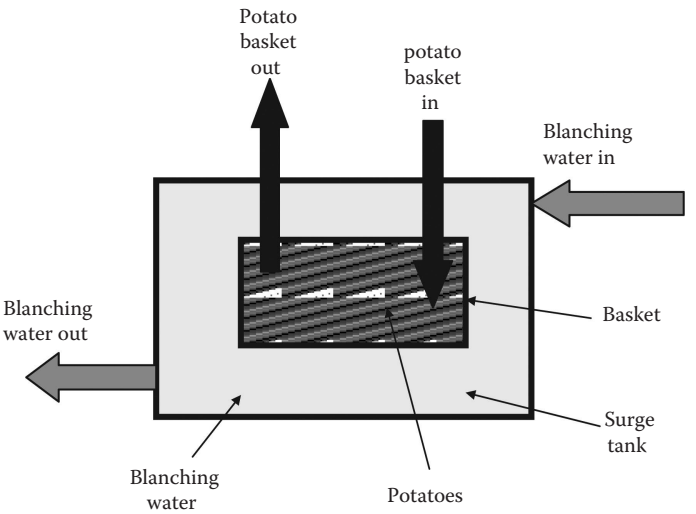


FIGURE E.4.35.1
Schematic drawing of the continuous blancher.

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When the French cut potatoes were considered as a slab of thickness 2*L*, then the solute concentration profile along the slab is simulated similarly as in Example 4.13:

$$\frac{\bar{c}-c^*}{c_0-c^*}=\frac{8}{\pi^2}\sum_{m=0}^{\infty}\frac{1}{(2m+1)^2}\exp\left[\frac{-D(2m+1)^2\pi^2 t}{L^2}\right]. \tag{E.4.35.3}$$

When only the first term of Equation E.4.35.3 is significant and $c^* = s_{out}$, therefore

$$c_{out}=s_{out}+(c_{in}-s_{out})\frac{8}{\pi^2}\exp\left[-\frac{D\pi^{2\tau}}{L^2}\right]. \tag{E.4.35.4}$$

French cuts are not actually infinite slabs with thickness 2*L*, therefore *L* is a nominal dimension and *D* is not exactly the diffusivity in Equation E.4.35.3. Equations E.4.35.1 and E.4.35.3 may be combined to eliminate c_{out}:

$$\begin{aligned}&\left[(W_{ps}x)c_{in}+W_w s_{in}\right]-s_{out}+(c_{in}-s_{out})\frac{8}{\pi^2}\exp\left[-\frac{D\pi^{2\tau}}{L^2}\right]-W_w s_{out}=\\&V\rho\frac{ds_{out}}{dt}+\frac{W_{ps}x\tau}{2}\frac{d}{dt}\left(s_{out}+(c_{in}-s_{out})\frac{8}{\pi^2}\exp\left[-\frac{D\pi^{2\tau}}{L^2}\right]\right).\end{aligned} \tag{E.4.35.5}$$

Equation E.4.35.5 may be rearranged as

$$\begin{aligned}&W_{ps}c_{in}\left\{1-\frac{8}{\pi^2}\exp\left[-\frac{D\pi^{2\tau}}{L^2}\right]\right\}-W_{ps}s_{out}\left\{1-\frac{8}{\pi^2}\exp\left[-\frac{D\pi^{2\tau}}{L^2}\right]\right\}+W_w(s_{in}-s_{out})\\&=\left[V\rho+\frac{W_{ps}x\tau}{2}\left\{1-\frac{8}{\pi^2}\exp\left[-\frac{D\pi^{2\tau}}{L^2}\right]\right\}\right]\frac{ds_{out}}{dt}.\end{aligned} \tag{E.4.35.6}$$

Under steady state conditions, when $ds_{out}/dt = 0$, the solution is

$$s_{out}=\frac{W_{ps}c_{in}\left\{1-\frac{8}{\pi^2}\exp\left[-\frac{D\pi^2\tau}{L^2}\right]\right\}+W_W s_{in}}{W_{ps}\left\{1-\frac{8}{\pi^2}\exp\left[-\frac{D\pi^2\tau}{L^2}\right]\right\}+W_W}. \tag{E.4.35.7}$$

MATLAB® code E.4.35 compares the model with the experimentally determined concentrations of potassium in precooked water.

MATLAB® CODE E.4.35

Command Window:

```
clear all
close all
format compact
```

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```
% enter the data
timeD=[0.4 1 1.4 2 3.1 4.6 6];
concentrationD=[120 185 235 250 260 260 285];

% plot the data
plot(timeD, concentrationD,'o') ; hold on
xlabel('Time (h)')
ylabel('concentration ((weight/weight)*1e6)')

% enter the constants
e = 0; D = 0.423; L = 2.0;
Sout = 275;
Cin = 0;

% modeling
for t = 0:0.1:6
    e = e + 1;
    C(e) = Sout + (Cin - Sout) * (8 / (pi^2)) * exp(-D * (pi^2) * t
/ (L^2));
    time(e) = t;
end

% plot the model
plot(time, C); hold on
legend('Data','Model','Location','SouthEast')
```

When we run the code Figure E.4.35.2 will appear on the screen.

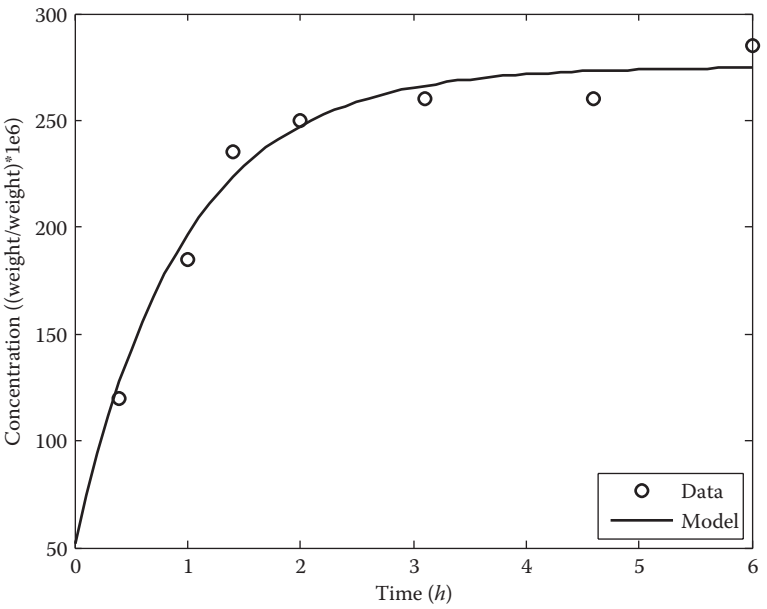


FIGURE E.4.35.2
Comparison of the predicted concentration of potassium in precooked water with the experimental data obtained during the blanching process of the potato slices (thickness = 095 cm). (Adapted from Kozempel, M. F., Sullivan, J. F., and Craig, J. C., *Lebensmittel-Wissenschaft und Technologie,* 14, 331–35, 1981.)

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Example 4.36: Extraction of Solutes From Plants by Breaking Down the Tissue

During extraction of the chemicals in a plant, first water diffuses into the plant and fills its pores. Chemicals dissolve in the water filling the pores, diffuse to the solids/water interface and go to the external water phase. In some extraction processes, solvent may not reach the solute, if it is enclosed in a well-protected environment. Steam extraction-distillation and microwave assisted extraction are among the processes where the plant tissue is gently broken down to help the solvent to reach to the solutes.

Most of the essential oils are produced with a combined extraction-steam distillation process (Figure E.4.36.1). In the extraction chamber, steam runs through the leaves and breaks down the cells. Essential oils diffuse through the leaves and join the liquid phase. Steam, which is running through the liquid phase evaporates the essential oils. Steam and essential oil vapors leave the extraction chamber together and condensed in the next stage. Essential oils are not soluble in water and easily recovered in the separator. Rosemary and lavender essential oils are important fragrances used in both perfume and food industries.

Material balance around the plant material requires

$$-V\frac{dc}{dt} = Ak(c - c^*), \tag{E.4.36.1}$$

where V is the volume and c is the average essential oil content of the plant material. A is the interfacial area, k is the mass transfer coefficient, and c^* is the essential oil concentration in the plant material that is in equilibrium with that of the liquid phase. When we assume that $c >> c^*$ Equation E.4.36.1 may be rearranged as

$$\int_{c0}^{c(t)} \frac{dc}{c} = -\kappa \int_0^c dt, \tag{E.4.36.2}$$

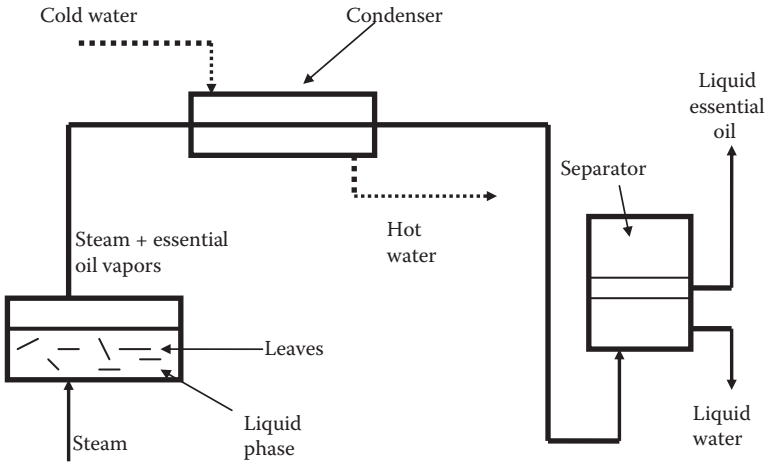


FIGURE E.4.36.1
Schematic description of the essential oil production by a combined extraction-steam distillation process.

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where $\kappa = Ak/V$. After integration, Equation E.4.36.2 becomes

$$c(t) = c_0 \exp(-\kappa t). \tag{E.4.36.3}$$

Equation E.4.36.3 may be rewritten in terms of the mass of the essential oils remaining in the plant material as

$$m(t) = m_0 \exp(-\kappa t), \tag{E.4.36.4}$$

where $m(t)$ is the total mass of the essential oil remaining in the plant material at time t and m_0 is the value of $m(t)$ at $t = 0$. The total amount of the extracted essential oil is

$$m_{\text{extracted}}(t) = m_0 - m(t) = m_0 - m_0 \exp(-\kappa t). \tag{E.4.36.5}$$

Equation E.4.36.5 may be rearranged as

$$m_{\text{extracted}}(t) = m_0 \left[1 - \exp\left(-\kappa t\right)\right], \tag{E.4.36.6}$$

since the extracted essential oils are immediately removed by the steam and collected, $m_{\text{extracted}}(t)$ may also be regarded as the total mass of the essential oils recovered by time t. MATLAB® code E.4.36.a simulates rosemary and lavender essential oil recovery processes.

MATLAB® CODE E.4.36.a

Command Window:

```
clear all
close all
format compact

mRosemary=[0.00 0.37 0.55 0.71 0.87 0.98 1.06 1.08 1.12 1.12 1.16
1.16 1.16 1.16 1.16 1.16]; % amount of rosemary oil extracted (g)
mLavender=[0.00 0.08 0.21 0.33 0.46 0.54 0.63 0.80 0.84 0.92 0.92
0.96 1.00 1.00 1.00 1.00]; % amount of lavender oil extracted (g)
tData=[0:2:30]; % times (min)

% plot the data
plot(tData,mRosemary,'+', tData,mLavender,'s'); hold on;
xlabel('Time (min)')
ylabel('Amount of essential oil extracted (g)')
legend('Rosemary','Lavender','Location','SouthEast')
mRosemary0=1.16; % initial amount of the essential oil in rosemary
(g)
mLavender0=1.00; % initial amount of the essential oil in rosemary
(g)
kRosemary=0.18; % lavender oil extraction constant
k0=0.015; % lavender oil extraction constant
k1=0.008;
t(1)=0;
mRosemary(1)=0; % amount of the rosemary oil produced by t=0
```

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```
mLavender(1)=0; % amount of the lavender oil produced by t=0
for i=2:1:30
t(i)=i;
kLavender=k0+k1*t(i);
mRosemary(i)=mRosemary0*(1-exp(-kRosemary*t(i))); % amount of the
rosemary oil produced by t(i)
mLavender(i)=mLavender0*(1-exp(-kLavender*t(i))); % amount of the
lavender oil produced by t(i)
end

% plot the model
plot(t,mRosemary,':', t,mLavender,'-'); hold on
```

When we run the code Figure E.4.36.2 will appear on the screen.

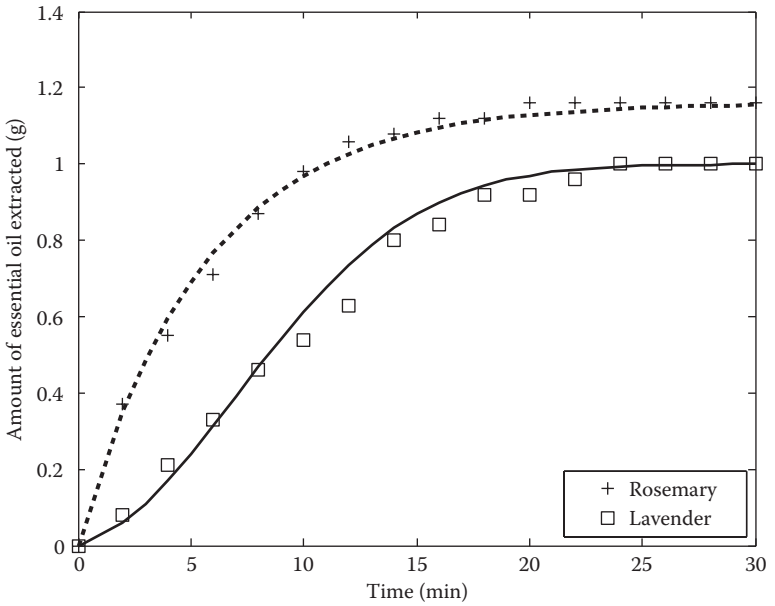


FIGURE E.4.36.2
Comparison of the steam extraction-distillation model with the data. (Adapted from Cassel, E., Vargas, R. M. F., Martinez, N., Lorenzo, D., and Dellacassa, E., *Industrial Crops and Products,* 29, 171–76, 2009.) Although the extraction parameter k_{Rosemary} was a constant through out the process, k_{Lavender} increased as time passed and was expressed as $k_{\text{Lavender}} = k_0 + k_1 \times t(i)$.

When extraction is carried out in a microwave field, heat that is absorbed by water located in the pores, may help to dissociate the solute from the tissue and increase the extraction rate, which is expressed as

$$-\frac{dm_{\text{water}}}{dt} = k_L a\, m_{\text{tea}}(c_{\text{pores}} - c_{\text{water}}). \tag{E.4.36.7}$$

After integrating Equation E.4.36.7 and substituting $c_0 = m_{\text{tea}} Y_{\text{sol}}/V_{\text{pores}}$, $c_{\text{pores}} = (c_0 V_{\text{pores}} - m_{\text{water}})/V_{\text{pores}}$, $c_{\text{water}} = m_{\text{water}}/V_{\text{water}}$, $V_{\text{pores}} = \beta\, m_{\text{pores}}$ we will obtain

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$$c_{water} = \frac{m_{tea}}{V_{water}}\left\{Y_{sol} - \beta \exp\left(\frac{V_{water}\, k_L a}{\beta\,(V_{water} - \beta\, m_{tea})}t\right)\right\}, \qquad \text{(E.4.36.8)}$$

where c_{water} = concentration of phenols in the external water phase, c_{pores} = phenols concentration in the pores, c_0 = concentration of phenols in the pores at time $t = 0$, m_{water} = mass of phenols in water at time t, m_{tea} = mass of tea, V_{pores} = volume of water retained in the pores, V_{water} = total volume of water used in the process, β = ratio of solution retained in the pores, Y_{sol} = fraction of phenols solubilized, k_L = interfacial mass transfer coefficient, a = specific interfacial mass transfer area, and t = time. MATLAB® code E.4.36.b computes the concentration of the phenols in the external water phase as a function of the water to tea ratio when t remains constant (Spigno and De Faveri 2009).

MATLAB® CODE E.4.36.b

Command Window:

```
clear all
close all

% enter the experimental data
xData= [10 20 30 40 50 75 100 125 150 175 200]; % xData=mTea/Vwater
data
cWaterData= [9.72e-3 5e-3 3.8e-3 2.7e-3 2.4e-3 1.8e-3 1.2e-3 1.1e-3
1.0e-3 0.9e-3 0.8e-3]; % phenols concentration in water (g/L)
plot(xData,cWaterData,'o'); hold on; % plot the data
xlabel('mTea/Vwater ratio (mL/g)')
ylabel('cWater (g/L)')

% enter the model constants
vWater=150; % volume (ml)
mTea = [15:-0.75: 0.75]; % amounts of tea addeed to 150 mL of water
(g)
Ysol = 0.27; % fraction of solubilized phenols
beta= 0.16; % solution retention (mL/g),
kla = 1.02E-5; % (mass transfer coefficient)*(specific interfacial
area) (m3/g s)
t=120; % duration of extraction process(s)

% modeling
i=1;
while i<21;
   xpre(i)=150/mTea(i); % liquid (water) to solid (tea) ratio
employed in the ith experiment
     cWaterModel(i)=((mTea(i)/vWater)*(Ysol-beta*exp((vWater*kla*t)/
(beta*(vWater-(mTea(i)-beta))))));
   i=i+1;
end

plot(xpre,cWaterModel);hold on; % plot the model
```

When we run the code Figure E.4.36.3 will appear on the screen.

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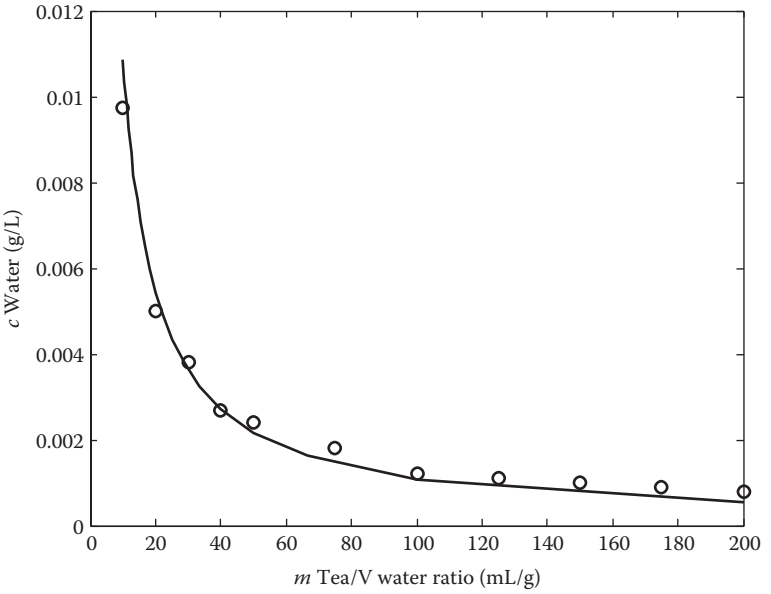


FIGURE E.4.36.3
Comparison of the model with the data when varying amounts of tea (solids) were added in 150 mL of water to obtain liquid to solids: the ratio of 20 to 200. Extraction lasted 120 s when the microwave oven was running at a power of 600 W. Concentration was expressed in g/L of gallic acid equivalents. (Adapted from Spigno, G., and De Faveri, D. M., *Journal of Food Engineering*, 93, 210–17, 2009.)

Solvents used in the food industry must be nontoxic and not leave any undesirable residues. The solvent also should be nonexplosive, inexpensive, readily available, plentiful in nature, easily separable from the substances extracted, and easy to regenerate or dispose. Water is a preferred solvent for the extraction of polar or ionic substances when its use is feasible in a process. Some organic solvents (i.e., hexane, heptane, thrichloroethylene, isopropyl alcohol, and ethyl alcohol) were also used in the past in the food industry for recovery of mostly nonpolar constituents, but extraction with supercritical carbon dioxide is preferred over the organic solvents in recent processes. Supercritical carbon dioxide exhibits polarity classifiable in between that of dichloromethane and ethyl ether, consequently nonpolar compounds (like fats, oils and aroma compounds) such as terpenes dissolve quite readily (Hierro and Santa-Maria 1992). Other compounds displaying a certain degree of solubility in supercritical carbon dioxide are low molecular weight compounds with average polarity, such as caffeine, nicotine, cholesterol, and alcohols (Hierro and Santa-Maria 1992). Supercritical carbon dioxide extraction was reported to be used for the extraction of fats, oils, hops, flavor, and perfume ingredients (Moyler 1988). Liquid carbon dioxide rejects protein, waxes, sugars, chlorophyll, and pigments to yield an extract that more closely resembles the aroma and taste of the botanical starting material of the essential oils then that of the products obtained with the steam distillation (Moyler 1988).

Liquid carbon dioxide is a very nonpolar solvent, ranging in polarity near hexane and pentane and its solvent power is not high compared with ordinary liquid solvents. The pressure–temperature phase diagram of carbon dioxide is shown in Figure 4.10. Subcritical liquid CO_2 is found in the triangle formed by the boiling line, the melting line, and the line of the critical pressure. From anywhere in this triangle the boiling line may be reached by heating at constant pressure or by decreasing the pressure at a constant temperature, which means that CO_2 can evaporate (Brogle 1982). In the supercritical region, separation of solute and solvent by a simple

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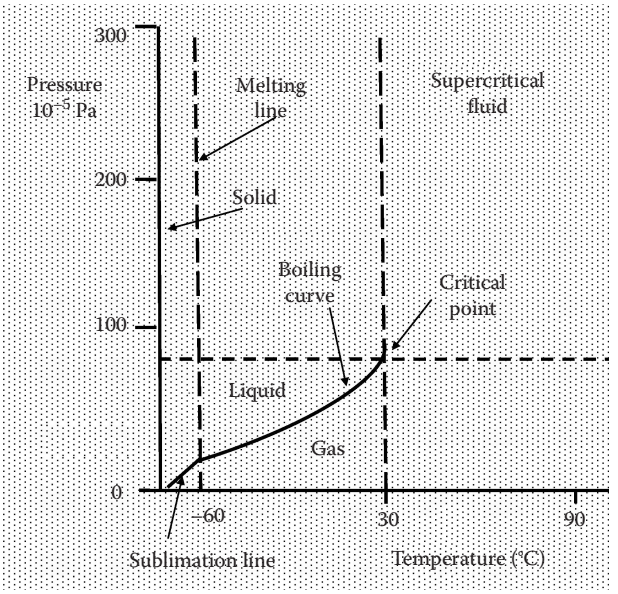


FIGURE 4.10
An approximate pressure–temperature phase diagram of carbon dioxide.

evaporation is not possible and also there is no principle difference between the liquid and the supercritical phases. Solvent power of supercritical carbon dioxide is highly dependent on its temperature and pressure (Brogle 1982). Generally solvent power of a supercritical solvent increases with (i) density at a given temperature and (ii) temperature at a given density. The supercritical area shown in Figure 4.10 spans the widest range of pressure and temperature and therefore the widest range of solvent power. The solvent power reaches very high levels at high temperatures and high pressures, but there is very low solvent power in the neighborhood of the critical point (Brogle 1982).

Example 4.37: Modeling Pneumatic Extraction of Citrus Juice and Juice Sacs

Pneumatic extraction is a new process (Figure E.4.37.1), which is at the experimental level yet, and expected to be used to extract juice from the fruits where the juice is located within the sacs or particles. Citrus fruit and promenade are among the fruits that the process is expected to be used. The process employs a high pressure air jet, which impinges on the fruit surface, breaks the tissue, and releases the juice sacs or the juice from the tissue.

The impingement force generated by the air jet is theoretically calculated as (Khazaei, Massah, and Mansouri 2008):

$$F = \rho_s a_s^2 A \left(\frac{2}{\gamma + 1} \right)^{1/(\gamma - 1)}, \tag{E.4.37.1}$$

where F = impingement force, ρ_s = density of the air in the jet, a_s = local speed of sound, A = initial air jet area, and γ = ratio of specific heats. Equation E.4.37.1 is a theoretical equation (Khazaei, Massah, and Mansouri 2008). In practical applications nonidealities may require multiplying Equation E.4.37.1 with a correction factor. MATLAB® code E.4.37 computes the impingement force applied by the jet on the surface of citrus fruit halves and describes the

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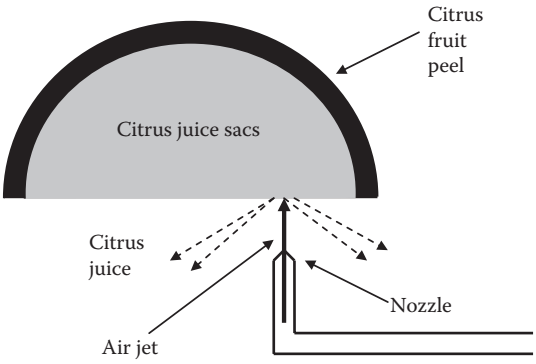


FIGURE E 4.37.1
Schematic drawing of juice and juice sacs removal process by the impinging air jet in a pneumatic extraction process.

MATLAB® CODE E.4.37

Command Window

```
clear all
close all

% enter the data
P=[300 400 600]; % operating air pressures (kPa)
Fexp1=[1.1 1.3 2]; % experimentally determined impingement force
with 2.5 mm nozzle diameter
Fexp2=[2.2 3 4.7]; % experimentally determined impingement force
with 3.5 mm nozzle diameter
Ps=192; % (kPa)
gamma=1.4;
r=[1.25e-3 1.75e-3] ; % nozzle radius (m)
A=pi*r.^2; % cross sectional area of the nozzle (m2)
rho=[3.50 4.67 7.01]; % supply air density (kg/m3)
cFactor=[0.80 0.9]; % correction factor

% plot the data
plot(P,Fexp1,'*', P,Fexp2,'o'); hold on; % plot the data
xlabel('air pressure (kPa)');
ylabel('impingement force (N)');
legend('nozzle diameter=2.5 mm', 'nozzle diameter=3.5
mm','Location','NorthWest')

% compute the force of impingement
for i=1:2
   for j=1:3
        a(j)=sqrt(1000*P(j)*gamma/rho(j)); % velocity of sound (m/s)
      F(j,i)=rho(j)*(a(j)^2)*A(i)*(2/(gamma+1)).^(1/(gamma-1)); %
theoretical impingement force (N)
```

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```
        Fcorrected(j,i)=cFactor(i)*F(j,i);
    end
end
plot(P,Fcorrected((1:3),1),'-', P,Fcorrected((1:3),2),':'); % plot
the model

%  relation between the removal rate of citrus juice and juice sacs
and the force applied
Yield(1,(1:3))=[28 38 55]; % yield with r=1.25 mm (%)
Yield(2,(1:3))=[38 47 72]; % yield with r=1.75 mm (%)
cFactor2=[0.4 0.5];
for i=1:2
     for j=1:3
         A(i)=pi*(r(i)^2);
          a(j)=sqrt(1000*P(j)*gamma/rho(j)); % velocity of sound
(m/s)
          F1(i,j)=rho(j)*(a(i)^2)*A(i)*(2/(gamma+1))^(1/(gamma-1));
% theoretical impingement force
    end
end

figure
plot(F1(1,(1:3)),Yield(1,(1:3)),'*', F1(2,(1:3)),Yield(2,(1:3)),'*')
; hold on; % plot the CJJS removal rate versus the impingement
surface
xlabel('impingement force (kPa)');
ylabel('yield  (%)'); % percentage of the citrus juice and juice
sacs removed
legend('nozzle diameter=2.5 mm', 'nozzle diameter=3.5
mm','Location','SouthEast')

%  fit a polynomial empirical model (line) to the data
N=1;

x1= F1(1,(1:3)); % when r=1.25 mm
c2= polyfit(x1,Yield(1,(1:3)),N); % when r=1.25 mm
Model1=polyval(c2, x1); % when r=1.25 mm

x2= F1(2,(1:3)); % when r=1.75 mm
c3= polyfit(x2,Yield(2,(1:3)),N); % when r=1.75 mm
Model2=polyval(c3, x2); % when r=1.75 mm

plot (x1, Model1,'-', x2, Model2,':'); hold on;
```

When we run the code the Figures E.37.2 and E.4.37.3 will appear on the screen.

relation between the extraction yield and the impingement force at two different nozzle diameters.

Example 4.38: Supercritical Extraction of Fish Oils

Objectionable components, such as odor compounds, free fatty acids and polychlorinated biphenyls (PCBs) are present in fish oils. The PCBs may be removed from the fish oils by a supercritical carbon dioxide extraction (Krukonis 1989).

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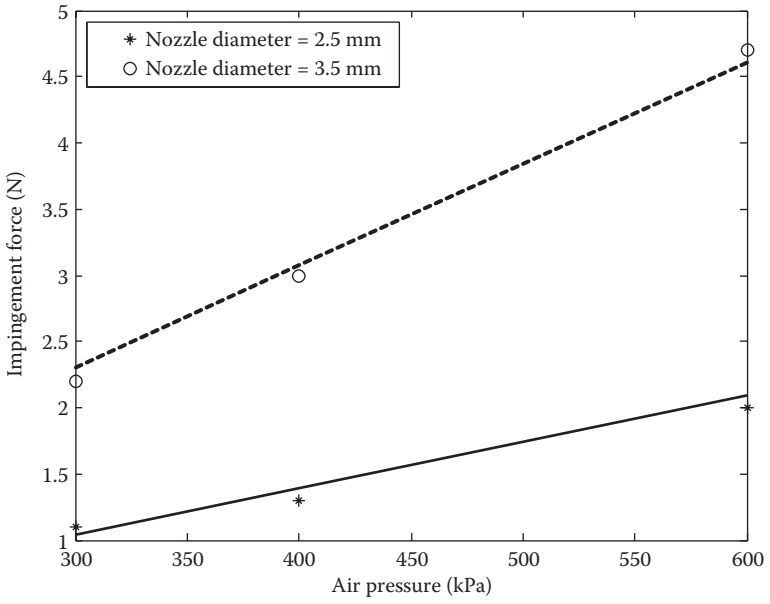


FIGURE E.4.37.2
Variation of the corrected impingement force with air pressure. (Adapted from Khazaei, J., Massah, J., and Mansouri, G.H., *Journal of food Engineering*, 88, 388–98, 2008.)

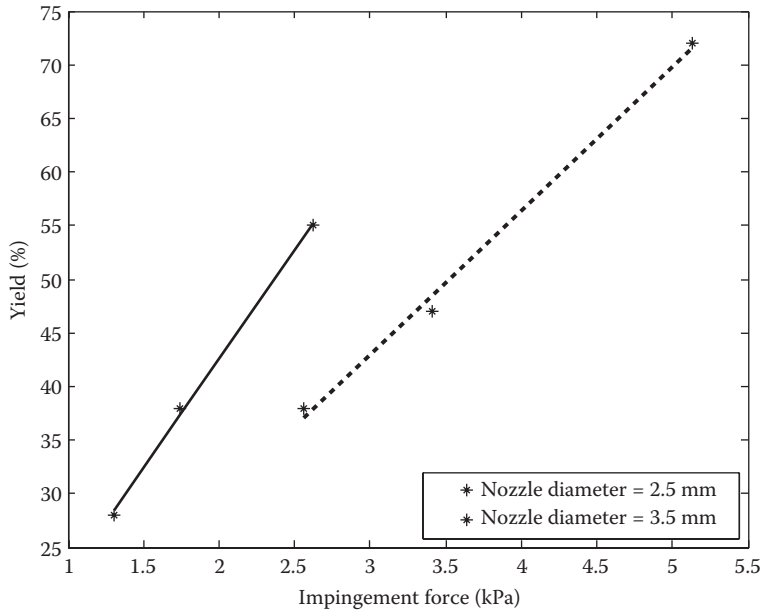


FIGURE E.4.37.3
Variation of the juice and juice sacs removal rate with the impingement force. Data were adapted from Khazaei, J., Massah, J., and Mansouri, G. H., *Journal of Food Engineering*, 88, 388–98, 2008.)

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The distribution coefficient of a component that is extracted from one phase into another is defined generally as the ratio of concentrations of the component in the respective phases; by convention, the component being extracted by the solvent is in the numerator. For the specific case of carbon dioxide, PCBs, and fish oil the distribution coefficient K is defined as

$$K = \frac{y_{\text{PCB/gas}}}{x^*_{\text{PCB/oil}}}, \tag{E.4.38.1}$$

where $c_{\text{PCB/gas}}$ is the PCB concentration in carbon dioxide and $c_{\text{PCB/oil}}$ is the PCB concentration in fish oil in equilibrium with $c_{\text{PCB/gas}}$. The distribution coefficient is not supposed to be a function of the PCB concentration. The selectivity β of extraction may be defined as

$$\beta = \frac{\left[y_{\text{PCB}} / y_{\text{triglycerides}}\right]_{\text{extract}}}{\left[x_{\text{PCB}} / x_{\text{triglycerides}}\right]_{\text{fish oil}}}, \tag{E.4.38.2}$$

where $(x_{\text{PCB}}/x_{\text{triglycerides}})_{\text{extract}}$ and $(x_{\text{PCB}}/x_{\text{triglycerides}})_{\text{fish oil}}$ are the ratio of PCBs to triglycerides in the extract and the equilibrium fish oil phases, respectively. Distribution coefficient K and the selectivity b of the process varies with pressure as depicted in Table E.4.38. MATLAB® code E.4.38 determines the variation of the PCBs in the fish oil during cross-flow filtration.

An equilibrium contacting stage for extraction of odorous compounds with supercritical CO_2 is depicted in Figure E.4.38.1, where raw fish oil and supercritical CO_2, free of odorous compounds, are brought into contact. The contacting process takes sufficient time so the odor compounds are distributed between the fish oil and super critical CO_2 phases to attain equilibrium. Super critical carbon dioxide and odorous compounds that dissolve in it are removed. We repeat this process until we have fish oil with an acceptable level of odorous compounds. The number of times we repeat this process is the number of the stages of the process. The stage is called an equilibrium stage if equilibrium is attained between the amounts of the odorous compounds distributed between the stages. During super extraction of the fish oils with supercritical carbon dioxide, the same batch of fish oil is total mass and odorous compounds balances around the nth stage are

$$L_{n-1}x_{n-1} + V_{n-1}y_{n-1} = V_n y_n + L_n x_n. \tag{E.4.38.3}$$

TABLE E.4.38

Variation of the Distribution Coefficient and the Selectivity with Pressure

Extraction Pressure (kPa)	Distribution Coefficient	Selectivity
1685	0.008	12.9
2224	0.015	9.7
3370	0.014	2.1
3707	0.014	1.3

Source: Krukonis, V. J., *Journal of the American Oil Chemists Society*, 66, 818–21, 1989.

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MATLAB® CODE E.4.38

Command Window:

```
clear all
close all

% PLOT VARIATION OF K AND BETA WITH PRESSURE

% enter the data
P=[1685 2224 3370 3707]; % extraction pressure (kPa)
K=[8e-3 15e-3 14e-3 14e-3];% distribution coefficient
beta=[12.9 9.7 2.1 1.3]; % selectivity

%  fit a polynomial empirical model to the data
N=3; % determine N by trial and error to obtain good agreement
between model & data
c = polyfit(P,K,N);

Pmodel=1500:100:4000;
Kmodel=polyval(c,Pmodel);

%  fit a best fitting line to the data
N=1; % determine N by trial and error to obtain good agreement
between model & data
c1 = polyfit(P,beta,N);
Pmodel=1500:100:4000;
betaModel =polyval(c1,Pmodel);

% plot the best fitting curves
[AX,H1,H2]=plotyy(Pmodel,Kmodel,Pmodel,betaModel); hold on;
set(H1,'LineStyle',':')
set(H2,'LineStyle','-')
ylim(AX(2), [0 15])

% plot the data
[AX,H1,H2]=plotyy(P,K,P,beta);  hold on;
xlabel('operating pressure (kPa)')
set(get(AX(1),'Ylabel'),'String','distribution coefficient')
set(get(AX(2),'Ylabel'),'String','selectivity')
set(H1,'LineStyle','*')
set(H2,'LineStyle','o')
ylim(AX(2), [0 15])
legend('K','beta','Location','NorthEast')

figure
for j=1:3
    counter=0;
    x(1)=0.03; % fraction of the odorous compounds in the fish oil
    L=100; % weight of  odorous compounds free fish oil
    V=2500; % weight of odorous compounds fee super critical carbon
dioxide
  for i=2:100
    x(i)=(L*x(i-1)+V*0)/(L+K(j)*V);
      if x(i)<=0.003
```

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```
       if counter==0
        fprintf('\n at P= %.4g kPa number of the stages needed to
reduce odorous compounds to 10 %% of its original fraction is = %2g
\n', P(j), i)
         counter=i;
       end
      end
  end
     if  j==1 plot((1:counter),x(1:counter),'p-'); hold on; end
     if  j==2 plot((1:counter),x(1:counter),'s-'); hold on; end
     if  j==3 plot((1:counter),x(1:counter),'o-'); hold on; end
end

ylabel('fraction of the odorous compounds in the fish oil')
xlabel('number of the stages')
legend('P=1685 kPa','P=2224 kPa','P=3370
kPa','Location','NorthEast')
```

When we run the code the following lines and Figures E.4.38.2 and E.4.38.3 will appear on the screen:

```
at P= 1685 kPa number of the stages needed to reduce odorous
compounds to 10 % of its original fraction is = 14

 at P= 2224 kPa number of the stages needed to reduce odorous
compounds to 10 % of its original fraction is =  9

 at P= 3370 kPa number of the stages needed to reduce odorous
compounds to 10 % of its original fraction is =  9
```

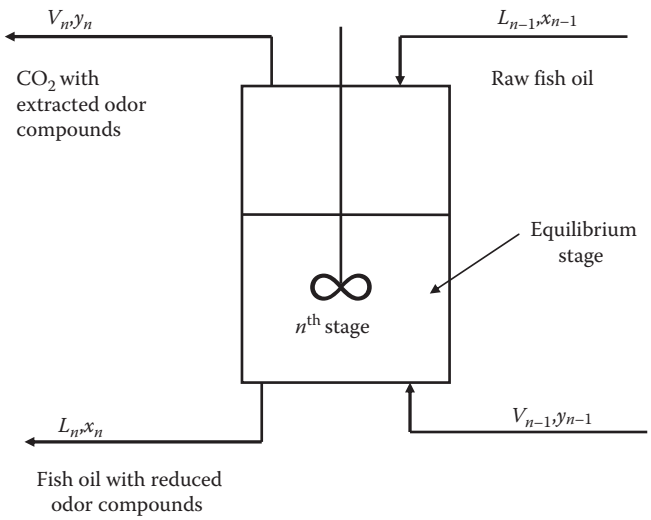


FIGURE E.4.38.1
Theoretical equilibrium contacting stage.

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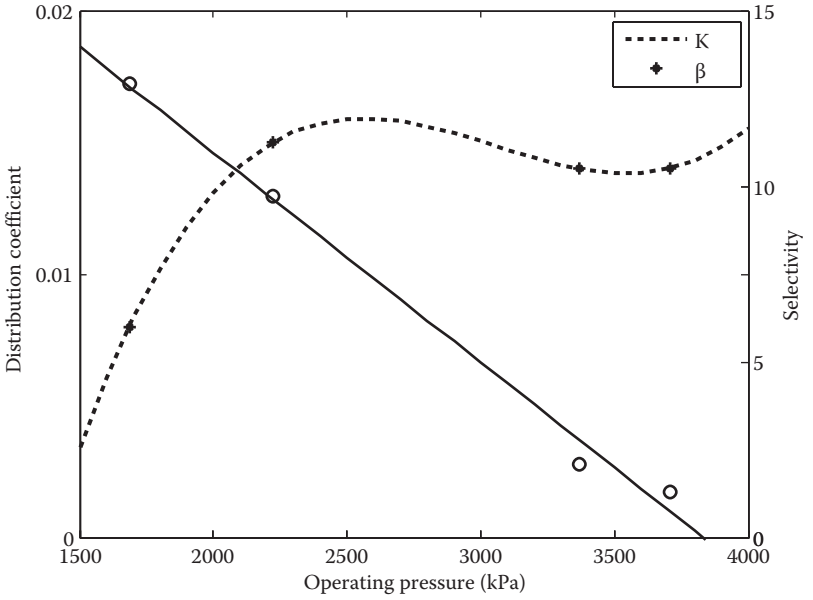


FIGURE E.4.38.2
Variation of the distribution coefficient, *K*, and selectivity, β, with operating pressure during supercritical extraction of odorous compounds from fish oil. (Adapted from Krukonis, V. J., *Journal of the American Oil Chemists Society*, 66, 818–21, 1989.)

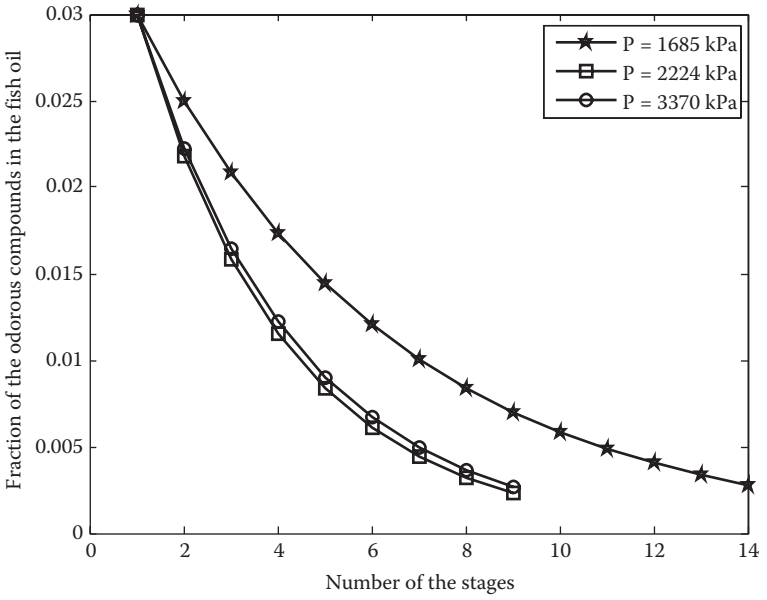


FIGURE E.4.38.3
Variation of the fraction of the odorous compounds in the fish oil with the number of the stages of the extraction process.

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We may combine Equation E.4.38.1 with Equation E.4.38.3 and obtain

$$x_n = \frac{L_{n-1}x_{n-1} + V_{n-1}y_{n-1}}{KV_n + L_n}. \tag{E.4.38.4}$$

We may combine Equations E.4.38.1 and E.4.38.2 to obtain

$$K_{\text{triglycerides}} = \frac{K_{\text{PCB}}}{\beta}. \tag{E.4.38.5}$$

MATLAB® code E.4.38 computes the fraction of the odor compounds remaining in the fish oil in a stagewise contacting process. Equation E.4.38.5 may also be used in a similar way to simulate the distribution of the triglycerides between the phases.

Example 4.39: Continuous Supercritical Carbon Dioxide Extraction of Vitamin E and Sterols From Olive Oil in a Packed Column

Vegetable oils and the residues of the oil refining process are important sources of high value raw materials for the chemical and nutraceutical industries. Hurtado-Benavides et al. (2004) employed the following column to extract vitamin E and sterols from olive oil.

When we consider a differential height *dz* of the packed column of Figure E.4.39, (cross-sectional area of the column = *A*) mass balance around the differential volume element of *Adz* requires

$$-Vdy = A\mathcal{K}_y a(y - y^*)Adz, \tag{E.4.39.1}$$

where *V* is the mass flow rate of gas, *A* is the cross-sectional area of the column, $\mathcal{K}_y a$ is the overall mass transfer coefficient, *a* is the interfacial area per unit volume, *y* is the weight fraction in the extract, and *y** is the weight fraction corresponding to the equilibrium with the liquid phase composition. Equation E.4.39.1 may be integrated as

$$Z_T = \frac{V}{AK_y a}\int_{\text{in}}^{\text{out}} \frac{dy}{y - y^*}, \tag{E.4.39.2}$$

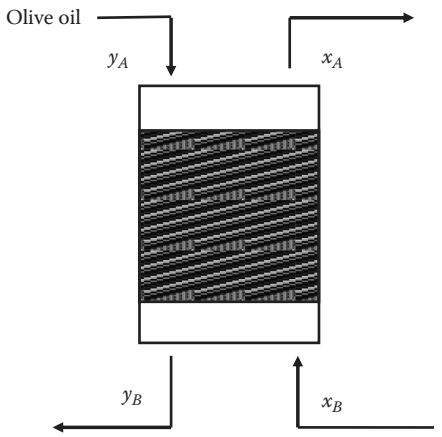


FIGURE E.4.39
Schematic description of the supercritical extraction process.

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where Z_T is the total height of the column. The integral part of Equation E.4.39.2 is called the number of transfer units, NTU:

$$\text{NTU} = \int_{\text{in}}^{\text{out}} \frac{dy}{y - y^*}. \tag{E.4.39.3}$$

The other part is the height of a transfer unit, HTU:

$$\text{HTU} = \frac{V}{AK_y a}. \tag{E.4.39.4}$$

The total bed height may be expressed as

$$Z_T = (\text{NTU})(\text{HTU}). \tag{E.4.39.5}$$

MATLAB® code E.4.39.a uses Equations E.4.39.3 and E.4.39.3 to compute the NTU and the packing height, by using the data presented by Hurtado-Benavides et al. (2004) during the supercritical carbon dioxide extraction of vitamin E from olive oil. The packing was glass beads and the supercritical CO_2 to oil olive flow rate ratio was 23.14.

The computations are repeated in MATLAB® code E.4.39.b for the extraction of sterols from olive oil by using the supercritical carbon dioxide in the same column.

It should be noticed that although the exact same conditions apply in the extraction of both vitamin E and sterols, the NTU and HTU are substantially different in both cases.

MATLAB® CODE E.4.39.a

Command Window:

```
clear all
close all
format compact
global yEquilibrium

% SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF VITAMINS

% enter the data
yA=0.019; % vitamins in the supercritical carbon dioxide at the top
of the column
yB=0.009; % sterols in the supercritical carbon dioxide at the
bottom of the column
HTU=0.25; % hight of a transfer unit

StepNumber=2000
deltaY=(yA-yB)/StepNumber;
yEquilibrium=0.008993; % estimated
y(1)=yB;

for i=2:StepNumber
     y(i)=y(i-1)-deltaY;
end

% compute the NTU
NTU=quad(@calculateNTU,yB,yA)
```

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```
fprintf('\n vitamin E in the supercritical carbon dioxide at the
bottom of the column, y= %.3g \n', yB)

z=HTU*NTU; % height of the packing in the column
fprintf('\n height of the packing in the column, z= %.2g m\n', z)
```

M-file:

```
function f=calculateNTU(y)
global yEquilibrium
f=1./(y-yEquilibrium);
```

When we run the code the following lines will appear on the screen:

```
StepNumber =
        2000
NTU =
    7.2651

 vitamin E in the supercritical carbon dioxide at the bottom of the
column, y= 0.009

 height of the packing in the column, z= 1.8 m
```

MATLAB® CODE E.4.39.b

Command Window:

```
clear all
close all
format compact
global yEquilibrium

% SUPERCRITICAL CARBON DIOXIDE EXTRACTION OF STEROLS

% enter the data
yA=0.334; % sterols in the supercritical carbon dioxide at the top
of the column
yB=0.319; % sterols in the supercritical carbon dioxide at the
bottom of the column
HTU=1.49; % hight of a transfer unit

StepNumber=2000
deltaY=(yA-yB)/StepNumber;
yEquilibrium=0.3132; % estimated
y(1)=yB;

for i=2:StepNumber
     y(i)=y(i-1)-deltaY;
end
```

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```
% compute the NTU
NTU=quad(@calculateNTU,yB,yA)
fprintf('\n sterols in the supercritical carbon dioxide at the
bottom of the column, y= %.3g \n', yB)

z=HTU*NTU; % hight of the packing in the column
fprintf('\n hight of the packing in the column, z= %.2g m\n', z)
```

When we run the code the following lines will appear on the screen:

```
StepNumber =
        2000
NTU =
    1.2771

 sterols in the supercritical carbon dioxide at the bottom of the
column, y= 0.319

 hight of the packing in the column, z= 1.9 m
```

4.4.4 Mathematical Analysis of Distilled Beverage Production Processes

Distillation is the major unit operation in distilled alcoholic beverage (i.e., brandy, whiskey, vodka, rum, tequila, raki, etc.) production processes. The first step in the distilled alcoholic beverage production is fermentation of an appropriate carbon source to produce alcohol. Although ethyl alcohol and water are the two major components of any distilled spirit, their aroma and flavor are attributable to minor compounds usually referred to as congeners. The congeners are mostly side products of alcoholic fermentation, some of them originate from the fruit. Distillation conditions affect the quantities of the congeners, which find their way to the final product and some of the flavor and aroma compounds arise from chemical reactions during distillation such as heat induced degradative changes (Guymon 1974).

Distillation is based on the separation of components of a liquid mixture by the help of the relative volatility differences. Relative volatility is defined as

$$\alpha_{AB} = \frac{y_A / x_A}{y_B / x_B}, \tag{4.97}$$

where y and x are the mole fractions in the vapor and liquid phases, respectively. The ratio y_i/x_i is called the volatility of component i. Easy separation is achieved when $\alpha_{AB} << 1$ or $\alpha_{AB} >> 1$. Components with higher vapor pressure (i.e., alcohol) will have a higher mole fraction in the vapor phase. It should be noticed that components with a similar relative volatility to ethanol will also appear in the distillate and contribute to the flavor. Appropriate cuts of distillates from the same or different fermentation products are blended to obtain the optimum product.

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Example 4.40: Analysis of Whiskey Production In a Pot Still

The earliest version of the industrial distillation equipment are the pot stills (Figure E.4.40.1), where direct heat is supplied to the fermented mixture in the pot, vapor rises into the head, passes through the coiled tube, then condenses and drains into a product tank. During whiskey production in a pot still, the product is distilled two or three times, than different cuts of the distillate are mixed together to attain the required taste and the ethanol content.

1. In a study made in a Turkish distillery with a steam heated pot still, Yazicioglu (1974) reported that the initial product for the second distillation operation contains 30% alcohol, the first cut of distillate was 80 L with 83% average alcohol content, the middle cut was 1750 L with 74% average alcohol content, the final cut of distillate was 1170 L with 20% average alcohol content. The remaining liquid in the pot still contains 2.2% ethanol. Calculate the initial volume of the fermentation product charged to the pot still.

   Solution: Total liquid balance requires

$$V_0 = 80 + 1750 + 1170 + V_R, \tag{E.4.40.1}$$

   where V_0 and V_R are the initial and the final remaining volumes of the liquid in the pot still. Ethanol balance requires

$$0.30\ V_0 = (80)(0.83) + (1750)(0.74) + (1170)(0.20) + (0.022)V_R. \tag{E.4.40.2}$$

   After solving Equations E.4.40.1 and E.4.40.2 together we will obtain $V_0 = 5500$ L and $V_R = 2500$ L.

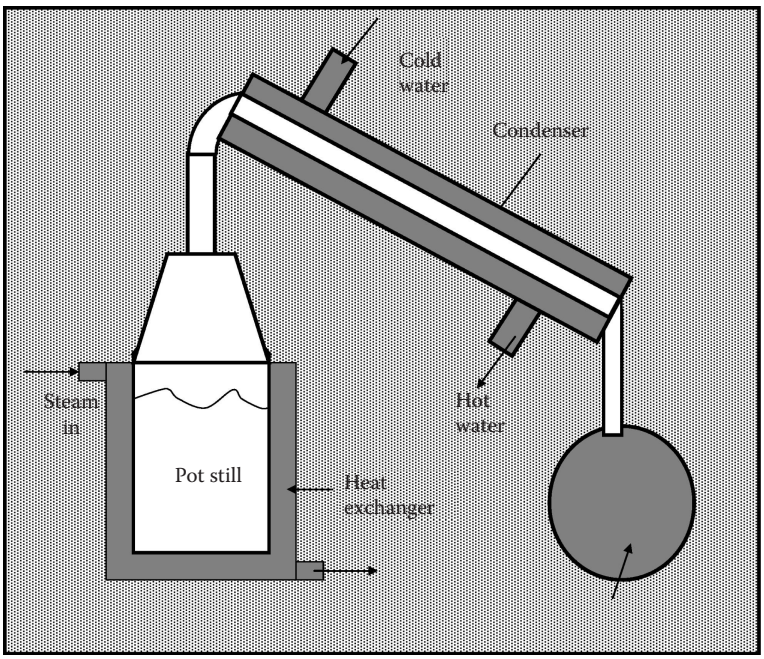


FIGURE E.4.40.1
Schematic drawing of the distillation equipment.

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a. Use the following data (Yazicioglu 1974) to compute the variation of the volume and average ethanol content of the middle cut, also compute the volume and ethanol content of the liquid remaining in the pot still.

Time (h)	T (°C)	F_i (L/h)	y_i (Volume Fraction)	Time (h)	T (°C)	F (L/h)	y_i (Volume Fraction)
1	84.5	50	0.83	17	85.5	50	0.789
2	82.5	60	0.845	18	85.5	60	0.792
3	82.5	60	0.845	19	86.5	50	0.771
4	82.6	60	0.835	20	87.5	60	0.73
5	83	60	0.835	21	88	60	0.73
6	83	60	0.829	22	88.5	60	0.723
7	83.5	60	0.845	23	88.5	60	0.718
8	83.6	60	0.835	24	89	60	0.68
9	83.8	50	0.832	25	89	60	0.68
10	83.8	60	0.83	26	89.5	60	0.65
11	84.5	50	0.834	27	90	60	0.63
12	84.5	50	0.834	28	90.5	60	0.62
13	84.5	50	0.84	29	90.5	50	0.61
14	85	50	0.83	30	90.5	50	0.60
15	85	50	0.83				
16	85	50	0.83				

F_i = distilled product flow rate from the pot stills during the time period, $\Delta t = 1$ h.

Solution: Total amounts of vapor removed from the pot still at $t = n\Delta t$ is $V(t) = \sum_{i=1}^{n} F_i \Delta t$ with average ethanol content $y_{av} = \sum_{i=1}^{n} F_i y_i \Delta t / \sum_{i=1}^{n} F_i \Delta t$. The amount of liquid remaining in the pot still is $L(t) = L_0 - V(t)$ with the fraction of ethanol of $x(t) = (L_0 x_0 - V(t) y_{av}(t))/L(t)$. MATLAB® code E.4.40 shows the details of the computations.

MATLAB® CODE E.4.40

Command Window:

```
clear all
close all
format compact

% enter the data
F=[50 60 60 60 60 60 60 60 50 60 50 50 50 50 50 50 50 60 50 60 60 60
60 60 60 60 60 60 50 50]; % distilled product flow rate from the pot
still
yVolume=[0.83 0.845 0.845 0.835 0.835 0.829 0.845 0.835 0.832 0.83
0.834 0.834 0.84 0.83 0.83 0.83 0.789 0.792 0.771 0.73 0.73 0.723
0.718 0.68 0.68 0.65 0.63 0.62 0.61 0.60]; % volume fraction of
ethanol in the product coming from the pot still
 T=[84.5 82.5 82.5 82.6  83 83 83.5 83.6 83.8 83.8 84.5 84.5 84.5 85
85 85 85.5 85.5 86.5 87.5 88 88.5 88.5 89 89 89.5 90 90.5 90.5
90.5]; % temperature of the pot stil (oC)
deltaTime=1; % time increment over which the sample is collected
V(1)=0; % initial volume of distillate
t(1)=0;
```

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```
xVolume(1)=0.29; % initial volumetric fraction of ethanol in the pot
still
L(1)=5420 ; % initial volume of the mixture in the pot stil (L)
t=[2:1:31]; % times that the data were recorded (h)
yVolumeAverage(1)=0;
deltaEthanol(1)=F(1)*yVolume(1);
for n=2:length(t)
   t(n)=t(n-1)+deltaTime;
   V(n)=V(n-1)+F(n-1)*deltaTime; % volume of the distillate (L)
   deltaEthanol(n)=F(n)*yVolume(n); % ethanol content of the
incremental distillate
   yVolumeAverage(n)=(sum(deltaEthanol(1:n)*deltaTime)/V(n)); %
volumetric fraction of ethanol remaining in the distillate
   L(n)=L(1)-V(n); % amount of mixture remaining in the pot still
(L)
   xVolume(n)=(L(1)*xVolume(1)-V(n)*yVolumeAverage(n))/L(n); %
volumetric fraction of ethanol remaining in the pot still
end

% plot the computations and the data
 plot(t,yVolume, 's') ; hold on
[AX,H1,H2]=plotyy(t,xVolume,t,T);  hold on;
xlabel('time (h)')
set(get(AX(1),'Ylabel'),'String','x, y (mole fraction)')
set(get(AX(2),'Ylabel'),'String','(T ^o C)')
set(H1,'LineStyle','*')
set(H2,'LineStyle','o')
legend('fraction of ethanol in the distillate','fraction of ethanol
in the pot still','Location','NorthEast')
legend(H2,'Temperature','Location','East')

figure
[AX,H1,H2]=plotyy(t,V,t,L);  hold on;
xlabel('time (h)')
set(get(AX(1),'Ylabel'),'String','V (liter)')
set(get(AX(2),'Ylabel'),'String','L (liter)')
set(H1,'LineStyle','*')
set(H2,'LineStyle','o')
legend('volume of the distillate','volume remaining in the pot
still','Location','SouthEast')
```

When we run the code Figures E.4.40.2 and E.4.40.3 will appear on the screen.

Mass balances may be performed to obtain the following equations for a continuous fractionating column with rectifying and stripping sections (Figure 4.11):

$$F = D + B, \tag{4.98}$$

where F, D, and B are the feed, distillate, and bottom product rates, respectively. The relation between the compositions of the phases in the enriching (above the feed plate) section of the column is

$$y_{n+1} = \frac{L_n}{V_{n+1}} x_n + \frac{Dx_D}{V_{n+1}}, \tag{4.99}$$

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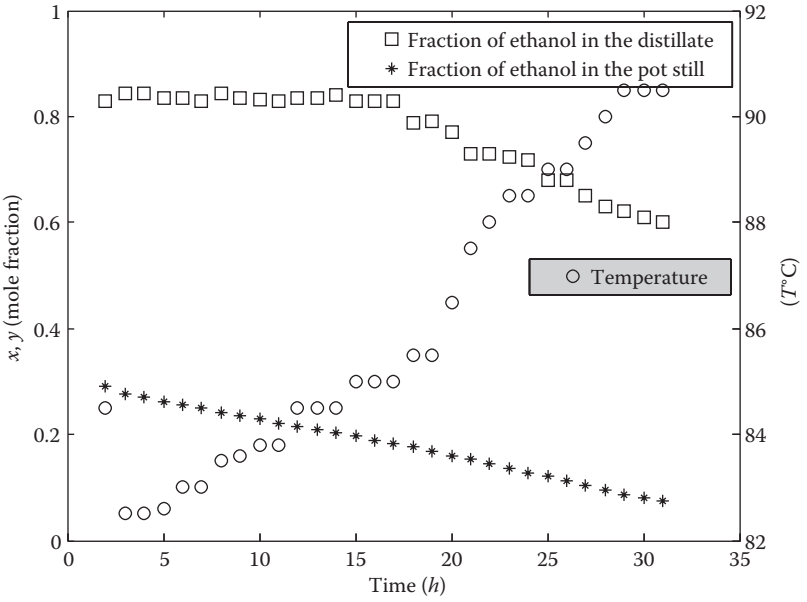


FIGURE E.4.40.2
Variation of the volumetric fractions of ethanol in the pot still and the distillate during the production of the "middle cut.

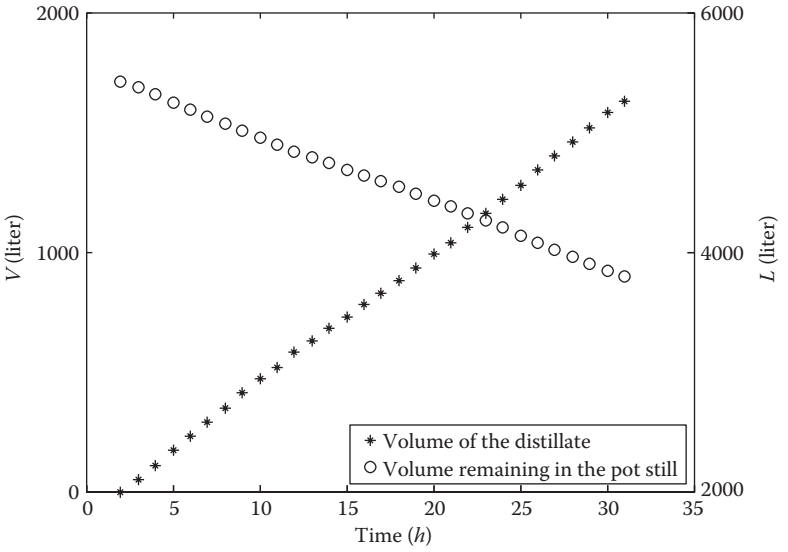


FIGURE E.4.40.3
Variation of the volumes of the content of the pot still and the distillate during the production of the "middle cut."

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and the relation between the compositions of the phases in the stripping section (below the feed plate) of the column is

$$y_{m+1} = \frac{L_m}{L_m - B} x_m + \frac{Bx_B}{L_m - B}, \tag{4.100}$$

where L and V are the flow rates of downward and upward flowing streams, respectively. Variables x and y denotes the ethanol concentrations in L and V, respectively. The subscripts describe the plate number that the stream is leaving. Generally heat is applied at the base of a tower by means of a reboiler (heat exchanger) as shown in Figure 4.11, but when a water solution is fractionated to give the nonaqueous solute as the distillate and the water is removed as the residue product, the heat may be provided by the use of an open steam (saturated at the pressure of the column) at the bottom of the tower; then the reboiler is not used, but more trays are needed in the stripping section of the tower. In such a column the enriching operating line (i.e., Equation 4.99) will be the same. The total material balance and the operating line for the stripping section needs to be reestablished as

$$F + S = D + B, \tag{4.101}$$

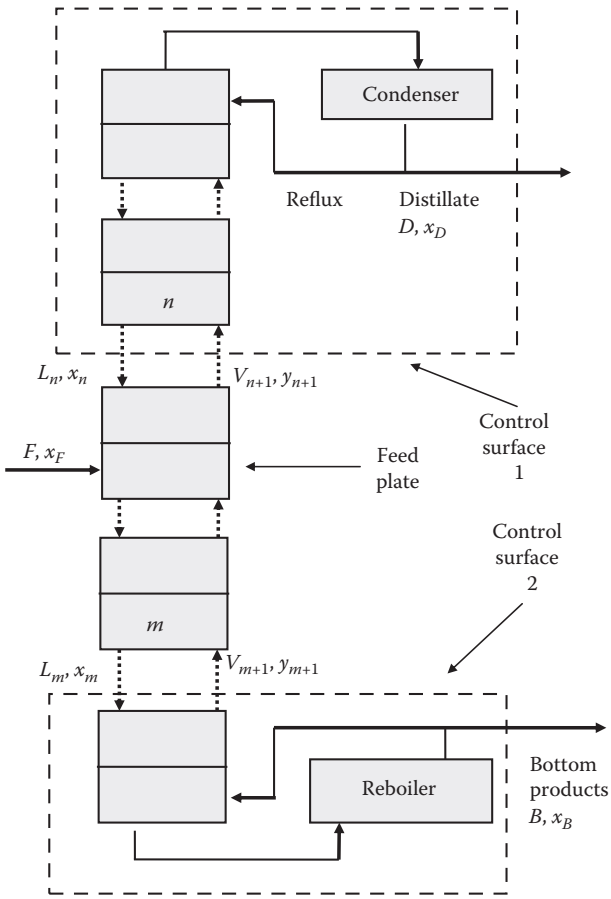


FIGURE 4.11
Material balance diagram for a continuous fractionating column.

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$$y_{m+1} = \frac{L_m}{L_m + S - B} x_m + \frac{Bx_B}{L_m + S - B}, \tag{4.102}$$

where S is the rate of steam input to the column. The liquid that is obtained by condensing the overhead vapors and returned to the top of the column is called the reflux. When all of the overhead products are condensed and returned the top of the column we will have the total reflux. The internal reflux ratio is defined as L/V where L and V are the molar flow rates of liquid and vapor streams, respectively; while designing a column using the McCabe and Thiele method, the molar liquid and vapor flow rates are assumed to be constant.

Example 4.41: Distillation Column Design With a McCabe and Thiele Method for Separation of Ethanol from a Fermentation Product

An ethanol–water mixture available at its bubble point with 0.3 mole fraction ethanol will be distilled to produce 0.80 mole fraction ethanol with negligible ethanol in the bottoms. The feed rate to the column is 910 kg/h, the column will contain 76 cm diameter cross-flow sieve trays (Figure E.4.41.1) and operate under atmospheric pressure (101.3 kPa). The net tray area for the flow of the vapor phase is 0.417 m^2. Determine a suitable reflux ratio, number of the trays needed, and the location of the feed plate needed for this separation. Saturated open steam at 169 kPa will be used for heating.

Solution: The feed composition corresponds to 52.27% (wt/wt) ethanol. Molecular weights of ethanol and water are 46.05 and 18.02 g/g mol, respectively; therefore, the feed contains (910)(0.5227)/(46.05) = 10.33 kmol ethanol and (910)(1–0.5227)/(18.02) = 24.10 kmol water. If almost all the ethanol will be removed from the residue, the distillate D = 10.33/0.80 = 12.91 kmol/h (12.91)(0.80)(46.05) + (12.91)(0.20)(18.02) = 522.2 kg/h. Equilibrium data for ethanol–water systems is depicted in Table E.4.41.

MATLAB® code E.4.41.a plots the equilibrium mass fraction of ethanol in the vapor and liquid phases as a function of temperature by using the data given in Table 4.41.1. It also produces an equilibrium curve and a polynomial function for the equilibrium curve.

At the top of the column, mole fraction of ethanol is 0.80 corresponding to a mass fraction y = (0.80)(46.05)/[(0.80)(46.05) + (0.20)(18.02)] = 0.91, the temperature of this plate may be estimated from Table E.4.41 as 78.28°C.

The diameter of the distillation columns are chosen to accommodate the pertinent liquid and vapor flow rates. The detailed design is made near flooding conditions. With a large pressure drop

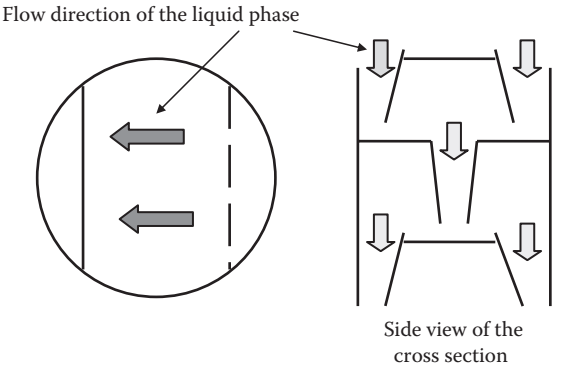


FIGURE E.4.41.1
A cross flow tray arrangement. Bubble-cap trays were used in almost all distillation columns during 1920–1950, but they have been abandoned for new installation because of their high cost.

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TABLE E.4.41

Equilibrium Mass Fractions for Ethanol–Water Systems at 101.3 kPa

T (°C)	x	y	T (°C)	x	y
100.0	0	0	81.0	0.60	0.794
98.1	0.02	0.192	80.1	0.70	0.822
95.2	0.05	0.377	79.1	0.80	0.858
91.8	0.10	0.527	78.3	0.90	0.912
87.3	0.20	0.656	78.2	0.94	0.942
84.7	0.30	0.713	78.1	0.96	0.959
83.2	0.40	0.746	78.2	0.98	0.978
82.0	0.50	0.771	78.3	1.00	1.00

Source: Geankoplis, C. J., and Toliver, P. R., Transport Processes and Separation Process Principles (Includes Unit Operations). Prentice Hall, Upper Saddle River, NJ, 2003.

MATLAB® CODE E.4.41.a

Command Window:

```
clear all
close all
format compact

% enter the data
xMass=[0 0.02 0.05 0.1 0.20 0.30 0.40 0.50 0.60 0.70 0.80 0.90 0.94
0.96 0.98 1.00]; % mass fraction of ethanol in the pot stil (liquid
phase)
yMass=[0 0.192 0.377 0.527 0.656 0.713 0.746 0.771 0.794 0.822 0.858
0.912 0.942 0.959 0.978 1.00]; % volume fraction of ethanol in the
vapor phase coming from the pot still
 T=[100 98.1 95.2 91.8 87.3 84.7 83.2 82 81 80.1 79.1 78.3 78.2 78.1
78.2 78.3]; % temperature of the pot stil (oC)
MWwater=18; % molecular weight of water (g/gmol)
MWethanol=46.05; % molecular weight of ethanol (g/gmol)

% convert the data ito mole fractions
for i=1:length(xMass)
yMol(i)=(yMass(i)/MWethanol)/((yMass(i)/MWethanol)+((1-yMass(i))/
MWwater));
xMol(i)=(xMass(i)/MWethanol)/((xMass(i)/MWethanol)+((1-xMass(i))/
MWwater));
end

% plot the data
plot(T,xMol,':o',T,yMol, '-*') ; hold on
legend('x','y',2,'Location','NorthEast')
xlabel('T (^oC)')
ylabel('x, y (mol fraction)')

% produce an equilibrium curve equation
figure(2)
```

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```
N=5;
c = polyfit(xMol,yMol,N)
% yModel=polyval(c,xMol);
for i=1:length(xMol)
yModel(i)=(19.4376*xMol(i)^5)- (55.2823*xMol(i)^4)+(
58.5526*xMol(i)^3)-(27.9642*xMol(i)^2)+6.2225*xMol(i)+0.0456;
end
plot(xMol,yMol, '*', xMol,yModel, '-') ; hold on % plot the
equilibrium data and the equilibrium curve
ylim([0 1.2])
legend('data','model','Location','SouthEast')
xlabel('x (mol fraction)')
ylabel('y_e_q (mol fraction)')
```

When we run the code Figures E.4.41.2 and E.4.41.3 and the following lines will appear on the screen:

```
c =
   19.4376  -55.2823   58.5526  -27.9642    6.2225    0.0456
```

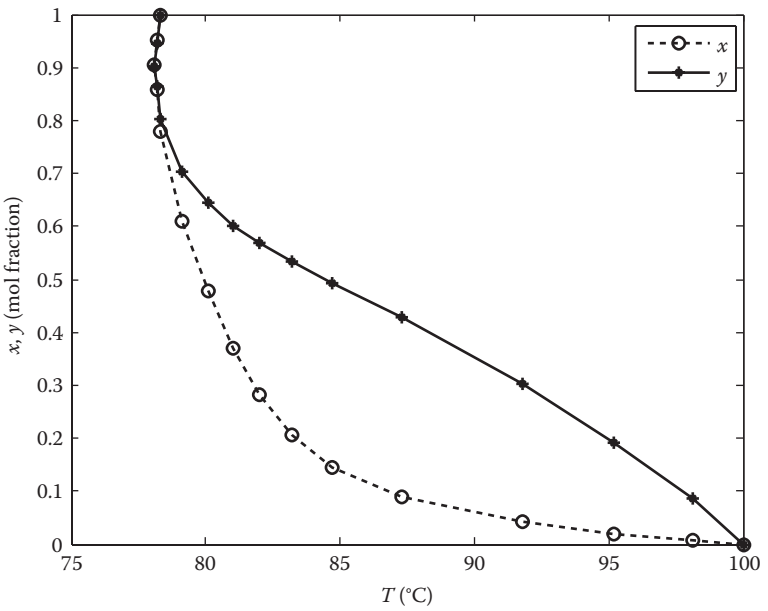


FIGURE E.4.41.2
When we bring ethanol–water mixture to temperature T and wait long enough to reach equilibrium, the system will set the x and y values as given in the plot.

in space between the trays, the level of liquid leaving a tray at a relatively low pressure and entering the one of high pressure must necessarily assume an elevated position in the downcomers. The liquid is led from one tray to the next by means of the downcomers. As the pressure difference increases further due to the increased rate of either vapor or liquid, the level in the downcomers will increase further, and eventually the liquid level will reach that of the tray above, then the increase in either flow rate will force the liquid to occupy the entire space between the trays, this

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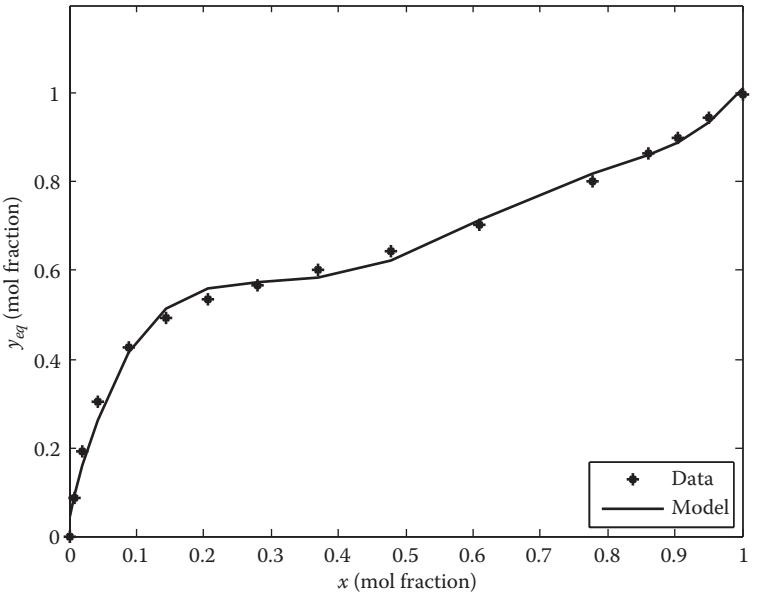


FIGURE E.4.41.3
Equilibrium curve. Equation of the curve is $y_{eq} = 19.4376x^5 - 55.2823x^4 + 58.5526x^3 - 27.9642x^2 + 6.2225x - 0.0456$.

is called flooding. For a given type of a column at flooding the superficial velocity of the vapor phase is (Treybal 1980):

$$v_F = C_F \sqrt{\frac{\rho_L - \rho_V}{\rho_V}}, \tag{E.4.41.1}$$

where ρ_L is the density of the liquid phase and ρ_v is the density of the vapor phase, C_F is flooding constant of the tray tower and may be expressed empirically as (Treybal 1980)

$$C_F = \alpha \log\left\{\frac{1}{(L_s/V_s)\sqrt{\rho_v/\rho_L}} + \beta\right\}\left(\frac{\sigma}{0.02}\right)^{0.2}, \tag{E.4.41.2}$$

where L_s and V_s are the superficial mass flow rates of liquid and vapor phases, respectively, σ is the surface tension of the liquid phase, α and β are constants and under the operating conditions given as $\alpha = 0.0452$ and $\beta = 0.0287$. At the temperature of the top of the column (tray number 20) $\rho_v = 1.405$ kg/m^3, $\rho_L = 744.9$ kg/m^3 and $\sigma = 0.021$ N/m. If we should tentatively take $(L_s/V_s)(\rho_V/\rho_L)^{0.5} = 0.1$, Equation E.4.41.2 will provide $C_F = 0.0746$, then we may use Equation E.4.41.1 to calculate $V_F = 1.72$ m/s. If we should choose a reflux ratio of 3 then we will have $V = D(3 + 1) = 12.91(3 + 1) = 51.64$ kmol/h vapor at the top, which (after using the ideal gas law) may be shown to correspond to 0.414 m^3/s volumetric vapor flow rate. The velocity of the vapor phase is 0.414/0.417 = 0.993 m/s (where 0.417 = the net tray area for the flow of the vapor phase). This net velocity of the vapor phase corresponds to only 58% of the flooding velocity of the tower and indicates that the choice of the reflux ratio is appropriate for the operation of the column.

The flow rate of the liquid phase is $L = 3D = (3)(12.91) = 38.73$ kmol/h = 38.73[(0.80)(46.05) + (0.20)(18.02)] = 1567 kg/h, and $V = (51.64)[(0.80)(46.05) + (0.20)(18.02)] = 2089$ kg/h. We may calculate $(L_s/V_s)(\rho_v/\rho_L)^{0.5} = (1567/2089)(1.405/744.9)^{0.5} = 0.033$. When $(L_s/V_s)(\rho_v/\rho_L)^{0.5} = 0.1$,

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Equation E.4.52.1 uses the C_F calculated for $(L_s/V_s)(\rho_V/\rho_L)^{0.5} = 0.1$, therefore the calculation of V_F is correct.

All the feed will join the liquid coming from the enriching section in the feed plate, then the flow rate of the liquid and the vapor phases in the stripping section will be

$$L_{\text{stripping}} = L + F, \tag{E.4.41.3}$$

$$V_{\text{stripping}} = V. \tag{E.4.41.4}$$

Therefore $L_{\text{stripping}} = 38.73 + 34.43 = 73.2$ kmol/h and $V_{\text{stripping}} = 51.64$ kmol/h. It should be noticed that Equations E.4.41.3 and E.4.41.4 are valid only with liquid feed at its bubble point, partitioning of the feed among the phases depends on its enthalpy.

Enthalpy of the saturated steam at 169 kPa is 2699 kJ/kg (reference: enthalpy of liquid water at 0°C is 0 kJ/kg). It will adiabatically expand to the column conditions, where enthalpy of the saturated steam under 101.3 kPa is 2676 kJ/kg and the latent heat ΔH_{vapor} is 2257 kJ/kg. We will use the following equation to relate the molar flow rates of steam and vapor phase at the bottom of the column:

$$V = S\left(1 + \frac{H_N + H_{\text{saturated}}}{\Delta H_{\text{vapor}}}\right). \tag{E.4.41.5}$$

After substituting the numbers in Equation E.4.41.5 we will have
$51.64 = S(1 + 2699 + 2676/2557)$, then we can easily calculate $S = 51.17$ kmol steam/h. The molar material balance between the phases requires

$$L = V - S + B. \tag{E.4.41.6}$$

After substituting the numbers $73.2 = 51.64 - 51.1 + B$, then we can easily calculate that $B = 72.7$ kmol/h.

We assumed that there is a saturated steam at the bottom plate of the column at 101.3 kPa, therefore the temperature of this plate may be assumed as 100°C. The locus of the intersection of the stripping and enriching operating lines is (Treybal 1980)

$$y = \frac{q}{q-1}x - \frac{x_F}{q-1}, \tag{E.4.41.7}$$

where

$$q = \frac{L_{\text{stripping}} - L_{\text{enriching}}}{F} = \frac{H_V - H_F}{H_V - H_L}. \tag{E.4.41.8}$$

$L_{\text{stripping}}$ = molar flow rate of the liquid phase in the stripping section, $L_{\text{enriching}}$ = molar flow rate of the liquid phase in the enriching section, F = molar feed rate to the column, H_V = molar enthalpy of the vapor phase, H_L = molar enthalpy of the liquid phase, H_F = molar enthalpy of the feed, and x_F is the average of the mole fraction of ethanol in both phases of the feed stream. Equation E.4.41.8 describes the q line. In the y versus x diagram (Figure E.4.41.4) the intersection of $y = x$ (45° line) with $y = z_F$ lines is found, than a line passing through the intercept with a slope of $q/(1 - q)$ is plotted to obtain the q line. The value of q is 1 for a mixture of ethanol–water feed at its bubble point.

MATLAB® code E.4.41.b determines the number of the ideal stages required for the separation.

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MATLAB® CODE E.4.41.b

Command Window:

```
clear all
close all
global y

% enter the data
xd=0.8; % mole percent of ethanol in the distillate
xb=0.02; % mole percent of ethanol in the bottoms
zf=0.3; % mole percent of ethanol in the feed
R=3; % reflux ratio
q=1; %  feed is a two-phase mixture with feed quality equal to 0.85

% plot and compute the equilibrium curve by using function
EthanolEquilibrium
for i=1:11
       y=0.1*(i-1);
       ye(i)=0.1*(i-1);
       xe(i)=fzero('EthanolEquilibrium',0.5); % find the value of
the independent variable, around 0.5, which makes the value of the
function zero
end

% compute the intersection of feed line and operating lines
yi=(zf+xd*q/R)/(1+q/R);
xi=(-(q-1)*(1-R/(R+1))*xd-zf)/((q-1)*R/(R+1)-q);

figure(1);
hold on;
axis([0 1 0 1]); % set scaling for the x- and y-axes (xMin xMax yMin
yMax)

% plote operating and feed lines and equilibrium curve
plot(xe,ye,':');
set(line([0  1],[0  1]),'Color',[0 0 0]); % draw black lines
set(line([xd xi],[xd yi]),'Color',[0 0 0]);
set(line([zf xi],[zf yi]),'Color',[0 0 0]);
set(line([xb xi],[xb yi]),'Color',[0 0 0]);

% computations for the rectifying section
i=1;
xp(1)=xd;
yp(1)=xd;
y=xd;
while (xp(i)>xi),
    xp(i+1)=fzero('EthanolEquilibrium',0.5);
    yp(i+1)=R/(R+1)*xp(i+1)+xd/(R+1);
    y=yp(i+1);
    set(line([xp(i) xp(i+1)],[yp(i) yp(i)]),'Color',[0 0 0]);
    if (xp(i+1)>xi) set(line([xp(i+1) xp(i+1)], [yp(i)
yp(i+1)]),'Color',[0 0 0]);
    end
        i=i+1;
end
```

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```
% computations for the stripping section
SS=(yi-xb)/(xi-xb);
yp(i)=SS*(xp(i)-xb)+xb;
y=yp(i);
set(line([xp(i) xp(i)],[yp(i-1) yp(i)]),'Color',[0 0 0]);

while (xp(i)>xb),
    xp(i+1)=fzero('EthanolEquilibrium',0.5);
    yp(i+1)=SS*(xp(i+1)-xb)+xb;
    y=yp(i+1);
    set(line([xp(i) xp(i+1)], [yp(i) yp(i)]),'Color',[0 0 0]);
    if (xp(i+1)>xb) set(line([xp(i+1) xp(i+1)], [yp(i)
yp(i+1)]),'Color',[0 0 0]);
    end
    i=i+1;
end

grid
xlabel('x')
ylabel('y, yeq')
hold off;
```

M-file:

```
function f=EthanolEquilibrium(x)
% function EthanolEquilibrium determines values of yeq for the given
values of x
global y
f=y-((19.4376*x^5)- (55.2823*x^4)+( 58.5526*x^3)-
(27.9642*x^2)+6.2225*x+0.0456);
end
```

When we run the code Figure E.4.41.4 will appear on the screen.

The number of ideal plates is the same as the number of the horizontal lines shown in Figure E.4.41.3 connecting the operating line to the equilibrium line. The horizontal stage lines of Figure E.4.41.3 indicate that when liquid and the vapor streams enter into a tray their compositions are related by the operating line; after remaining in contact they attain equilibrium in an ideal plate, then the relation between their compositions is described by the equilibrium curve. The number of the ideal stages required for the given separation were determined from Figure E.4.41.3 as 8.

The actual number of the plates may be calculated by using the Murphree column efficiency defined as

$$\eta = \frac{\text{number of ideal trays required for separation}}{\text{number of the real trays}}. \tag{E.4.41.9}$$

The temperature of the top and the bottom plates were reported as 78.28 and 100°C, respectively. The average temperature of the column may be assumed to be 89.5°C, where the

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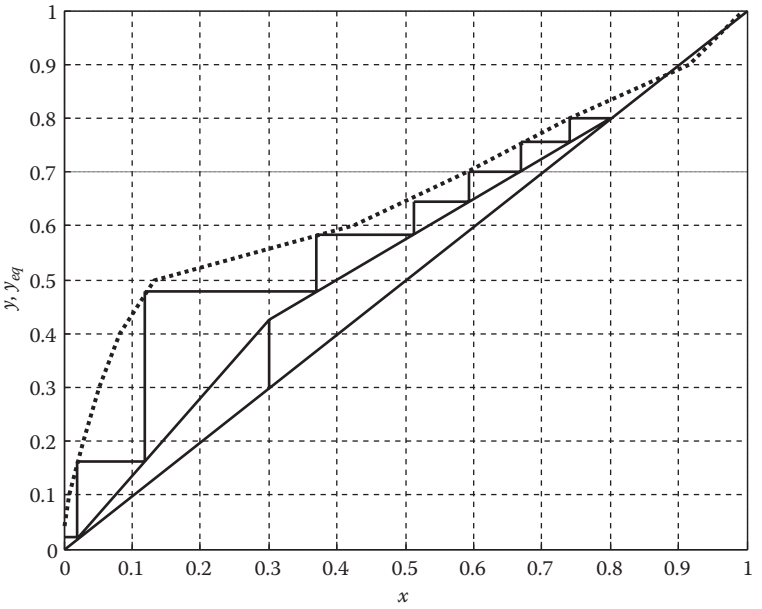


FIGURE E.4.41.4
Determination of the number of the ideal stages to achieve the required separation: The number of the steps in the stairway-like drawing is eight, meaning that the number of the ideal stages required for the required separation is eight.

equilibrium mass fractions of ethanol and water are $x_{ethanol} = 0.066$, $x_{water} = 0.934$, $y_{ethanol} = 0.36$, and $y_{water} = 0.64$. The relative volatility of ethanol–water mixture at the average column temperature may be calculated after substituting the numbers in Equation 4.52:

$$\alpha_{ethanol/water} = \frac{y_{ethanol}/x_{ethanol}}{y_{water}/x_{water}} = 7.96.$$

Viscosity of the ethanol–water mixtures may be calculated by using the Kendall–Monroe equation:

$$\mu_{mixture}^{1/3} = x_{ethanol}\mu_{ethanol}^{1/3} + x_{water}\mu_{water}^{1/3}, \tag{E.4.41.10}$$

where we may substitute the mass fractions of ethanol and water in the feed stream for x_{water} and $x_{ethanol}$. After substituting $x_{water} = 0.447$, $x_{ethanol} = 0.523$ and the viscosities at 89.5°C $\mu_{ethanol} = 0.95 \times 10^{-3}$ kg/ms and $\mu_{water} = 0.8 \times 10^{-3}$ kg/ms in Equation E.4.41.6 we will calculate $\mu_{mixture} = 0.8 \times 10^{-3}$ kg/ms. Then $\alpha_{average}\mu_{average} = 6.4 \times 10^{-3}$. The Murphree plate efficiency may be determined from a correlation obtained with O'Connell's (1946) data as

$$\eta = 0.492\left(100 \times \alpha_{average}\mu_{average}\right)^{-0.245} \tag{E.4.41.11}$$

as $\eta = 0.55$. After substituting the numbers in Equation E.4.41.9 we will determine the number of the real trays required for this separation as 15. Figure E.4.41.4 shows that the feed enters to the ideal stage number 6. We may calculate the corresponding real tray number for the entrance of the feed as 11 after using the Murphree plate efficiency.

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Example 4.42: Estimation of the Tray Number for the Maximum Accumulation of the Congeners During Brandy Production

Congeners, which may originate from the plant raw material or produced in the fermentation process, make an important contribution to the taste of the distilled beverages. Congeners may undergo chemical changes in the column (Figure E.4.42.1) during distillation therefore information, as given in Table E.4.42, about the tray number with its temperature and congeners concentration is important for the alcoholic beverage producers.

In the United States, two times the volumetric percentage of ethanol is referred to as the proof strength of an alcoholic beverage. The proof strength at which the volatility curve of a particular component intersects that of the ethyl alcohol indicates that proof at which the minor constituent will be concentrated in a fractionating column at the limiting condition of total reflux. MATLAB® code E.4.42.a produces a plot for the variation of the congeners concentration along the column and fits empirical (polynomial) models to the data.

The maximum concentration of a particular congener or minor component may be assumed to occur at a proof in the column at which its volatility is approximately equal to the internal reflux ratio (Guymon 1974). MATLAB® code E.4.42.b plots the volatility of each congener and predicts the tray number for the maximum concentration of each congener.

Reading the curves of Figure E.4.42.3 at 0.7 volatility indicates that the maximum n-propyl alcohol concentration should occur at 170°proof, the maximum isobutyl alcohol concentration should

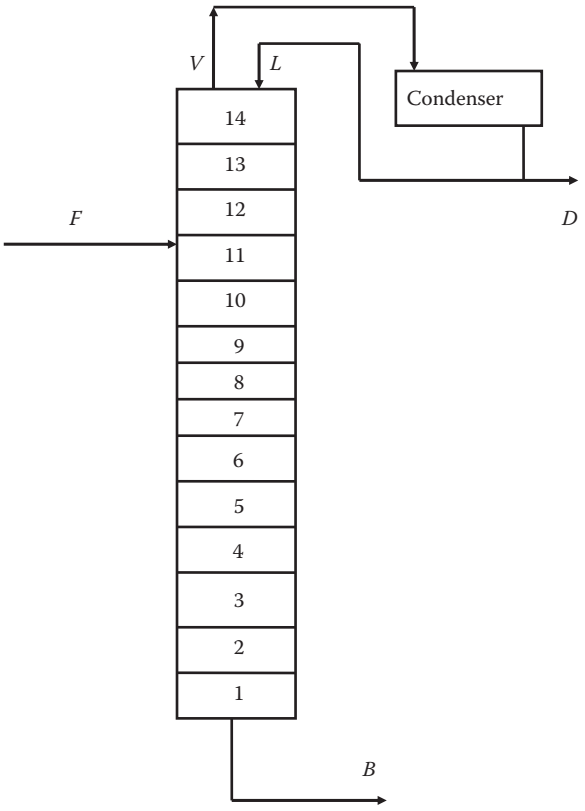


FIGURE E.4.42.1
Schematic description of the distillation column. When V and L do not change along the column, the reflux ratio is $R = L/V$.

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TABLE E.4.42

Ethanol and Higher Alcohol Concentrations in the Plates of a Distillation Column During Brandy Production

Tray Number	°Proof	*n*-Propyl alcohol[a]	Isobutyl Alcohol[a]	Amyls[a]
Overhead	189.8	—	2.3	—
14	189.2	—	7.1	2.4
13	188.6	11.8	11.8	5.9
12	187.5	19.9	16.4	14.0
Product	186.0	25.4	25.4	25.4
11	186.6	25.7	22.2	23.4
10	184.0	42.5	42.5	64.0
9	181.9	62.3	65.6	158
8	179.2	65.0	85.0	207.5
7	176.8	88.0	110.0	354
6	171.9	107.5	150.5	688
5	166.4	120.5	177	1000
4	160.2	135	200	1500
3	148.5	116	190	2150
2	128.5	128	208	3210
1	94.4	53	71	1178

Source: Guymon, J. F., In *Chemistry of Winemaking,* Table 2, American Chemical Society, Washington, DC, 1974.

[a] Grams per 100 liters at existing proof.

MATLAB® CODE E.4.42.a

Command Window:

```
clear all
close all

% enter the data
TrayNumber=[1:15];
Proof=[94.4 128.5 148.5 160.2 166.4 171.9 176.8 179.2 181.9 184.0
186.6 187.5 188.6 189.2 189.8 ];
Propyl=[53 128 116 135 120.5 107.5 88.0 65.0 62.3 42.5 25.7 19.9
11.8]; % alpha propyl alcohol (g/100L)
TrayPropyl=[1:13]; % trays where the prophy alcohol measured
 Isobutyl=[71 208 190 200 177 150.5 110.0 85.0 65.6 42.5 22.2 16.4
11.8 7.1 2.3]; % isobutyl alcohol (g/100L)
Amyls=[1178 3210 2150 1500 1000 688 354 207.5 158 64.0 23.4 14.0 5.9
2.4]; % amyls (g/100L)
TrayAmyls=[1:14]; % trays where the amyls were measured

% plot the data
semilogy(TrayNumber,Isobutyl,'*', TrayAmyls,Amyls,'o', TrayPropyl,
Propyl,'s'); hold on
ylim([1e0 1e5]);
 [AX,H1,H2] = plotyy(TrayPropyl, Propyl, TrayNumber, Proof); hold on
```

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```
ylim([1e0 1e5]);
ylim(AX(2), [0 250])
set(H1,'LineStyle','none')
set(H2,'LineStyle','p')
xlabel('Tray Number')
ylabel('Congeners (g/100 L)')
set(get(AX(2),'ylabel'), 'string', '^o Proof')

legend('iso-butyl alcohol','amyls',' n-propyl alcohol','Location','S
outhWest')
legend(H2,'proof','Location','East')

%  fit a polynomial empirical model to the data
N=4; % determine N by trial and error to obtain good agreement
between model & data

c = polyfit(TrayNumber, log(Isobutyl),N);
IsobutylModel=polyval(c,TrayNumber);
semilogy(TrayNumber,exp(IsobutylModel),'-'); hold on;
ylim([1e0 1e5]);

c = polyfit(TrayAmyls, log(Amyls),N);
AmylsModel=polyval(c,TrayAmyls);
semilogy(TrayAmyls,exp(AmylsModel),':'); hold on;
ylim([1e0 1e5]);

c = polyfit(TrayPropyl, log(Propyl),N);
PropylModel=polyval(c,TrayPropyl);
semilogy(TrayPropyl,exp(PropylModel),'--'); hold on;
ylim([1e0 1e5]);

N=2;
c = polyfit(TrayNumber, Proof,N);
ProofModel=polyval(c,TrayNumber);
semilogy(TrayNumber,Isobutyl,'*', TrayAmyls,Amyls,'o', TrayPropyl,
Propyl,'s'); hold on
ylim([1e0 1e5]);
 [AX,H1,H2] = plotyy(TrayPropyl, Propyl, TrayNumber, ProofModel);
hold on
ylim([1e0 1e5]);
ylim(AX(2), [0 250])
set(H1,'LineStyle','none')
set(H2,'LineStyle','-')
```

When we run the code Figure E.4.42.2 will appear on the screen:

be at 158° proof and the maximum amyls concentration should be at 128° proof. Figure E.4.42.1 or Table E.4.42 shows that the maximum n-propyl alcohol concentration was in tray number 4 (160.2° proof), the maximum isobutyl alcohol concentration was in tray number 2 (128.5° proof) and the maximum amyls concentration was in tray number 2 (128.5° proof), which indicates that the estimates are in good agreement with the experimental results.

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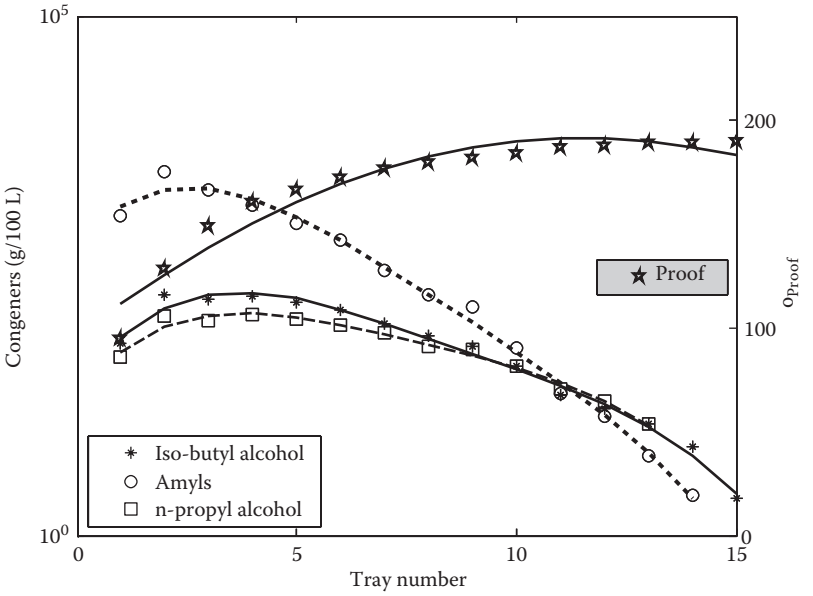


FIGURE E.4.42.2
Variation of the proof strength and congener concentration along the distillation column. (Data, shown with markers, adapted from Guymon, J. F., *Chemistry of Winemaking,* American Chemical Society, Washington, DC, 137, 1974.) It is clearly seen from the figure that the ethyl alcohol content (proof strength) increases with the plate number (as we go up), amyls content is higher at the bottom. The lines are empirical (polynomial) models. It is stated in the original reference that the product is taken between the 11th and 12th trays. Tray number 15 represents the overheads.

MATLAB® CODE E.4.42.b

Command Window:

```
clear all
close all

% enter the data
EthylAlcohol=[0:10:100]; % volume percent
IsoAmyl=[20 15 9.1 4.4 2.2 1.4 0.87 0.59 0.37 0.25 0.17]; %
volatility
IsoButyl=[20 15 9.1 7.2 3.6 2.2 1.4 1.2 0.7 0.58 0.39]; % volatility
Propyl=[18 12 7.1 4.4 3.1 2 1.6 1.2 0.84 0.68 0.62]; % volatility
Proofs=2.*EthylAlcohol; % convert the ethyl alcohol percentages into
proofs

% plot the data
semilogy(Proofs,IsoAmyl, '*', Proofs,IsoButyl, 'o', Proofs,Propyl,
's'); hold on
ylim([0.1 40]);
xlabel('Ethyl Alcohol (proof)')
ylabel('Volatility (y/x)')
```

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```
%  fit a polynomial empirical model to the data
N=2; % determine N by trial and error to obtain good agreement
between model & data

c1 = polyfit(Proofs,log( IsoAmyl),N);
IsoAmylModel=polyval(c1,Proofs);
semilogy(Proofs,exp(IsoAmylModel),'-'); hold on;

c2 = polyfit(Proofs, log(IsoButyl),N);
IsoButylModel=polyval(c2,Proofs);
semilogy(Proofs,exp(IsoButylModel),':'); hold on;

c3 = polyfit(Proofs, log(Propyl),N);
PropylModel=polyval(c3,Proofs);
semilogy(Proofs,exp(PropylModel),'--'); hold on;

legend('iso-amyl data','iso-butyl data',' propyl data', 'iso-amyl
model','iso-butyl model',' propyl model','Location','SouthWest')
```

When we run the code Figure E.4.42.3 will appear in the screen:

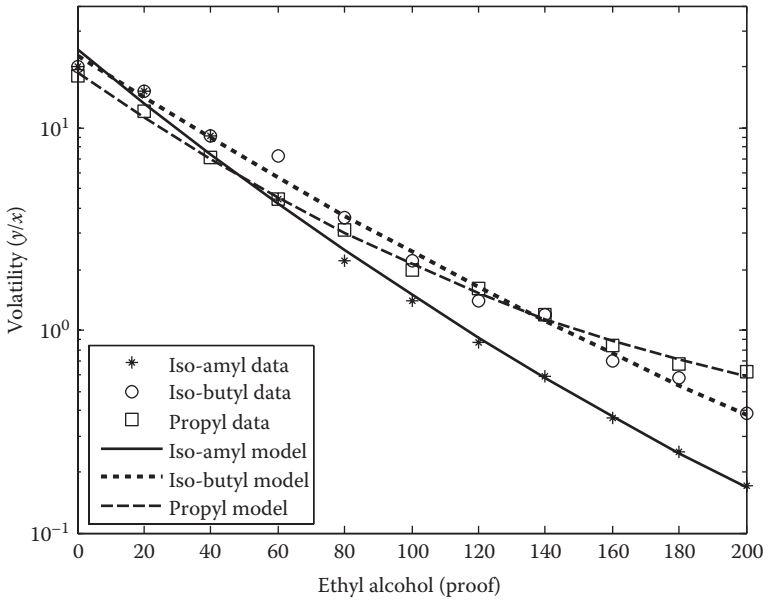


FIGURE E.4.42.3
Variation of the volatility ratio with the percentage of the ethyl alcohol. (Data, shown with markers, were adapted from Guymon, J. F., *Chemistry of Winemaking,* American Chemical Society, Washington, DC, 137, 1974.) The lines are empirical (polynomial) models.

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Questions for Discussion and Problems

A. Thermal Process Problems

1. Although the Ball's formula method does not have strong theoretical basis, it is preferred over the perfect conduction and perfect convection models in practice. Why?

B. Transport Phenomena Problems for the Processes Involving Phase Change

1. Drying rate of a food is

$$R_c = 0.1 \text{ when } 0.7 \le x \le 0.25$$

$$R_{f1} = 0.056 + 0.1x + 0.3x^2 \text{ when } 0.25 \le x \le 0.10$$

$$R_{f2} = 0.016 + 0.5x + 0.4x^2 \text{ when } 0.10 \le x \le 0.03$$

where R_c, R_{f1}, and R_{f2} are the rate in the constant, first falling, and the second falling rate periods, respectively (kg H_2O/kg dry solids h m^2); x is the free moisture content of the food (kg H_2O/kg dry solids). Compute the drying time required to reduce the moisture content from $x_0 = 0.65$ to $x_f = 0.05$.

2. Variation of the drying rate of a solid food with moisture content is described in Figure Q.4.B.2:

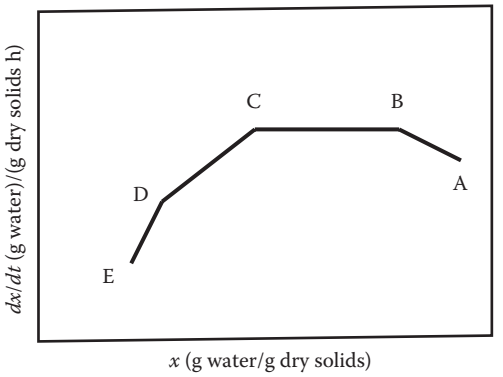


FIGURE Q.4.B.2
Variation of the drying rate of a solid food with moisture content.

What happens at each stage of drying? Explain in terms of the surface moisture content, surface temperature, temperature at the depths of the solids, location of the water front, and the phase of the diffusing water.

3. Infinite slab cookies are baked in a constant temperature oven. Suggest a simplified form of the equation of continuity to describe the drying behavior of a single cookie. Under what conditions is the solution to this equation:

$$\frac{x - x^*}{x_0 - x^*} = \frac{8}{\pi^2} \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \exp\left[\frac{(2n+1)^2 \pi^2}{4} \frac{Dt}{L^2}\right].$$

Simplify the given solution after assuming that one term approximation. Under what conditions is this approximation valid? Assume that D/L^2 is a constant and describe an experimental procedure to calculate the apparent diffusivity. Why do we prefer to use the term "apparent diffusivity"?

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C. Crystallization Kinetics Problems

1. Explain how nuclei are formed at the molecular level? Why larger crystals tend to get larger when crystals with a size distribution range are stored in the solution for a long time?

D. Unit Operations Problems

1. Evaporation, membrane filtration, and crystallization may be used to concentrate the same product. Explain the benefit and disadvantages of each process.
2. 300,000 kg of tomato paste ($x = 0.30$) will be produced in a double effect evaporator.
   i. Determine how many tomatoes ($x = 0.85$) are needed.
   ii. How much water will be removed?
   iii. The total temperature drop in the steam side for the entire process is $\Sigma T = 40°C$. If the overall heat transfer coefficients for each evaporator is $U_1 = 3000$ W/m^{2}K, $U_2 = 1000$ W/m^{2}K, predict the average temperature driving force in each evaporator ($\Delta T_1 = ?$, $\Delta T_2 = ?$).
   iv. Determine the heat transfer areas of the evaporators.
   v. Amount of the steam to be supplied to the process.
   vi. You may obtain all the missing data from the related examples.
3. In a triple effect evaporator system, the total temperature drop in the steam side for the entire process is $\Sigma\Delta T = 65.97°C$. If the overall heat transfer coefficients for each evaporator is $U_1 = 3123$ W/m^{2}K, $U_2 = 1987$ W/m^{2}K, $U_3 = 1136$ W/m^{2}K, predict the average temperature driving force in each evaporator ($\Delta T_1 = ?$, $\Delta T_2 = ?$,$\Delta T_3 = ?$).
4. An ultrafiltration system has a membrane area of 0.75 m^2 and permeability of water through the membrane is 180 kg water/h m^2.
   i. How much water will be removed after 1 hour of operation?
   ii. These systems will be used to concentrate a whey solution from 7 to 25%. How much product will be produced after 1 hour of operation.
   iii. If the concentrate contains 11% lactose, and the feed contains 5.3% lactose, calculate how much lactose is removed with the permeate (liquid passing through the membrane).
5. i. Draw a simple batch distillation equipment. If the initial amount of a fermentation product to be distilled is L_0, and the initial ethanol content is x_0, make the mass balance to calculate the amount of ethanol leaving the fermentation product after a portion shown with ΔL is distilled off. You may assume that the equilibrium relation between the ethanol concentrations in vapor (y) and liquid (x) phases is related with $K = y/x$ where K is a constant.
   ii. If the relative volatility of water and ethanol can be shown as

$$\alpha_{\text{ethanol/water}} = \frac{y_{\text{ethanol}}/x_{\text{ethanol}}}{y_{\text{water}}/x_{\text{water}}},$$

   explain the degree of difficulty in the separation of ethanol and water depending on the values of the relative volatilities.
   iii. If there are two other components, A and B, in the mixture with $\alpha_{A/\text{water}} = \alpha_{\text{ethanol/water}}$ and $\alpha_{B/\text{water}} >> \alpha_{\text{ethanol/water}}$, explain how A and B will appear in the distillate in relation with ethanol (together or at different times, etc.).
   iv. If the distilled product is an alcoholic drink, why will the taste of the distilled product collected between 10 and 15 minutes of distillation be different than the one collected between 20 and 30 minutes of distillation?

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5

Statistical Process Analysis and Quality Control

5.1 Statistical Quality Control

The application of the statistical techniques to maintain the desired quality level during all stages of production or storage is called *statistical quality control*. The quality of the commodities may be evaluated after comparing the measurements or attributes of the quality factor with the desired standard. If their difference is greater than the *tolerable limits* than the process inputs are readjusted to decrease or eliminate the difference. This is called the *closed-loop feed-back control* (Figure 5.1).

Usually a process is divided into stages and the principles of statistical quality control are applied to the individual stages separately. The raw materials, intermediary, or the final products are not permitted to pass to the next stage if they fail to satisfy the prespecified quality standards. The *stagewise quality control* scheme helps to maintain the desired quality level at all levels of the process, and makes it possible to react rapidly if anything is going wrong. Corrective actions, including reprocessing, may be applied on the rejected items. If it is not possible to correct the cause of the rejection these commodities may be discarded.

Example 5.1: Stagewise Quality Control in Winemaking

Stagewise quality control practiced in a winery (Figure E.5.1) may include the following steps:

i. The variety of the grapes is confirmed. Their maturity, sugar, mildew, rot and foreign matter levels, pesticide residue, color, and firmness are checked while receiving the raw material. Grapes must be picked early in the morning and rushed to the winery. The temperature of the grapes is an indicator of the time they are picked. If these requirements are not satisfied the grapes are rejected.
ii. The sanitary situation, condition of the fly proof screens, and an addition of SO_2 is monitored timely in the crushing area to prevent *Acetobacter* infections. The yeast inoculum should be checked frequently for purity. Temperature and proper circulation of the fermentation medium should also be checked. New wine should be removed as soon as possible after fermentation lees settle. Microbial growth and sugar consumption should be checked against standard curves to prevent unusual fermentation. If these requirements are not satisfied corrective actions must be taken to prevent quality loss.
iii. Wine tanks must be checked for unusual oxygen entry or heating. Visual and taste inspections, malic acid, and lactic acid measurements should be done. Volatile acidity, SO_2, alcohol, pH, and total acidity are monitored. Organoleptic analyses are made to obtain the right blends. The sanitary condition of the equipment, temperature, and the volume

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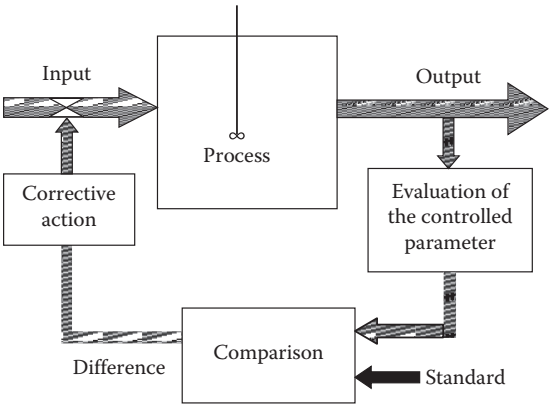


FIGURE 5.1
Feedback control in a closed-loop. Evaluation of the controlled parameter may be based on measured property or attributes (without measurement by visual observation, etc.).

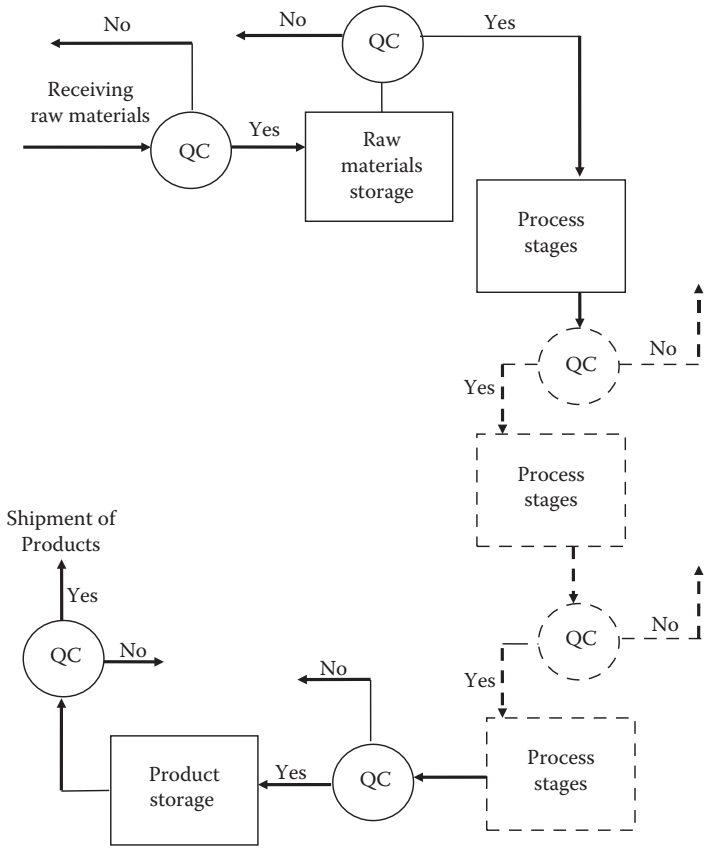


FIGURE E.5.1
A simple flow diagram of the wine making process. Feedback control is applied after every stage. It is not permitted to go to the next stage, if the commodities fail to pass (denoted as NO) the QC tests. Any rejected product may either be processed again or discarded. Crushing, fermentation, aging, and bottling are among the processing stages.

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and composition of the head space of the storage tanks are also monitored. If any of these requirements are not satisfied corrective actions are taken to prevent quality loss.

iv. The right packaging material should be used. The bottling room and the bottles should be clean. Input and output of the filters are continuously sampled and microbiological analyses are made.

v. In the warehousing and shipment stage precautions should be taken not to confuse different wines. Temperature and humidity of the warehouse is monitored. Cork finish bottles are stored with the cork pointed down to prevent drying of the cork. Wine should be handled delicately by the fork lift operators to prevent physical damaging. Stock rotation and chronology of bottling date should be carefully controlled. The loading practices are controlled and the follow-up information to distributors is carefully analyzed. An interested reader may refer to Peterson (1974) for a detailed process flow diagram or Christaki and Tzia (2002) for a detailed description of quality and safety assurance in wine making.

Total quality management of a food plant is achieved in three levels: Quality control by line employees, assurance by midmanagement to be certain that the control job is done effectively, and improvement of safer and more effective new procedures by top management. Procedures of quality control and product safety are integrated with the production process. The statistical techniques explained in Chapter 5 are usually applied by the line employees. Implementation of the quality control in the food industry is subject to numerous international and national standards in all countries.

5.2 Statistical Process Analysis

Quality control may be done via measuring the quality factors, or on the basis of the more practical judgments not involving measurements. Data may be collected manually, mechanically, or may involve acquisition of electrical signals. Sensors convert measurable physical phenomenon into digital electric signals. The signal may be amplified or may require filtering. Data acquisition hardware interfaces between the signal and a PC. Digital data is displayed, analyzed, and stored on a computer. We will use MATLAB® for data analysis.

A variety of sampling methods can be employed for the acquisition of the data. In *random sampling* each element has equal probability of sampling. Throwing a dice or using a random number generator to determine the items to be sampled are ways of random sampling. *Grab* or *opportunity* sampling is another method of choosing the items randomly. In *systematic sampling* we may select every other *k*th item in a row. Solids, liquids, and gases are usually sampled mechanically by using devices such as grabs, scoops, and so on. There are many analytical techniques available for the measurement of the quality parameters. Spectroscopic analysis measures the interaction of the material with electromagnetic radiation. Electrochemical and gravimetric analysis measures the interaction of the material with electric and gravitational field, respectively.

The major statistical distribution models commonly used in the food industry are depicted in Table 5.1. A typical bar chart to visualize variation of the cell size distribution of the log (cell area) of the corn extrudates is shown in Figure E.5.2.1; cell size distribution of the ice crystals in meat tissue during storage are depicted in Figure E.4.31.1. In an infinite data set, if the variations in the measured quantity x are random, the distribution of the values of x around the population mean μ may be described with a normal (Gaussian)

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TABLE 5.1

Statistical Distribution Models Commonly Used in Food and Bioprocess Engineering Analysis

Normal (Gaussian) distribution

Probability (relative frequency) $f(\mu,\sigma)$ of obtaining the measurement x from a population with mean μ and standard deviation σ

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left\{-\frac{1}{2}\left(\frac{x-\mu}{\sigma}\right)^2\right\} \tag{5.1}$$

where

$$f = \frac{\text{group} \times \text{frequency}}{\text{total} \times \text{number} \times \text{of} \times \text{data} \times \text{points}} \tag{5.2}$$

MATLAB® function: `f = normpdf(x,mu,sigma)`

Binomial distribution

Probability $f(x,n,p)$ of getting x failures in n trials from a population where the overall probability of failure is p

$$f(x,n,p) = \frac{n!}{x!(n-x)!} p^x (1-p)^{(n-x)} \tag{5.3}$$

The mean and the standard deviation:

$$\mu = np \tag{5.4}$$

$$\sigma = \sqrt{np(1-p)} \tag{5.5}$$

MATLAB function: `f = binopdf(x,n,p)`

Poisson distribution

Probability $f(x,\lambda)$ of getting x failures in n trials from a population where the overall probability of failure is p

$$f(x,\lambda) = e^{-\lambda} \frac{\lambda^x}{x!} \tag{5.6}$$

where

$$\lambda = np \tag{5.7}$$

The mean and the standard deviation:

$$\mu = \lambda \tag{5.8}$$

$$\sigma = \sqrt{\lambda} \tag{5.9}$$

MATLAB function: `f = poisspdf(x,lambda)`

distribution model (Equation 5.1 in Table 5.1). Major properties of the normal distribution curve are depicted in Table 5.2.

We may classify the apples according to their size after measuring them individually, or we may role them over a slanted surface with holes, such that the apples smaller than a certain diameter pass through, but the larger ones are retained. In such analysis, if the apples smaller than the hole size are detrimental, they may be classified as the non-confirming units (failure) while the ones retained on the screen are called the confirming ones (success). In some cases using visual observations may be more practical and less costly than measuring the quality aspects. We may use binomial or Poisson distribution models when

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TABLE 5.2

Common Statistical Terms Used to Describe a Normally Distributed Data Set

Size of the data sets	A data set is considered a population when it is large enough for sufficient representation of an actual population. In practical applications a large data set consisting of 100 or more measurements ($n \geq 100$) may be treated as a population. When $30 \leq n \leq 100$, the data set may be considered as a large sample. A data set with $n \leq 30$ is referred to as a small sample (LaMont et al. 1977). MATLAB® function: `a = length(x)`
Median	When the data set is written in an order of increasing measurements, the reading or observation above or below that equal the number of observations fall (with a data set including an even number of measurements the two measurements above or below that equal the number of observations fall are averaged to calculate the median). MATLAB function: a=median(x)
Mode	Value that occurs most frequently (the longest bar in the bar chart) MATLAB function: a=mode(x)
range	Difference between the largest and the smallest observations MATLAB function: a=range(x)
Sample mean (average)	$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i \quad (5.10)$$ MATLAB function: a=mean(x)
Population mean	$$\mu = \frac{1}{n}\sum_{i=1}^{n} x_i \quad (5.11)$$ (n represents the whole population) MATLAB function: a=mean(x)
Population standard deviation (σ)	Measure of the scatter of the data around the population mean MATLAB function : s=std(x)
Sample standard deviation (s)	Measure of the scatter of the data around the sample mean MATLAB function : s = std(x,1)
Population variance (σ^2)	$$s^2 = \frac{1}{n}\sum_{i=1}^{n} (x_i - \mu)^2 \quad (5.12)$$ MATLAB function : a=var(x)
Sample variance (s^2)	$$s^2 = \frac{1}{n-1}\sum_{i=1}^{n} \cdot (x_i - \bar{x})^2 \quad (5.13)$$ or $$s^2 = \frac{1}{n-1}\left\{\sum_{i=1}^{n} x_i^2 - \frac{1}{n}\left(\sum_{i=1}^{n} x_i\right)^2\right\} \quad (5.14)$$ MATLAB function : a=var(x,1)
Population variance of the sample means	$$\sigma_{\bar{x}} = \frac{\sigma}{\sqrt{n}} \quad (5.15)$$
Variance of the sample means	$$s_{\bar{x}} = \frac{s}{\sqrt{n}} \quad (5.16)$$

(*Continued*)

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TABLE 5.2 (CONTINUED)

Common Statistical Terms Used to Describe a Normally Distributed Data Set

Skewness

$$\text{skewness} = \frac{1}{n}(\sigma^{-3})\sum_{i=1}^{n}(x_i - \mu)^3 \tag{5.17}$$

MATLAB function: a=skewness(x)

Kurtosis

$$\text{kurtosis} = \frac{1}{n}(\sigma^{-4})\sum_{i=1}^{n}(x_i - \mu)^4 \tag{5.18}$$

MATLAB function: a=kurtosis(x)

Mean of the added properties

$$\mu = \sum_{i=1}^{k}\mu_i, \tag{5.19}$$

where μ_i = population mean of the ith added property,

$$\mu = \sum_{i=1}^{k}\omega_i\mu_i, \tag{5.20}$$

where

$$\omega_i = (n_i)\left(\sum_{j=1}^{k} n_j\right)^{-1}. \tag{5.21}$$

MATLAB function: a=wmean(x,w)

Variance of the added properties

$$\sigma^2 = \sum_{i=1}^{k}\sigma_i^2, \tag{5.22}$$

where σ_i = population standard deviation of the ith added property,

$$\sigma^2 = \sum_{i=1}^{k}\omega_i\sigma_i^2. \tag{5.23}$$

Notes: In the following MATLAB functions a = function(x) or a = function (x,w), a represents the value returned by the function, x describes the data set, w describes the weights of elements of x; example: w(1) is the weight of x(1).

we determine the quality attributes on the basis of the counts or fractions of the confirming or nonconfirming units (Table 5.1).

In order to use the binomial distribution model, analysis should be done with a constant sample size n, we must have two possible outcomes of an observation either as confirming or nonconfirming. There should be a constant probability of each outcome. If we know that a process produces 0.1% defective chocolate bars, this constant probability level is $p = .001$. If $p = .5$ binomial distribution curve is symmetrical, for the other values of p it is skew. For a large number of observations (i.e., $np \geq 10$), the binomial distribution curve approaches the normal distribution curve then the properties of the normal distribution may be applied to the binomial distribution. Binomial distribution is not practical to use with large data sets. Poisson distribution is a good approximation of the binomial distribution to analyze large data sets with rare defects, especially when $n \geq 20$ and $p \leq 0.05$ or $n \geq 100$ and $np \leq 10$. For large values of λ, the Poisson distribution curve approaches the normal distribution curve then the properties of the normal distribution may be applied to the Poisson distribution.

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TABLE 5.3

Confidence Limits

Confidence limits of μ with normal distribution (σ is available, p = 0.9973)	$\bar{x} - 3\sigma_{\bar{x}} \le \mu \le \bar{x} + 3\sigma_{\bar{x}}$	(5.24)
	MATLAB® Version: [mu,sigma,muCI,sigmaCI] = normfit(x,alpha) returns estimates of μ, σ and their confidence intervals with 100*(1-alpha)% probability	
Confidence limits of μ with normal distribution (σ is not available, p = 0.9973)	$\bar{x} - 3\frac{s}{\sqrt{n}} \le \mu \le \bar{x} + 3\frac{s}{\sqrt{n}}$	(5.25)
Confidence limits of μ with normal distribution (variable p, σ is not known)	$\bar{x} - t\frac{s}{\sqrt{n}} \le \mu \le \bar{x} + t\frac{s}{\sqrt{n}}$	(5.26)
	where $t = \frac{\bar{x} - \mu}{s/\sqrt{n}}$	(5.27)
Confidence limits with binomial distribution (p = 0.9973)	$np - 3\sqrt{np(1-p)} \le (np)_{\exp} \le np + 3\sqrt{np(1-p)}$	(5.28)
	MATLAB Version: `[p,pCI] = binofit(x,n,alpha)` returns estimates of p and its confidence limits with 100*(1-alpha)% probability	
Confidence limits with Poisson distribution (p = 0.9973)	$np - 3\sqrt{\lambda} \le (np)_{\exp} \le np + 3\sqrt{\lambda}$	(5.29)
	MATLAB Version: `[lambda,lambdaCI]=poissfit(x,alpha)` returns estimates of lambda and its confidence limits with 100*(1-alpha)% probability	
Confidence limits of σ^2 with $p = \gamma - \beta$	$\frac{s^2\nu}{\chi^2_{\beta}} \le \sigma^2 \le \frac{s^2\nu}{\chi^2_{\gamma}}$	(5.30)
	where $\chi^2 = \frac{(n-1)s^2}{\sigma^2}$	(5.31)

The distribution models may be used to find the confidence limits of a statistical parameter (Table 5.3) or to test the validity of hypothesis (Table 5.4).

Example 5.2: Cell Size Distribution in Corn Extrudates

Nonnormal distributions may be converted into (reasonably) normal distribution after appropriate transformation. Barrett and Peleg (1991) transformed x into $\zeta = \log(x)$, where x = cell area, while studying the cell size distribution in the corn extrudates. The cell size area distribution data may be modeled as

$$f(\zeta) = \frac{1}{\sigma_\zeta\sqrt{2\pi}}\exp\left\{-\frac{1}{2}\left(\frac{\zeta - \mu}{\sigma_\zeta}\right)^2\right\}, \tag{E.5.2.1}$$

where σ_ζ is the population standard deviation obtained after transformation of the data into a new variable. MATLAB® code E.5.2 prepares a bar chart of the transformed data (Figure E.5.2.1). It also plots the experimental and model cell size distributions frequencies (Figure E.5.2.2).

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TABLE 5.4

Statistical Tests

Sample mean $\bar{x}_A$ is obtained from a normally distributed population. Check if μ_A = a specific value? Population standard deviation σ_A is known

$$\mu - z_{1-\alpha/2}\frac{\sigma}{\sqrt{n}} \le \bar{x} \le \mu + z_{1-\alpha/2}\frac{\sigma}{\sqrt{n}} \tag{5.32}$$

where

$$z = \frac{x-\mu}{\sigma} \tag{5.33}$$

MATLAB® Version:
H=ztest(x,mu,sigma) performs a *z*-test. H=1 indicates that with 95 % probability x comes from a normally distributed population described with μ and σ. H=0 indicates the opposite.

Sample mean $\bar{x}_A$ is obtained from a normally distributed population. Checkif μ_A = a specific value? Population standard deviation σ_A is not known

$$\mu - t_{1-\alpha/2}\frac{s}{\sqrt{n_A}} \le \bar{x}_A \le \mu + t_{1-\alpha/2}\frac{s}{\sqrt{n_A}} \tag{5.34}$$

Sample means $\bar{x}_A$ and are obtained from normally distributed populations. Check if $\mu_A = \mu_B$? Values of σ_A and σ_B are available

$$-z_{1-a/2}\left(\frac{\sigma_A^2}{n_A}+\frac{\sigma_B^2}{n_B}\right)^{1/2} \le \bar{x}_A - \bar{x}_B \le z_{1-a/2}\left(\frac{\sigma_A^2}{n_A}+\frac{\sigma_B^2}{n_B}\right)^{1/2} \tag{5.35}$$

where

$$z = \frac{\bar{x}_A - \bar{x}_B}{\left(\frac{\sigma_A^2}{n_A}+\frac{\sigma_B^2}{n_B}\right)^{1/2}} \tag{5.36}$$

MATLAB Version:
`[H,p,CI] = ttest(x,y,alpha)` returns a 100*(1–α)% confidence interval (CI) on μ_A-μ_B. H=0 means μ_A-μ_B with the returned probability p. Notice length(x) should be the same as length(y)

Sample means $\bar{x}_A$ and $\bar{x}_B$ are obtained from normally distributed populations. Check if $\mu_A = \mu_B$? It is assumed that $\sigma_A = \sigma_B$, but their values are not available

$$-t_{1-a/2}s_p\left(\frac{1}{n_A}+\frac{1}{n_B}\right)^{1/2} \le \bar{x}_A - \bar{x}_B \le t_{1-a/2}s_p\left(\frac{1}{n_A}+\frac{1}{n_B}\right)^{1/2} \tag{5.37}$$

where

$$s_p^2 = \left(\nu_A s_A^2 + \nu_B s_B^2\right)/\left(\nu_A + \nu_B\right) \tag{5.38}$$

s_p = pooled variance (degrees of freedom $\nu = \nu_A + \nu_B$)
s_A = sample variance of the data set A (degrees of freedom of ν_A)
s_B = sample variance of the data set B (degrees of freedom of ν_B)

$$t = \frac{\bar{x}_A - \bar{x}_B}{s_p\left(\frac{1}{n_A}-\frac{1}{n_B}\right)} \tag{5.39}$$

Is the data set distributed normally?

$$-\frac{7.35}{\sqrt{N}} \le \text{skewness} \le \frac{7.35}{\sqrt{N}} \tag{5.40}$$

$$3-\frac{14.7}{\sqrt{N}} \le \text{kurtosis} \le 3+\frac{14.7}{\sqrt{N}} \tag{5.41}$$

where N = total number of data points in the set

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TABLE 5.4 (CONTINUED)

Statistical Tests

Check if the assumed distribution model is correct

$$\chi^2_{\text{observed}} \le \chi^2_{\text{Table}} \tag{5.42}$$

where

$$\chi^2_{\text{observed}} = \sum_{i=1}^{n}\left(\frac{f_o - f_e}{f_e}\right)^2 \tag{5.43}$$

where
f_o = observed frequencies
f_e = frequencies estimated with a distribution model

Check if $\sigma_A = \sigma_B$?

$$\frac{1}{F_{\alpha/2}(\nu_A,\nu_B)} \le (s_A/s_B)^2 \le F_{\alpha/2}(\nu_A,\nu_B) \tag{5.44}$$

where

$$F_{\alpha/2}(\nu_A,\nu_B) = \frac{s_A^2/\sigma_A^2}{s_B^2/\sigma_B^2} \tag{5.45}$$

when $\sigma_A = \sigma_B$, then

$$F(\nu_A,\nu_B) = s_A^2/s_B^2 \tag{5.46}$$

Important property:

$$F_{1-\gamma}(\nu_A,\nu_B) = \frac{1}{F_{\gamma}(\nu_A,\nu_B)} \tag{5.47}$$

MATLAB Version:
H = vartest2(x,y,alpha) performs the F test of the hypothesis that two independent samples, in the vectors x and y, come from normal distributions with the same variance, at the significance level (100*alpha)%. H=1 means that vectors x and y, are not coming from normal distributions with the same variance, H=0 is the opposite.

MATLAB® CODE E.5.2

Command Window:

```
clear all
close all
format compact

% introduce the data
frequency=[0.01 0.05 0.05 0.05 0.16 0.27 0.32 0.27 0.4 0.20 0.04
0.09 0.03];
logCellArea=[-1.4 -0.9 -0.3 0.2 0.8 1.3 1.8 2.2 2.8 3.3 3.8 4.2
4.8];

% prepare a bar chart of the data
bar(frequency);
set(gca, 'xTickLabels',logCellArea)
ylabel('frequency')
xlabel('log(cell area)')
grid on
title('bar chart of the log cell areas')
```

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```
% plot the data
figure
plot(logCellArea, frequency,'o') ; hold on
xlabel('frequency')
ylabel('log(cell area)')
grid on
alpha=0.1; % parameter needed to calculate confidence limits of mu
(muCI) and confidence limits of sigma (sigmaCI) with probability of
100*(1-alpha) %

% fit normal distribution model
[mu,sigma,muCI,sigmaCI] = normfit(logCellArea,alpha)

% compute the model frequencies
fModel = normpdf(logCellArea,mu,sigma)
% plot the model
plot(logCellArea, fModel,'-') ; hold on
```

When we run the code the following lines and Figures E.5.2.1 and E.5.2.2 will appear on the screen:

```
mu =
    1.7385
sigma =
    1.9973
muCI =
    0.7512
    2.7258
sigmaCI =
    1.5089
    3.0266
fModel =
    0.0581    0.0835    0.1187    0.1485    0.1789    0.1950    0.1996
0.1945    0.1734    0.1471    0.1173    0.0935    0.0617
```

Example 5.3: Probability of Having More than a Limiting Weight of Contents in the Cans

a. What is the probability of having *exactly* six cans with more than 500 g of contents when eight cans are taken randomly from a population where 80% of the whole cans have more than 500 g of contents?

   Solution: The quality factor has been reported on the basis of confirming/nonconfirming units, and the conditions of the problem implies the binomial distribution as $f(x,n,p) = n!/x!(n-x)!p^x(1-p)^{(n-x)}$ (Equation 5.3 in Table 5.1) when $n = 8$, $x = 6$, $p = 0.80$ $f(6,8,0.80) = 0.29$. Exactly six cans will have at least 500 g contents with 29% probability. MATLAB® code E.5.3.a performs the same computations.

b. What is the probability of getting at least six cans with 500 g contents?

   Solution: The total probability of getting six, seven, or eight cans with 500 g contents is

$$f(6,8,0.80)+f(7,8,0.80)+f(8,8,0.80)=0.29+0.34+0.17=80\%.$$

   MATLAB code E.5.3.b shows the details of the computations.

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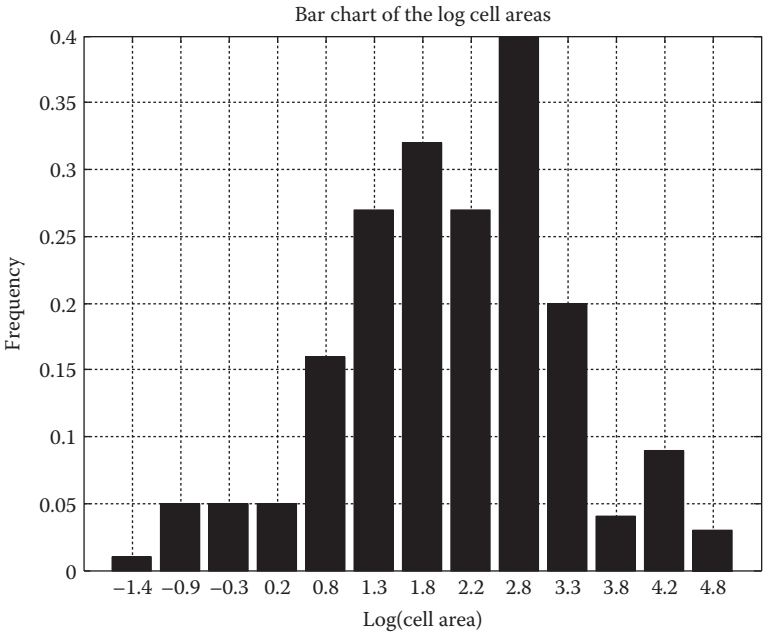


FIGURE E.5.2.1
Bar chart of the frequency of the log (cell area) of the corn extrudates visualizes the distribution. Further analysis, as given in Figure E.5.2.2, are needed for better understanding of the distribution. (Adapted from Barrett, A. M. and Peleg, M., *Journal of Food Science,* 57, 146–48, 154, 1991.)

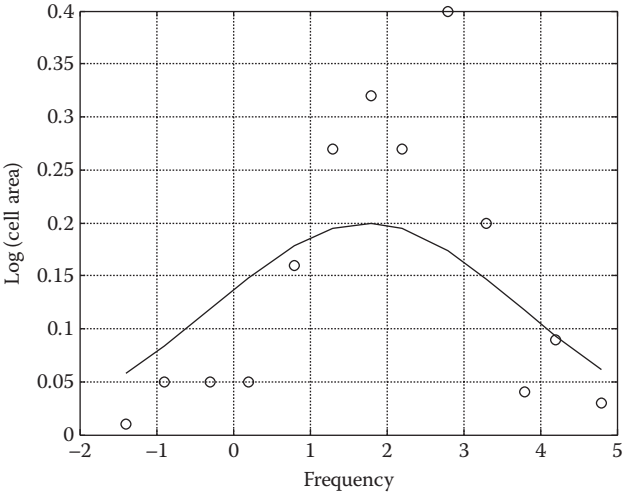


FIGURE E.5.2.2
The model and the experimentally determined distribution frequencies of the log (cell area) of the corn extrudates. The large scatter of the data points around the model is caused by the large confident limits of μ and σ. A data set, which would produce smaller confidence intervals, would represent the data more closely. (Adapted from Barrett, A. M., and Peleg, M., *Journal of Food Science,* 57, 146–48, 154, 1991.)

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MATLAB® CODE E.5.3.a

Command Window:

```
clear all
close all

% input the data
x=6;
n=8;
p=0.8;

% calculate f(x,n,p) with binomial distribution model
sum=0;
sum=binopdf(x,n,p);
sum=sum*100;
fprintf('\nexactly %d cans with have at least 500 g of contents with
%.2g %% probability',x,sum);
```

When we run the code the following line will appear on the screen:

```
exactly 6 cans with have at least 500 g of contents with 29 %
probability
```

MATLAB® CODE E.5.3.b

Command Window:

```
clear all
close all

% input the data
n=8;
p=0.8;

% calculate f(x,n,p) with the binomial distribution model
sum1=0;
for x=6:1:8
sum=binopdf(x,n,p);
sum1=sum1+sum;
end
sum1=sum1*100;
fprintf('\nexactly %d cans will have at least 500 g of contents with
%.2g %% probability',n,sum1);
```

When we run the code the following line will appear on the screen:

```
exactly 8 cans will have at least 500 g of contents with 80 %
probability
```

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Example 5.4: Probability of Having a Certain Fraction of Loss in Fruit Packing

A fruit packing company discards, on the average, 5% of the incoming produce to confirm a standard minimum quality level. In a lot of 120 kg, what is the probability of having about 10 kg of fruits discarded?

Solution: The quality factor has been reported on the basis of confirming/nonconfirming units; and the defect is a rare defect, therefore Poisson distribution may be used. The problem statement implies that $n = 120$, $p = 0.05$, and $x = 10$ after substituting the numbers in Equation 7.7 we will get $\lambda = np = 6$. Equation 5.6 requires that the probability of having 10 kg defectives is

$$f(x,\lambda) = e^{-\lambda}\frac{\lambda^x}{x!} = 0.042 = 4.2\%.$$

The solution is also obtained with MATLAB® code E.5.4.

A normal distribution curve is characterized by the parameters μ and σ. Parameter μ is the mean around the data distributed; parameter σ determines the width of the distribution curve. Distributions of the variables of most natural phenomena are approximately normal. MATLAB code 5.1 gives the plots of two normal distribution curves with the same μ and different σ values (Figure 5.2a and b).

There is a different distribution curve for every pair of distribution described with parameters μ and σ. Standard normal distribution of the x values around μ with standard deviation σ is defined to overcome the difficulties associated with the distribution curves of varying shapes as $z = (x - \mu)/\sigma$. Values of p corresponding to z_p for the normal curve are listed in Table 5.5. The z values listed in Table 5.5 may be computed after running MATLAB code 5.2.

MATLAB® CODE E.5.4

Command Window

```
clear all
close all

% input the data
x=10;
n=120;
p=0.05;
lambda=n*p;

% calculate f(x,lambda) with the Poisson distribution model
f=poisspdf(x,lambda);
PercentDefectives=f*100;
fprintf('\nprobability of having 10 kg of fruit discarded is %.2g
%%',PercentDefectives);
```

When we run the code the following line will appear on the screen:

```
probability of having 10 kg of fruit discarded is 4.1 %
```

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MATLAB® CODE 5.1

Command Window:

```
clear all
close all
global mu sigma  % functions get mu and sigma from the calling
command file

% plot the normal distribution function with same mu and different
sigmas
mu=8; % common mu
sigma=0.3; % sigma1
dx=6*sigma/100;
x=mu-3*sigma : dx : mu+3*sigma;
normal=norm_fcn(x);
plot(x,normal, '-'); hold on
text(mu, 1.35, 'sigma=0.7'), % insert text to the figure (0.6 is the
distance from the bottom)
xlabel('x')
ylabel('Probability')
grid on
sigma=0.7; % sigma2
dx=6*sigma/100;
x=mu-3*sigma : dx : mu+3*sigma;
normal=norm_fcn(x);
plot(x,normal, ':'); hold on
text(mu, 0.6, 'sigma=0.3')

% plot the normal distribution function with different  mu values and
same sigma
figure
sigma=0.6; % sigma
mu=4; %  mu1
dx=6*sigma/100;
x=mu-3*sigma : dx : mu+3*sigma;
normal=norm_fcn(x);
plot(x,normal, '-'); hold on
text(mu, 0.3, 'mu=4'), % insert text to the figure (mu is the
distance from the x axis)
xlabel('x')
ylabel('Probability')
grid on
mu=8; %  mu2
dx=6*sigma/100;
x=mu-3*sigma : dx : mu+3*sigma;
normal=norm_fcn(x);
plot(x,normal, ':'); hold on
text(mu, 0.3, 'mu=8'), % insert text to the figure (mu is the
distance from the x axis)
```

When we run the code Figures 5.2.a and 5.2.b will appear on the screen.

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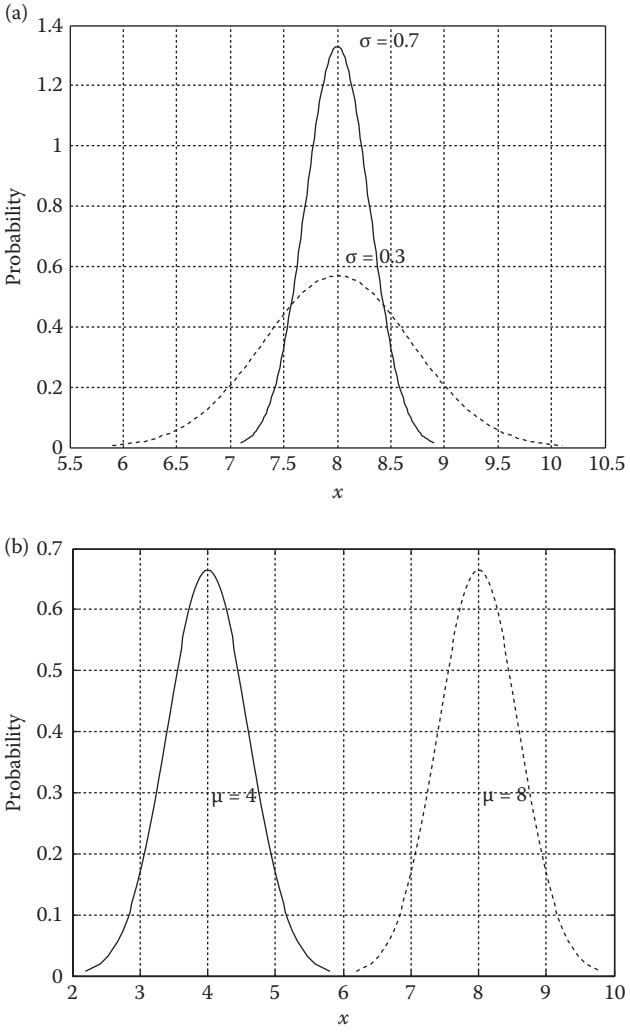


FIGURE 5.2
(a) Plots of normal probability density function with $\mu = 8$, $\sigma_1 = 0.3$ and $\sigma_2 = 0.7$. (b) Plots of normal probability density function with $\mu_1 = 4$, $\mu_2 = 8$, and $\sigma = 0.6$.

In a normal distribution curve 68.26, 95.46, and 99.73% of the total area is enclosed within the limits of $\mu \pm \sigma$, $\mu \pm 2\sigma$ and $\mu \pm 3\sigma$, respectively (Figure 5.4) as depicted by MATLAB code 5.3.

The normality of a data set may be assessed with the skewness or kurtosis tests (Table 5.4; Levinson 1990). The skewness Equation 5.17 measures the symmetry of the data; the kurtosis, Equation 5.18, measures the tendency of the data to have long "tail" regions and a high center. When a population is formed by additive contributions from different sources; that is, weight of a packaged food = weight of the package material + weight of the food; protein content of a food = protein content of the each individual making up the food, and so on, the composite nature of the population should be considered in the statistical analysis. With such a population mean and the variance of the added properties are

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TABLE 5.5

Values of the Normal Distribution Function $F(z) = (1/\sqrt{2\pi})\int_{-\infty}^{z}\exp(-(1/2)\zeta^2)d\zeta$ as Produced by MATLAB® Function p=normcdf(z)

z_p	0.00	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09
0.0	0.5000	0.5040	0.5080	0.5120	0.5160	0.5199	0.5239	0.5279	0.5319	0.5359
0.1	0.5398	0.5438	0.5478	0.5517	0.5557	0.5596	0.5636	0.5675	0.5714	0.5753
0.2	0.5793	0.5832	0.5871	0.5910	0.5948	0.5987	0.6026	0.6064	0.6103	0.6141
0.3	0.6179	0.6217	0.6255	0.6293	0.6331	0.6368	0.6406	0.6443	0.6480	0.6517
0.4	0.6554	0.6591	0.6628	0.6664	0.6700	0.6736	0.6772	0.6808	0.6844	0.6879
0.5	0.6915	0.6950	0.6985	0.7019	0.7054	0.7088	0.7123	0.7157	0.7190	0.7224
0.6	0.7257	0.7291	0.7324	0.7357	0.7389	0.7422	0.7454	0.7486	0.7517	0.7549
0.7	0.7580	0.7611	0.7642	0.7673	0.7704	0.7734	0.7764	0.7794	0.7823	0.7852
0.8	0.7881	0.7910	0.7939	0.7967	0.7995	0.8023	0.8051	0.8078	0.8106	0.8133
0.9	0.8159	0.8186	0.8212	0.8238	0.8264	0.8289	0.8315	0.8340	0.8365	0.8389
1.0	0.8413	0.8438	0.8461	0.8485	0.8508	0.8531	0.8554	0.8577	0.8599	0.8621
1.1	0.8643	0.8665	0.8686	0.8708	0.8729	0.8749	0.8770	0.8790	0.8810	0.8830
1.2	0.8849	0.8869	0.8888	0.8907	0.8925	0.8944	0.8962	0.8980	0.8997	0.9015
1.3	0.9032	0.9049	0.9066	0.9082	0.9091	0.9115	0.9131	0.9147	0.9162	0.9177
1.4	0.9192	0.9207	0.9222	0.9236	0.9251	0.9265	0.9279	0.9292	0.9306	0.9319
1.5	0.9332	0.9345	0.9357	0.9370	0.9382	0.9394	0.9406	0.9418	0.9429	0.9441
1.6	0.9452	0.9463	0.9474	0.9484	0.9495	0.9505	0.9515	0.9525	0.9535	0.9545
1.7	0.9554	0.9564	0.9573	0.9582	0.9591	0.9599	0.9608	0.9616	0.9625	0.9633
1.8	0.9641	0.9649	0.9656	0.9664	0.9671	0.9678	0.9686	0.9693	0.9699	0.9706
1.9	0.9713	0.9719	0.9726	0.9732	0.9738	0.9744	0.9750	0.9756	0.9761	0.9767
2.0	0.9772	0.9778	0.9783	0.9788	0.9793	0.9798	0.9803	0.9808	0.9812	0.9817
2.1	0.9821	0.9826	0.9830	0.9834	0.9838	0.9842	0.9846	0.9850	0.9854	0.9857
2.2	0.9861	0.9864	0.9868	0.9871	0.9875	0.9878	0.9881	0.9884	0.9887	0.9890
2.3	0.9893	0.9896	0.9898	0.9901	0.9904	0.9906	0.9909	0.9911	0.9913	0.9916
2.4	0.9918	0.9920	0.9922	0.9925	0.9927	0.9929	0.9931	0.9932	0.9934	0.9936
2.5	0.9938	0.9940	0.9941	0.9943	0.9945	0.9946	0.9948	0.9949	0.9951	0.9952
2.6	0.9953	0.9955	0.9956	0.9957	0.9959	0.9960	0.9961	0.9962	0.9963	0.9964
2.7	0.9965	0.9966	0.9967	0.9968	0.9969	0.9970	0.9971	0.9972	0.9973	0.9974
2.8	0.9974	0.9975	0.9976	0.9977	0.9977	0.9978	0.9979	0.9979	0.9980	0.9981
2.9	0.9981	0.9982	0.9982	0.9983	0.9984	0.9984	0.9985	0.9985	0.9986	0.9986

calculated with Equations 5.19 through 5.23 (Table 5.2). It should be noticed that these rules are applied while calculating the difference of the population mean and the variance as $\mu_2 = \mu - \mu_1$ and $\sigma_2^2 = \sigma^2 + \sigma_1^2$.

Example 5.5: Fraction of the Total Production Falling Between Given Limits

A fruit juice is produced with a sugar content of $\mu = 8\%$ and $\sigma = 0.5\%$. What percentage of the products contain between 6.7 and 9.15% sugar?

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MATLAB® CODE 5.2

Command Window:

```
clear all
close all

% plot the standard normal probability density curve
z= -5:0.05:5; % range of the standard normal variable
f=normpdf(z);
plot(z,f)
xlabel('z')
ylabel('f(z)')
grid on

figure(2)
z=0:0.1:3; % range of the standard normal variable
p=normcdf(z);  % plot the standard normal variable probability
density curve
plot(z,p)
xlabel('z')
ylabel('cumulative probability density function')
grid on
```

When we run the code Figures 5.3.a and 5.3.b will appear on the screen.

Solution: After using Equation 5.33 we will determine $z_1 = 9.15–8/0.5 = 2.3$, $p_{2.3} = 0.9893$ (Table 5.5) and $z_2 = 6.7–8/0.5 = –2.6$. The probability corresponding to $z = –2.6$ is not given in Table 5.5. The z distribution is symmetrical. The fraction of the area in z distribution curve between $z = –\infty$ and $z = –2.6$ is the same as the area between $z = 2.6$ and $z = \infty$, therefore $p_{–2.6} = 1 – p_{2.6}$ or after substituting the numbers $p_{–2.6} = 1 – 0.9953 = 0.0047$, indicating that 0.47% of the whole production contains less than 6.7% sugar. The required interval of probability is $p(–2.6 \le z \le 2.3) = 0.9893–0.0047 = 0.9846$. Indicating that 98.46% of the total production contains 6.7% to 9.15% sugar. MATLAB® code E.5.5 shows the details of the solution.

Example 5.6: The Maximum Tolerable Standard Deviation

a. Concentration of a certain food additive is required to be 0.2 ±0.02%. If the population mean of the additive concentration in the food is $\mu = 0.2\%$, what should be the standard deviation?

   Solution: Additive contents of the food should be $\mu – 3\sigma \pounds x \pounds \mu + 3\sigma$ ($p = 0.9973$) (Table 5.3), since $\mu = 0.2\%$, the tolerance limits should correspond to $6\sigma = (2)(0.02\%)$, therefore $\sigma = 0.007\%$. The same calculations are also performed with MATLAB® code E.5.6.a.

b. If the additive is added with $\mu = 0.19\%$ and $\sigma = 0.021\%$, what percentage of the foods satisfy the required tolerance limits?

   Solution: Allowed limits of the additive concentration:

$$x_{\text{lower}} = (0.2) – (0.02) = 0.18\% \text{ and } x_{\text{upper}} = (0.2) + (0.02) = 0.22\%.$$

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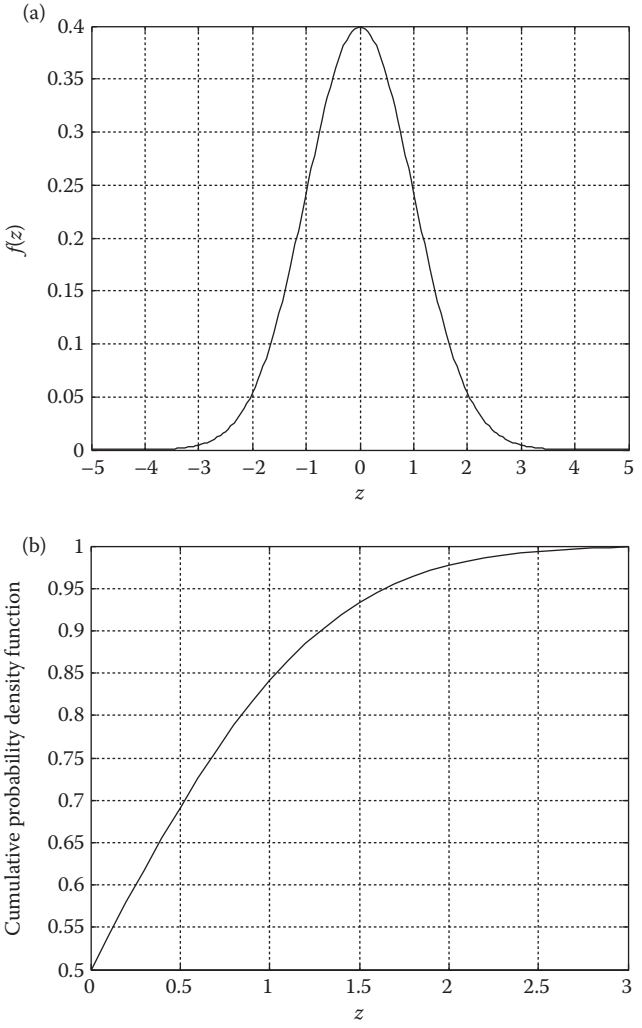


FIGURE 5.3
(a) Probability of occurrences of the standard normal variable at any value of z as described in the horizontal axis. (b) Cumulative probabilities of the standard normal variable. The code that is employed to prepare this figure may also be employed to tabulate the values given in Table 5.5 after some minor modifications.

The z values corresponding to x_{lower} and x_{upper} are

$$z_{lower} = \frac{x_{lower} - \mu}{\sigma} = \frac{0.18 - 0.19}{0.021} = -0.48p - 0.48$$

and

$$z_{lower} = \frac{x_{upper} - \mu}{\sigma} = \frac{0.22 - 0.19}{0.021} = 1.43.$$

A fraction of the production with fewer additives than 0.18% is: $p_{-0.48} = 1 - p_{0.48} = 1 - 0.6844 = 31.56\%$. The fraction of the production with fewer additives than 0.22% is

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MATLAB® CODE 5.3

Command Window:

```
clear all
close all

% compute and plot the fraction of the area remaining outside of the
mu-i*sigma and mu+i*sigma range
mu=0.32
sigma=0.18
alpha=0.05
for i=1:1:3
p = normspec([mu-i*sigma,mu+i*sigma],mu,sigma,'inside')
end
grid on
```

When we run the code three different versions of Figure 5.4 showing the area enclosed between $\mu - i\sigma$ and $\mu + i\sigma$ will appear on the screen.

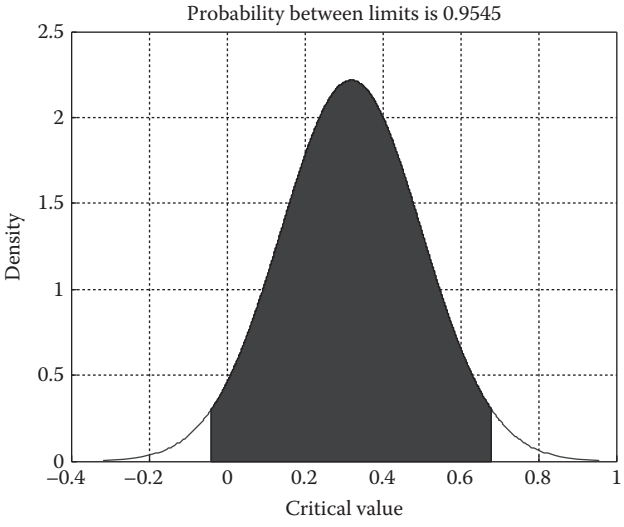


FIGURE 5.4
Area enclosed between $\mu - 2\sigma$ and $\mu + 2\sigma$. Fraction of the area enclosed between $\mu - i\sigma$ and $\mu + i\sigma$ is 0.6827 when $i = 1$, 0.9545 when $i = 2$ and 0.9973 when $i = 3$.

MATLAB® CODE E.5.5

Command Window:

```
clear all
close all

% input the data
xup=9.15;
```

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```
xlow=6.7;
mu=8;
sigma=0.5;

% compute the normal cumulative distribution functions
z1 = normcdf(xup,mu,sigma);
z2 = normcdf(xlow,mu,sigma);
z=(z1-z2);
PercentProduct=z*100; % percentage of the product with 6.7 to 9.15 %
sugar content
% print the results
display(z1);
display(z2);
fprintf('probability of having fruit juice with 6.7 to 9.15 %% sugar
content is %.2f %%',PercentProduct );
```

When we run the code the following lines will appear on the screen:

```
z1 =
    0.9893

z2 =
    0.0047

probability of having fruit juice with 6.7 to 9.15 % sugar content
is 98.46 %
```

MATLAB® CODE E.5.6.a

Command Window:

```
clear all
close all

% input the data
threesigma=0.02;

% compute the standard deviation
sigma=threesigma/3;
fprintf('\n\nThe standart deviation is %.3f %%\n\n',sigma);
```

When we run the code the following line will appear on the screen:

```
The standart deviation is 0.007 %
```

$p_{1.43} = 92.36\%$. Amounts of the products with the allowed amounts of additive = (92.36 – 31.56)% = 60.80%. The same calculations are also performed with MATLAB code E.5.6.b.

c. If only 3% of the product is permitted to contain less than 0.2% additive, $\sigma = 0.02\%$, and no upper limit is specified what should be the population mean additive concentration?

Solution: $p = 0.03$, $x = 0.2\%$, Equation 5.33 requires $z_{0.03} = (0.2 - \mu)/0.02$. The value of $z_{0.03}$ is not given in Table 5.5; therefore, we should read $z_{0.97} = 0.8340$, then calculate

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MATLAB® CODE E.5.6.b

Command Window:

```
clear all
close all
format compact

% input the data
xup=0.22;
xlow=0.18;
mu=0.19; % percent
sigma=0.021; % percent
x=0.2; % percent

% compute the normal cumulative distribution functions
mu=0.19;
sigma=0.021;
z1 = normcdf(xlow,mu,sigma);
z2 = normcdf(xup,mu,sigma);
z=z2-z1;
display(z1);
display(z2);
fprintf('probability of having additive content between %.2f to %.2f
%% is %.3f\n', xlow,xup,z );
```

When we run the code the following lines will appear on the screen:

```
z1 =
    0.3170

z2 =
    0.9234

probability of having additive content between 0.18 to 0.22 % is
0.606
```

$z_{0.03} = -z_{0.97} = -0.8340$. After substituting the value of $z_{0.03}$ in Equation 5.33, we will calculate $\mu = 0.217\%$. The same calculations are also performed with MATLAB code E.5.6.c.

Example 5.7: Probability of Having a Sample Mean Smaller than a Given Value

A margarine packaging machine was adjusted to pack 125 g of margarine ($\mu = 125$ g) with $\sigma = 5$ g. What is the probability of having less than 122 g of a sample mean with a sample of 25 packages?

Solution: A population standard deviation is available, therefore we will use the z values in the test. The standard normal deviate was defined as

$$z = \frac{x - \mu}{\sigma}. \tag{5.33}$$

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MATLAB® CODE E.5.6.c

Command Window:

```
clear all
close all

% input the data
x=0.2;
sigma=0.021;
z3=-normcdf(0.97); % z(0.03)=z(0.97)

% compute the population mean
mu=x-sigma*z3;
fprintf('\npopulation mean additive concentration is %.3f %%\n', mu
);
```

When we run the code the following line will appear on the screen:

```
population mean additive concentration is 0.218 %
```

Since the distribution of the sample mean around the population mean follows the normal behavior, the same expression may be stated for the distribution of the sample mean as $z = \bar{x} - \mu/\sigma_{\bar{x}}$ after substituting the numerical values

$$z = \frac{122-125}{5/\sqrt{25}} = -3.$$

The probability corresponding $z = 3$ is $p_{-3} = 1 - p_{+3} = 1 - 0.9987 = 0.0013$ (Table 5.5). Therefore the probability of having less than 122 g of a sample mean with a sample of 25 packages is 0.13%. The same calculations are also performed with MATLAB® code E.5.7.

Example 5.8: Use of the Standard Normal Variable Due to the Similarity of Poisson and Gaussian Distribution Curves

If 5% of a packaged product is known to be underweight, what is the probability that a random sample of 100 packages will contain 7 or more underweight packages?

Solution: It is given in the problem statement that $p = 0.05$, $n = 100$, and $\lambda = \mu = np = 5$. Since $\lambda < 10$, $n \geq 100$, and p = constant we may use the Poisson distribution with $\sigma = \sqrt{\lambda} = \sqrt{5}$. Similarity of Poisson and Gaussian distribution curves allows us to use the standard normal variable $z = (x - \mu)/\sigma = (7 - 5)/\sqrt{5} = 0.89$. Probability of having 7 or less underweight packages is 81.3% implying that the probability of having 7 or more underweight packages is 100 – 81.3 = 18.7%. The same calculations are also performed with MATLAB® code E.5.8.

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MATLAB® CODE E.5.7

Command Window:

```
clear all
close all

% input the data
xlow=122;
mu=125;
sigma=5;
n=25;

z1=normcdf(122,125,(5/sqrt(n)));
z1=z1*100;
fprintf('probability of having less than 122 g of sample mean with
25 packages is %.2f %%\n',z1 );
```

When we run the code the following line will appear on the screen:

```
probability of having less than 122 g of sample mean with 25
packages is 0.13 %
```

MATLAB® CODE E.5.8

Command Window:

```
clear all
close all

% input the data
x=7;
mu=5;
sigma=sqrt(mu);

% calculate the normal cumulative distribution function
z1=normcdf(x,mu,sigma);
fprintf('probability of having 7 or more underweight packages is =
%.1f %%\n',(1-z1)*100);
```

When we run the code the following line will appear on the screen:

```
probability of having 7 or more underweight packages is = 18.6 %
```

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Example 5.9: Statistical Properties of Broiler Feeds and their Raw Materials

Statistical properties related to the distribution of protein in broiler feed raw materials (rendering meal, meat and bone meal, sorghum, soybean meal, tapioca, corn, wheat) and final products (starter, grower, finisher) are given as (Alti and Özilgen 1994)

Raw Material or Feed	μ (%)	σ (%)	Kurtosis	Skewness	*N*
Rendering meal	55.0	1.7	2.19	–0.05	8
Meat and bone meal	39.4	1.2	2.59	–0.52	16
Sorghum	9.3	0.4	2.72	–0.21	16
Soybean meal	45.7	1.7	3.20	–0.75	76
Tapioca	2.7	0.3	3.83	0.71	22
Corn	7.5	0.6	4.63	0.04	57
Wheat	12.6	0.4	3.53	0.93	28
Starter	23.6	0.8	3.87	–0.56	66
Grower	21.6	0.9	4.28	–0.24	95
Finisher	20.4	0.9	5.12	–0.94	110

A simple test as described in Table 5.4 says that a data set is distributed normally if its skewness and kurtosis are within the following limits:

$$-\frac{7.35}{\sqrt{N}} \le \text{skewness} \le \frac{7.35}{\sqrt{N}}, \tag{5.40}$$

$$3-\frac{14.7}{\sqrt{N}} \le \text{kurtosis} \le 3+\frac{14.7}{\sqrt{N}}, \tag{5.41}$$

where N = total number of the measurements in a data set. MATLAB® code E.5.9 tests the normality of the distribution of proteins in each feed and prints out the result.

MATLAB® CODE E.5.9

Command Window:

```
clear all
close all

% input the data
Rmaterial=['Rendering Meal' 'Meat Bone Meal' 'Sorghum       '
'Soybean Meal  ' 'Tapioca       ' 'Corn          '  'Wheat         '
'Starter       '  'Grower        ' 'Finisher      '];
N=[8 16 16 76 22 57 28 66 95 110]';
mu=[55,39.4,9.3,45.7,2.7,7.5,12.6,23.6,21.6,20.4]';
sigma=[1.7,1.2,0.4,1.7,0.3,0.6,0.4,0.8,0.9,0.9]';
kurtosis=[2.19,2.59,2.72,3.2,3.83,4.63,3.53,3.87,4.28,5.12]';
skewness=[-0.05,-0.52,-0.21,-0.75,0.71,0.04,0.93,-0.56,-0.24,-0.94];

% compute the upper and lower limits
for i=1:1:10
```

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```
kurtlow(i)=3-14.7./sqrt(N(i));
kurthigh(i)=3+14.7./sqrt(N(i));
skwlow(i)=-7.35./sqrt(N(i));
skwhigh(i)=7.35./sqrt(N(i));
end

% perform the test
for i=1:1:10
    if (kurtosis(i)<kurtlow(i) || kurtosis(i) >kurthigh(i))
    fprintf('kurtosis test shows that protein content of %1.14s is
not distributed normally \n', Rmaterial(((i*14-13):(i*14))));
    end
end
for i=1:1:10
    if (skewness(i)<skwlow(i) || skewness(i)>skwhigh(i))
        fprintf('skewness test shows that the protein content of
%1.14s is not distributed normally \n', Rmaterial(((i*14-
13):(i*14))));
    end
end
```

When we run the code the following lines will appear on the screen:

```
kurtosis test shows that protein content of Finisher       are not
distributed normally
skewness test shows that the protein content of Finisher       are
not distributed normally
```

Example 5.10: Estimation of the Population Mean and Variance from those of the Additive Contributing Factors

Population mean and standard deviation of the contents of fruit juice containers is 500 g and 10 g, respectively. There are 24 containers packed in a box. An empty container weighs 30 g with a standard deviation of 2 g. The mean weight of an empty box is 200 g with a standard deviation of 20 g. Find the limits of the weight of a single box filled with juice.

Solution: Equations 5.19 and 5.22 require

$$\mu = \sum_{i=1}^{k} \mu_i = (24)(500) + (24)(30) + 200 = 12{,}920 \text{ g},$$

$$\sigma^2 = \sum_{i=1}^{k} \sigma_i^2 = (24)(10)^2 + (24)(2)^2 + (20)^2 = 2\ 896 \text{ g}, \quad \sigma = 53\text{g}.$$

Limits of x were given in Figure 5.3 as

$$\mu - 3\sigma \le x \le \mu + 3\sigma.$$

After substituting the numbers we will obtain $12,761 \le x \le 13,079$ implying that with $p = 99.73\%$ the weight of the single box filled with juice will be between these limits. The same solution is also obtained with MATLAB® code E.5.10.

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MATLAB® CODE E.5.10

Command Window:

```
clear all
close all

MeanWeights=[500 30 200]; % population mean weights of  juice, container
and box
Sigmas=[10 2 20]; % standard deviations of the weights of  juice,
container and box
Numbers=[24 24 1]; % numbers of  juice, container and box weights
entering in a batch
muFilledBox=sum(MeanWeights.*Numbers);
Variances=Sigmas.^2;
VarianceFilledBox=sum(Variances.*Numbers);
SigmaFilledBox=sqrt(VarianceFilledBox);
muLow=muFilledBox-3*SigmaFilledBox;
muHigh=muFilledBox+3*SigmaFilledBox;

% print the confidence limits of muFilledBox
fprintf('\nconfidence limits of the weight of the filled box:\n')
fprintf('%.2f g < Weight of the Filled Box  < %.2f g\n',muLow,muHigh)
```

When we run the code the following statement will appear on the screen:

```
confidence limits of the weight of the filled box:
12758.56 g < Weight of the Filled Box  < 13081.44 g
```

Example 5.11: Estimation of the Population Mean and Variance from Food Formulation and those of the Contributing Factors

The recipe of a certain food includes three protein-containing ingredients. A fraction of the ingredients in the recipe with their mean and standard deviation of protein contents are

Ingredient	ω_i	μ_i (%)	σ_i^2 (%)
1	0.10	30	6
2	0.15	7	1
3	0.05	6	0.5
Others	0.70	0	0

Determine the confidence limits of the protein contents of the food.

Solution: Equations 5.20 and 5.23 require

$$\mu = \sum_{i=1}^{k} \varpi_i \mu_i = (0.10)(30) + (0.15)(7) + (0.05)(6) + (0.70)(0) = 4.35\%,$$

$$\sigma^2 = \sum_{i=1}^{k} \varpi_i \sigma_i^2 = (0.10)(6) + (0.15)(1) + (0.05)(0.5) + (0.70)(0) = 0.775.$$

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MATLAB® CODE E.5.11

Command Window:

```
clear all
close all
format compact

% enter the data
w=[0.1 0.15 0.05 0.7];
mu=[30 7 6 0];
variance=[6 1 0.5 0];

% compute the population mean, variance and standard deviation
musum=sum(w.*mu);
variancesum=sum(w.*variance);
sigma=sqrt(variancesum);

% compute the confidence limits
xlow=musum-3*sigma;
xhigh=musum+3*sigma;

% print out the confidence limits
fprintf('protein content of a serving will be between %.2f and %.2f
%% \n',xlow,xhigh);
```

When we run the code the following statement will appear on the screen:

```
protein content of a serving will be between 1.71 and 6.99 %
```

Limits of x were given in Figure 5.3 as
$\mu - 3\sigma \le x \le \mu + 3\sigma$,, $1.71(\%) \le x \le 6.99(\%)$ implying that with $p = 99.73\%$, the protein content of a serving will be between these limits.

MATLAB® code E.5.11 gives the details of the computations.

Example 5.12: Additive Property of Population Mean and Variance

A vegetable with 85% population mean and 2% standard deviation of water contents is dried in three successive dryers. The following percentages of the initial moisture content were removed in each dryer:

Dryer	μ_i (%)	σ (%)
1	35	2
2	21	1
3	12	0.5

Calculate the confidence limits of the final moisture contents of the product.

Solution: $\mu = \mu_{\text{initial}} - (\mu_1 + \mu_2 + \mu_3) = 85\% - (35\% + 21\% + 12\%) = 17\%, \sigma^2 = \sigma^2_{\text{initial}} + \sigma_1^2 + \sigma_2^2 + \sigma_3^2 = 0.0004 + 0.0004 + 0.0001 + 2.5 \times 10^{-7} = 9 \times 10^{-4}$, $\sigma = 3\%$. It should be noticed here that although

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MATLAB® CODE E.5.12

Command Window:

```
clear all
close all
format compact

% enter initial population mean and initial variance
mu0=0.85;
sigma0=0.02;
variance0=sigma0^2;

% enter process population means and process variances
mup=[0.35 0.21 0.12];
sigmap=[0.02 0.01 0.005];

% compute mean and variance at the end of the process
sigmapsqr=sigmap.^2;

% compute the sum of the process variances
pvariancesum=sum(sigmapsqr);
variance=variance0+pvariancesum;
mupsum=sum(mup);
mu=(mu0-mupsum)*100
sigma=100*sqrt(variance)

% compute the confidence limits
xlow=mu-3*sigma;
xhigh=mu+3*sigma;

% print the confidence limits
fprintf('water content of the product will be between %.2f and %.2f
%%\n',xlow,xhigh);
```

When we run the code the following statement will appear on the screen:

```
mu =
   17.0000
sigma =
    3.0414
water content of the product will be between 7.88 and 26.12 %
```

the population mean has been subtracted, the variances are added. The limits of the moisture of the product are calculated according to Figure 7.3 as

$$\mu - 3\sigma \le x \le \mu + 3\sigma,\ 8\% \le x\ 26\%(p = 99.73\%).$$

Details of the computations are presented in MATLAB® code E.5.12.

Production of a single commodity usually consists of numerous stages with many control loops involving multiple measurements. In most processes intermediate or finished products pass through these stages at very high rates. When quality assurance is based on

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the individual items, due to the complex nature of this system, extremely large data sets are formed. These large data sets are usually impossible to analyze totally, therefore sampling is made. Each sample is made of different members; therefore, the sample mean shows a range of variation depending on the properties of the original population. The *Central Limit Theorem* states that *regardless of the distribution behavior of the individual values within their own population, distribution of the sample mean will approach the normal distribution as the sample size increases.* In most cases the sample size, *n*, required to achieve an acceptable near normal distribution of the sample mean around the population mean is four or five (Jacobs 1990). The variance of the sample mean decreases with the square root of the sample size (Equation 5.15 in Table 5.2). In a typical normal distribution curve of the sample mean, the area confined between $\mu \pm i\sigma_{\bar{x}}$ or $\mu \pm is_{\bar{x}}$ ($i = 1,2,3$) corresponds to 68.26%, 95.46%, and 99.73% of the total area under the curve when i is 1, 2, and 3, respectively; implying that if a very large number of samples should be drawn from the population, we may expect 68.26% of the sample mean to fall between $\mu \pm \sigma_{\bar{x}}$ or $\mu \pm s_{\bar{x}}$, and so on (Figure 5.5).

When the number of the items in a data set (n) is less than about 30 and values of μ and σ are not known we may drive information from the sample to discuss the properties of the population by using t-distribution. The definition of parameter t is given with Equation 5.27 in Table 5.3. The shape of the t-curves depends on the degrees of freedom of the data set as explained in the output of MATLAB® code 5.4 (Figure 5.5a and b).

MATLAB® CODE 5.4

Command Window:

```
clear all
close all

t= -4:0.04:4; % range of the standard normal variable
nu= [1 5 30]; % degrees of freedom

% plot the t probability density curve
for i=1:3
f=tpdf(t,nu(i));
if i==1; plot(t,f, '-'); hold on; end
if i==2; plot(t,f, ':'); hold on; end
if i==3; plot(t,f, '.-'); hold on; end
end
xlabel('t')
ylabel('f(t)')
grid on
legend('nu=1', 'nu=5', 'nu=30', 'Location','NorthEast')

% plot the cumulative t probability density curve
figure(2)
for i=1:3
t=0:0.1:3; % range of the standard normal variable
p=tcdf(t,nu(i));  % plot the standard normal variable probability
density curve
if i==1; plot(t,p, '-'); hold on; end
if i==2; plot(t,p, ':'); hold on; end
if i==3; plot(t,p, '.-'); hold on; end
```

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```
end
xlabel('t')
ylabel('cumulative probability density of t')
grid on
legend('nu=1', 'nu=5', 'nu=30', 'Location','SouthEast')
```

When we run the code Figure 5.5a and b will appear on the screen.

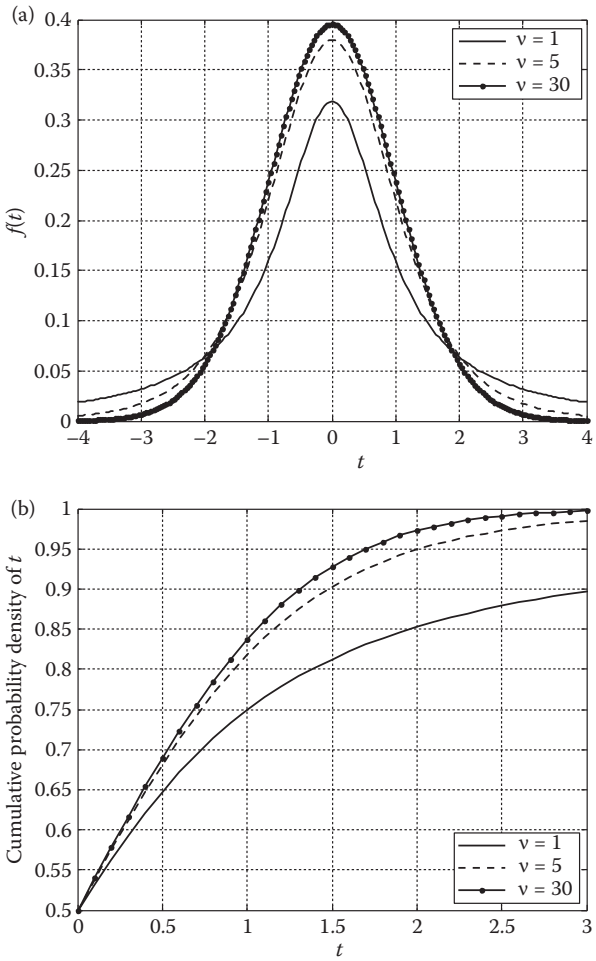


FIGURE 5.5
(a) The *t* distribution curves. (b) The cumulative probability density of the *t* distribution curves.

The probability *p* of having the population mean μ within the limits of $-t$ and $+t$ is listed in Table 5.6. Critical values for the student's *t* test of Table 5.6 are produced after running MATLAB code 5.5.

When the actual value of statistical parameters are not known, we may use statistical techniques (Table 5.3) and estimate the interval where the exact value may fall with a given

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TABLE 5.6

Two-Tailed Critical Student's t Values as produced by MATLAB® Function criticalT=tinv(p,nu)

$\nu\downarrow$ $p\rightarrow$	0.9	0.95	0.975	0.99
1	6.31	12.71	25.45	63.66
2	2.92	4.30	6.20	9.93
3	2.35	3.18	4.18	5.84
4	2.13	2.78	3.50	4.60
5	2.02	2.57	3.16	4.03
6	1.94	2.45	2.97	3.71
7	1.90	2.37	2.84	3.50
8	1.86	2.31	2.75	3.36
9	1.83	2.26	2.69	3.25
10	1.81	2.23	2.63	3.17
11	1.80	2.20	2.59	3.11
12	1.78	2.18	2.56	3.06
13	1.77	2.16	2.53	3.01
14	1.76	2.15	2.51	2.98
15	1.75	2.13	2.49	2.95
16	1.75	2.12	2.47	2.92
17	1.74	2.11	2.46	2.81
18	1.73	2.10	2.45	2.88
19	1.73	2.09	2.43	2.86
20	1.73	2.09	2.42	2.85
21	1.72	2.08	2.41	2.83
22	1.72	2.07	2.41	2.82
23	1.71	2.70	2.40	2.81
24	1.71	2.06	2.39	2.80
25	1.71	2.06	2.39	2.79
26	1.71	2.06	2.38	2.78
27	1.70	2.05	2.37	2.77
28	1.70	2.05	2.37	2.76
29	1.70	2.05	2.36	2.76
30	1.70	2.04	2.36	2.75
∞	1.65	1.96	2.24	2.58

Source: Table 5.6 was originally prepared by Merrington, M., *Biometrika*, 32, 300, 1942. Reproduced with permission from Biometrica trustees.

probability level. The limits of this interval are called the *confidence limits*. When we do not know the population mean and the population variance we may estimate the confidence limits of the population mean with Equation 5.26 and the confidence limits of the population variance with Equation 5.30. Confidence limits are estimated better as the sample size increases. The possibility in having an actual value of the statistical parameter beyond these

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MATLAB® CODE 5.5

Command Window:

```
clear all
close all

alpha=0.01; % values of alpha=[0.10 0.05 0.025 0.01]
nu=1:30;
p=1-alpha/2;
criticalT=tinv(p,nu);
criticalTinv=criticalT'
% substitute nu=1000 and run the code to produce the last number of
the column
```

When we run the code the related column of Table 5.6 will appear on the screen.

limits is only $1 - p$. The following example shows the computation of the confidence limits of the population mean and the population standard deviation from a sample by using the MATLAB® function normfit and the dependence of the confidence limits on the sample size.

Example 5.13: Computation of the Confidence Limits

a. There is 0.05 g/serving of population standard deviation in a sodium-free diet food. Write a MATLAB® code to compute the confidence limits of the population mean salt content. The following salt content of the samples were measured experimentally:

Sample Number	1	2	3	4	5	6	7	8	9	10
x	0.23	0.19	0.24	0.22	0.15	0.18	0.20	0.18	0.21	0.20

What are the confidence limits of the population mean salt content of the food based on this sample?

Details of the solution are presented in MATLAB code E.5.13.a.

b. The sample mean salt content of a sodium-free diet food was detected as 0.10 g/serving after making 25 replicate measurements. There is 0.05 g/serving of population standard deviation due to variations in production. What are the confidence limits of the population mean salt content of the food based on this sample? What would be the confidence limits if the same result had been obtained with a sample size of $n = 10$?

Solution: The sample standard deviation according to Equation 5.15 (Table 5.2) is $\sigma_{\bar{x}} = \sigma/\sqrt{n}$. Since the population standard deviation is known when $p = 0.9973$, the confidence limits are calculated as $\bar{x} - 3\sigma_{\bar{x}} \le \mu \le \bar{x} + 3\sigma_{\bar{x}}$ (Equation 5.24 in Table 5.3). When $n = 25$ $\sigma_{\bar{x}} = 0.01$ and the confidence limits are $0.07 \le \mu \le 0.13$ g. When $n = 10$ $\sigma_{\bar{x}} = 0.016$ and the confidence limits are $0.05 \le \mu \le 0.15$ g. It should be noticed that decreasing the sample size n increases the confidence interval of μ.

c. What should be the sample size if the difference between the confidence limits of μ is required to be less than 0.04 g/serving?

Solution: The difference between the confidence limits of μ is $6\sigma_{\bar{x}}$, therefore $6\sigma_x = (0.04/6) = 0.0067$. After substituting the values of σ and $\sigma_{\bar{x}}$ in Equation 5.15 we will obtain $n = 56$.

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MATLAB® CODE E.5.13.a

Command Window:

```
clear all
close all
format compact
format short g

% enter the data
SampleNumber=[1 2 3 4 5 6 7 8 9 10];
x=[0.23 0.19 0.24 0.22 0.15 0.18 0.20 0.18 0.21 0.20];
alpha= 0.5;

% use the function normfit to compute the confidence limits of mu
and sigma
[xbar,sigma,muLimits,sigmaLimits]=normfit(x,alpha)
```

When we run the code the following lines will appear on the screen:

```
xbar =
          0.2
sigma =
     0.026667
muLimits =
      0.19407
      0.20593
sigmaLimits =
     0.023706
     0.032939
```

MATLAB® CODE E.5.13.b

Command Window:

```
clear all
close all
format compact

% enter the data
mu=0.10; % g/serving
sigmaS=0.05; % sample standard deviation
n=[10 25];

% compute the population standard deviation
N=sqrt(n);
sigmaP=sigmaS./N;

% compute the confidence limits
xHigh=mu+3.*sigmaP;
xLow=mu-3.*sigmaP;
```

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```
% print the confidence limits
for i=1:1:2
fprintf('\nwhen n=  %2.0f salt content of the product will be
between %4.2f and %4.2f g per serving\n',n(i), xLow(i),xHigh(i));
end

% when 6*sigmaP=0.04 g/serving
sigmaP=0.04/6;
xHigh=mu+3.*sigmaP;
xLow=mu-3.*sigmaP;
n=(sigmaS/sigmaP)^2;
fprintf('\nn= %2.0f when xHigh-xLow= 0.04 g/serving\n', n)
```

When we run the code the following lines will appear on the screen:

```
when n=  10 salt content of the product will be between 0.05 and
0.15 g per serving

when n=  25 salt content of the product will be between 0.07 and
0.13 g per serving

n= 56 when xHigh-xLow= 0.04 g/serving
```

MATLAB® code E.5.13.b computes the same results.

We will try to find answers to the questions: *Does the population mean equal a specific number?* or *Are the means of two populations equal?* with hypothesis testing (Table 5.4). The answers to these questions are sought with the hypotheses concerning one or two means, respectively. If samples should be taken from a population repeatedly, it will be seen that the sample mean is scattered around the population mean over a range determined by the variance of the data. With hypothesis testing concerning one mean, we are actually trying to see if the mean of the sample with unknown origin falls into this range. If the answer to this question is yes, the sample may be a member of the suggested distribution curve. In Figure 5.6, the acceptance region is the range that the samples that are taken from a population with mean μ and variance σ fall with probability p. The possibility of having a sample from that population with mean outside the given limits is $1 - p = \alpha$. Since the distribution curve is symmetrical, having a sample from this population with mean in either rejection region is only $\alpha/2$. A sample may actually belong to the population, but its mean may fall into the rejection range with probability α (Figure 5.6). We may erroneously conclude from these data that the sample is not a member of the population described with μ and σ. This is called a *type I error* in statistics. In quality control, making a type I error means rejecting a batch of commodities with information based on a bad sample. MATLAB code 5.6 plots Figure 5.6.

Rejection of a good population with such an unlucky sample usually hurts the producers and it is called the *producer's risk*. The way that we make our judgments in hypothesis testing is weak in the sense that it is based on the criterion whether a sample mean falls into a predetermined range or not. It is possible that a sample may actually belong to another population but the two populations may overlap (Figure 5.7). We may accept a hypothesis erroneously under these conditions. This is called a *type II* error in statistics. A type II error may cause accepting a wrong population due to overlapping samples and may cause purchasing a batch of commodities with wrong specifications. It is called the *consumer's risk* in quality control. When a population with satisfactory properties is rejected due to a type I error, the hypothesis testing is usually repeated with a new sample. The probability

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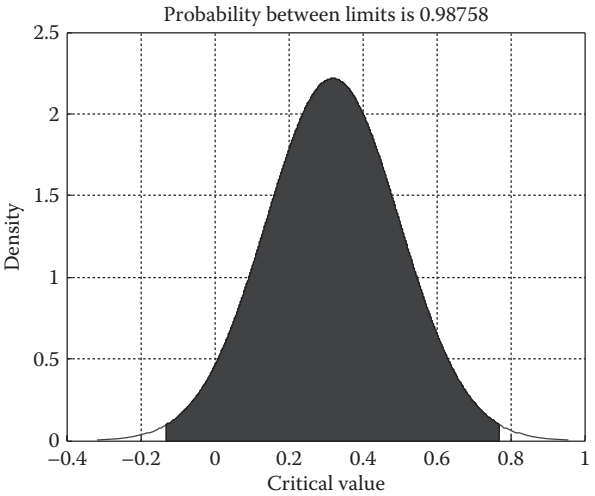


FIGURE 5.6
Schematic description of the acceptance (shaded area) and rejection regions (outside of the shaded area) of a normal distribution curve. In the present figure the acceptable region was between $\mu \pm 2.5\sigma$. Any sample that belong to this population but remain outside of these limits may be rejected because of a type I error (α = 1-0.98758) = 1.24%.

MATLAB® CODE 5.6

Command Window:

```
clear all
close all

% compute and plot the fraction of the area remaining outside of the
mu-2.5*sigma and mu+2.5*sigma range
mu=0.32
sigma=0.18
p = normspec([mu-2.5*sigma,mu+2.5*sigma],mu,sigma,'inside')
grid on
```

When we run the code Figure 5.6 will appear on the screen.

of making a type I error in two consecutive trials is very small and equals α^2. On the other hand the damage caused by a type II error may have more serious consequences in practical applications, since once a batch of commodities are accepted, a second test is not usually performed. MATLAB code 5.7 plots Figure 5.7 to visualize a type II error.

The values χ^2 may be calculated by using Equation 5.43. They may range between 0 and +¥ and their distribution is not symmetrical (Figure 5.8). When the value of χ^2 is tested for significance, we are interested only in the probability of exceeding the observed value as a result of random errors. Critical values of χ^2, a value that exceeds $1 - \alpha$% of the samples from χ^2 distribution with ν degrees of freedom are calculated by MATLAB® code 5.8 and given in Table 5.6.

Table 5.7 provides the χ^2 values that are reached or exceeded with probability $p = 1 - \alpha$. The χ^2 values may also be used to determine the confidence limits of σ^2 (Table 5.3).

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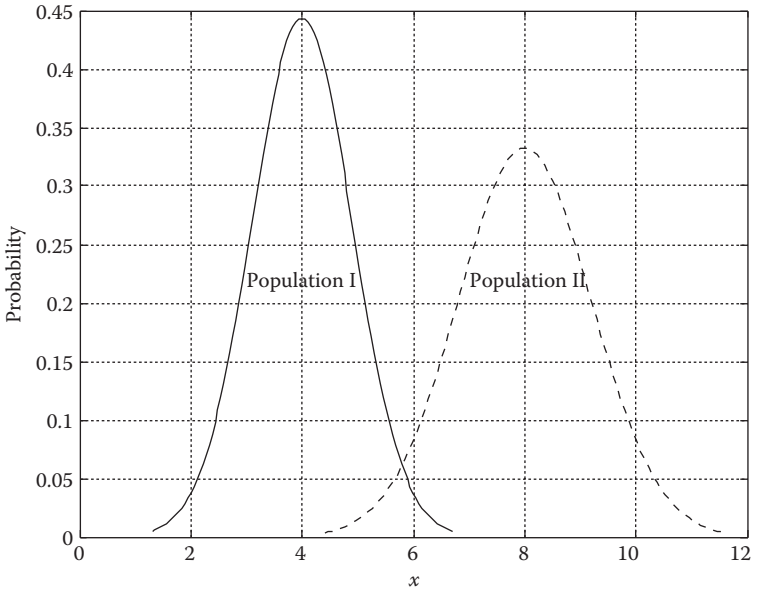


FIGURE 5.7
Overlapping population distribution curves with μ_1, σ_1, and μ_2, σ_2. Samples from the region where $4.2 \le x \le 6.6$ may cause type II error.

MATLAB® CODE 5.7

Command Window:

```
clear all
close all
format compact
global mu1 mu2 sigma1 sigma2 % functions get mu and sigma from the
calling command file

% plot the normal distribution function with different  mu values and
same sigma
sigma1=0.9;
sigma2=1.2;

mu1=4; %  mu1
dx1=6*sigma1/100;
x1=mu1-3*sigma1 : dx1 : mu1+3*sigma1;
normal=norm_fcn1(x1);
plot(x1,normal, '-'); hold on
text(3, 0.22, 'population I'), % insert text to the figure (mu is the
distance from the x axis)
xlabel('x')
ylabel('Probability')
mu2=8; %  mu2
dx2=6*sigma2/100;
x2=mu2-3*sigma2 : dx2 : mu2+3*sigma2;
```

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```
normal=norm_fcn2(x2);
plot(x2,normal, ':'); hold on
text(7, 0.22, 'population II'), % insert text to the figure (mu is
the distance from the x axis)
grid on
```

M-File1:

```
function f1=norm_fcn1(x)

% this function computes the normal distribution function
global mu1 sigma1  % get mu and sigma from the calling command file
f1 = zeros(size(x)); % create an output vector whose size matches the
input
f1 = 1./sqrt(2.*pi)./sigma1.*exp(-(x-mu1).^2./2./sigma1.^2); %
compute the normal distribution function
```

M-File2:

```
function f2=norm_fcn1(x)

% this function computes the normal distribution function
global mu2 sigma2  % get mu and sigma from the calling command file
f2 = zeros(size(x)); % create an output vector whose size matches the
input
f2 = 1./sqrt(2.*pi)./sigma2.*exp(-(x-mu2).^2./2./sigma2.^2); %
compute the normal distribution function
```

When we run the code Figure 5.7 will appear on the screen.

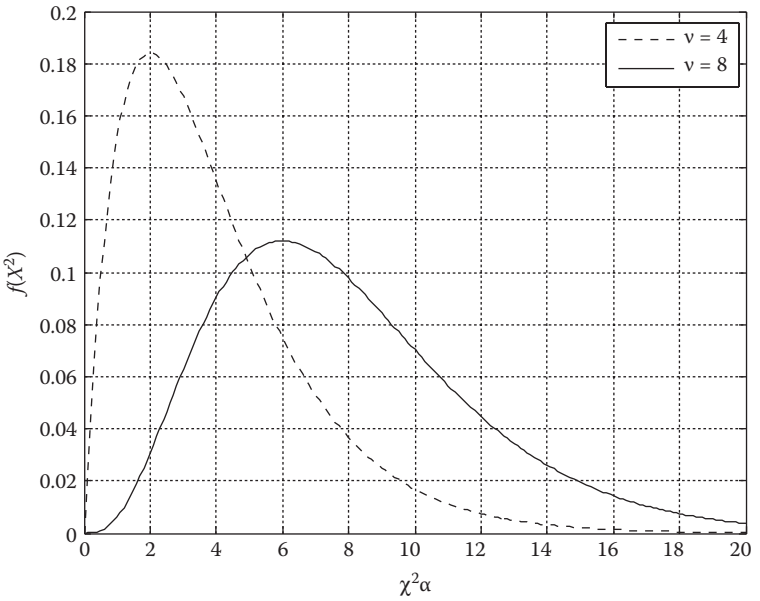


FIGURE 5.8
Cumulative probability of having values of χ^2 between 0 and χ^2_α as a function of χ^2_α.

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MATLAB® CODE 5.8

Command Window:

```
clear all
close all

alpha=0.05 % values of alpha=[0.005 0.01 0.025 0.05 0.975 0.99 0.995]
nu=1:30;
criticalChi2=chi2inv(alpha,nu)
```

When we run the code the related column of Table 5.7 will appear on the screen.

TABLE 5.7

Critical χ^2 Values as Produced by MATLAB® Function criticalChi2=chi2inv(alpha,nu)

$\nu\downarrow$ $p\rightarrow$	**0.995**	**0.99**	**0.975**	**0.95**	**0.05**	**0.025**	**0.01**	**0.005**
1	0.00	0.00	0.00	0.00	3.84	5.02	6.64	7.88
2	0.01	0.02	0.05	0.10	5.99	7.38	9.21	10.60
3	0.07	0.12	0.22	0.35	7.82	9.35	11.35	12.84
4	0.21	0.30	0.48	0.71	9.49	11.14	13.28	14.86
5	0.41	0.55	0.83	1.15	11.07	12.83	15.09	16.75
6	0.68	0.87	1.24	1.64	12.59	14.45	16.81	18.55
7	0.99	1.24	1.69	2.17	14.07	16.01	18.48	20.28
8	1.34	1.65	2.18	2.73	15.51	17.54	20.09	21.96
9	1.74	2.09	2.70	3.33	16.92	19.02	21.67	23.59
10	2.16	2.56	3.25	3.94	18.30	20.48	23.21	25.19
11	2.60	3.05	3.82	4.58	19.68	21.92	24.73	26.76
12	3.07	3.57	4.40	5.23	21.03	23.34	26.22	28.30
13	3.57	4.11	5.01	5.89	22.36	24.74	27.69	29.82
14	4.08	4.66	5.63	6.57	23.69	26.12	29.14	31.32
15	4.60	5.23	6.26	7.26	25.00	27.49	30.58	32.80
16	5.14	5.81	6.91	7.96	26.30	28.85	32.00	34.27
17	5.70	6.41	7.56	8.67	27.59	30.19	33.41	35.72
18	6.27	7.02	8.23	9.39	28.87	31.53	34.81	37.16
19	6.84	7.63	8.91	10.12	30.14	32.85	36.19	38.53
20	7.43	8.26	9.59	10.85	31.41	34.17	37.57	40.00
21	8.03	8.90	10.28	11.59	32.67	35.48	38.93	41.40
22	8.64	9.54	10.98	12.34	33.92	36.78	40.29	42.80
23	9.26	10.20	11.69	13.09	35.17	38.08	41.64	44.18
24	9.89	10.86	12.40	13.85	36.42	39.36	42.98	45.56
25	10.52	11.52	13.12	14.61	37.65	40.65	44.31	46.93
26	11.16	12.20	13.84	15.38	38.89	41.92	45.64	48.29
27	11.81	12.88	14.57	16.15	40.11	43.19	46.96	49.65
28	12.46	13.57	15.31	16.93	41.34	44.46	48.28	50.99
29	13.12	14.26	16.05	17.71	42.56	45.72	49.59	52.34
30	13.79	14.95	16.79	18.49	43.77	46.98	50.89	53.67

Source: Table 5.7 was originally prepared by Merrington, M. and Thomson, C. M., *Biometrika*, 32, 187–191, 1941. Reproduced with permission from Biometrica trustees.

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MATLAB code 5.9 computes and plots cumulative probability of having values of χ^2 between 0 and χ^2_α as a function of χ^2_α.

When the value of *F* is tested for significance, we are interested only in the probability of exceeding the observed value as a result of random errors. Critical values of *F*, a value that exceeds 1 – α% of the samples from *F* distribution with $\nu_{numerator}$ and $\nu_{denominator}$ degrees of freedom are calculated with the MATLAB code 5.10 and given in Tables 5.8 and 5.9.

MATLAB® CODE 5.9

Command Window:

```
clear all
close all

% compute the probability of having values of chi square between 0
and chi square alpha
chiSquareAlpha= 0:0.1:20;
nu=[4 8];
f1= chi2pdf(chiSquareAlpha,nu(1));
f2= chi2pdf(chiSquareAlpha,nu(2));

% plot cumulative probability function of occurences of f(chiSquare)
for the given values of  chiSquareAlpha
plot(chiSquareAlpha,f1, ':' , chiSquareAlpha,f2, '-'); hold on
ylabel('f(X^2)')
xlabel('X^2alpha')
grid on
legend('nu=4', 'nu=8', 'Location','NorthEast')
```

When we run the code Figure 5.8 will appear on the screen.

MATLAB® CODE 5.10

Command Window:

```
clear all
close all

alpha=0.01;
p=1-alpha;
infinity=1000
nun=40; % degrees of freedom of the numerator
nud=[1:25 30 40 60 120 infinity]; % degrees of freedom of the
denominator

F= finv(p,nun,nud);
Fcritical=F'
```

When we run the code the related column of Tables 5.8 and 5.9 will appear on the screen.

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TABLE 5.8

Values of $F_{0.01}(\nu_n,\nu_d)$ as produced by MATLAB® Function F= finv(p,nun,nud); ν_n = degrees of freedom for numerator, ν_d = degrees of freedom for denominator

$\nu\downarrow$ $p\rightarrow$	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	4052	5000	5403	5625	5744	5859	5928	5982	6023	6056	6106	6157	6209	6235	6261	6287	6313	6339	6366
2	98.5	99.0	99.2	99.2	99.3	99.3	99.4	99.4	99.4	99.4	99.4	99.4	99.4	99.5	99.5	99.5	99.5	99.5	99.5
3	34.1	30.8	29.5	28.7	28.2	27.9	27.7	27.5	27.3	27.2	27.1	26.9	26.7	26.6	26.5	26.4	26.3	26.2	26.1
4	21.2	18.0	16.7	16.0	15.5	15.2	15.0	14.8	14.7	14.5	14.4	14.2	14.0	13.9	13.8	13.7	13.7	13.6	13.5
5	16.3	13.3	12.1	11.4	11.0	10.7	10.5	10.3	10.2	10.1	9.89	9.72	9.55	9.47	9.38	9.29	9.20	9.11	9.02
6	13.7	10.9	9.78	9.15	8.75	8.47	8.26	8.10	7.98	7.87	7.72	7.56	7.40	7.31	7.23	7.14	7.06	6.97	6.88
7	12.2	9.55	8.45	7.85	7.46	7.19	6.99	6.84	6.72	6.62	6.47	6.31	6.16	6.06	5.99	5.91	5.82	5.74	5.65
8	11.3	8.65	7.59	7.01	6.63	6.37	6.18	6.03	5.91	5.81	5.67	5.52	5.36	5.28	5.20	5.12	5.03	4.95	4.83
9	10.6	8.02	6.99	6.42	6.06	5.80	5.61	5.47	5.35	5.26	5.11	4.96	4.81	4.73	4.65	4.57	4.48	4.40	4.31
10	10.0	7.56	6.55	5.99	5.64	5.39	5.20	5.06	4.94	4.85	4.71	4.56	4.41	4.33	4.25	4.17	4.08	4.00	3.91
11	9.65	7.21	6.22	5.67	5.32	5.07	4.89	4.74	4.63	4.54	4.40	4.25	4.10	4.02	3.94	3.86	3.78	3.69	3.60
12	9.33	6.93	5.95	5.41	5.06	4.82	4.64	4.50	4.39	4.30	4.16	4.01	3.86	3.78	3.70	3.62	3.54	3.45	3.36
13	9.07	6.70	5.74	5.21	4.86	4.62	4.44	4.30	4.19	4.10	3.96	3.82	3.66	3.59	3.51	3.43	3.34	3.25	3.17
14	8.86	6.51	5.56	5.04	4.70	4.46	4.28	4.14	4.03	3.94	3.80	3.66	3.51	3.43	3.35	3.27	3.18	3.09	3.00
15	8.68	6.36	5.42	4.89	4.56	4.32	4.14	4.00	3.89	3.80	3.67	3.52	3.37	3.29	3.21	3.13	3.05	2.96	2.87
16	8.53	6.23	5.29	4.77	4.44	4.20	4.03	3.89	3.78	3.69	3.55	3.41	3.26	3.18	3.10	3.02	2.93	2.84	2.75
17	8.40	6.11	5.19	4.67	4.34	4.10	3.93	3.79	3.68	3.59	3.46	3.31	3.16	3.08	3.00	2.92	2.83	2.75	2.65
18	8.29	6.01	5.09	4.58	4.25	4.01	3.84	3.71	3.60	3.51	3.37	3.23	3.08	3.00	2.92	2.84	2.75	2.66	2.57
19	8.19	5.93	5.01	4.50	4.17	3.94	3.77	3.63	3.52	3.43	3.30	3.15	3.00	2.92	2.84	2.76	2.67	2.58	2.49
20	8.10	5.85	4.94	4.43	4.10	3.87	3.70	3.56	3.46	3.37	3.23	3.09	2.94	2.86	2.78	2.69	2.61	2.52	2.42

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21	8.02	5.78	4.87	4.37	4.04	3.81	3.64	3.51	3.40	3.31	3.17	3.03	2.88	2.80	2.72	2.64	2.55	2.46	2.36
22	7.95	5.72	4.82	4.31	3.99	3.76	3.59	3.45	3.35	3.26	3.12	2.98	2.83	2.75	2.67	2.58	2.50	2.40	2.31
23	7.88	5.66	4.76	4.26	3.94	3.71	3.54	3.41	3.30	3.21	3.07	2.93	2.78	2.70	2.62	2.54	2.45	2.35	2.26
24	7.82	5.61	4.72	4.22	3.90	3.67	3.50	3.36	3.26	3.17	3.03	2.89	2.74	2.66	2.58	2.49	2.40	2.31	2.21
25	7.77	5.57	4.68	4.18	3.86	3.63	3.46	3.32	3.22	3.13	2.99	2.85	2.70	2.62	2.53	2.45	2.36	2.27	2.17
30	7.56	5.39	4.51	4.02	3.70	3.47	3.30	3.17	3.07	2.98	2.84	2.70	2.55	2.47	2.39	2.30	2.21	2.11	2.01
40	7.31	5.18	4.31	3.83	3.51	3.29	3.12	2.99	2.89	2.80	2.66	2.52	2.37	2.29	2.20	2.11	2.02	1.92	1.80
60	7.08	4.98	4.13	3.65	3.34	3.12	2.95	2.82	2.72	2.63	2.50	2.35	2.20	2.12	2.03	1.94	1.84	1.73	1.60
120	6.65	4.79	3.95	3.48	3.17	2.96	2.79	2.66	2.56	2.47	2.34	2.19	2.03	1.95	1.86	1.76	1.66	1.53	1.38
∞	6.63	4.61	3.78	3.32	3.02	2.80	2.64	2.51	2.41	2.32	2.18	2.04	1.88	1.79	1.70	1.59	1.47	1.32	1.00

Source: Table 5.8 was originally prepared by Merrington, M., and Thomson, C. M., *Biometrika*, 33, 73–88, 1943. Reproduced with permission from Biometrica trustees.

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TABLE 5.9

Values of $F_{0.05}(\nu_n,\nu_d)$ as produced by MATLAB® Function F= finv(p,nun,nud); ν_n = degrees of freedom for numerator, ν_d = degrees of freedom for denominator

$\nu\downarrow$ $p\rightarrow$	1	2	3	4	5	6	7	8	9	10	12	15	20	24	30	40	60	120	∞
1	161	200	216	225	230	234	237	239	241	242	244	246	248	249	250	251	252	253	254
2	18.5	19.0	19.2	19.3	19.3	19.3	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.4	19.5	19.5	19.5	19.5	19.5
3	10.1	9.55	9.28	9.12	9.01	8.94	8.89	8.85	8.81	8.79	8.74	8.70	8.66	8.66	8.62	8.59	8.57	8.55	8.63
4	7.71	6.94	6.59	6.39	6.26	6.16	6.09	6.04	6.00	5.96	5.91	5.86	5.80	5.80	5.75	5.72	5.69	5.66	5.63
5	6.61	5.79	5.41	5.19	5.05	4.95	4.88	4.82	4.77	4.74	4.68	4.62	4.56	4.56	4.50	4.46	4.43	4.40	4.37
6	5.99	5.14	4.76	4.53	4.39	4.28	4.21	4.15	4.10	4.06	4.00	3.94	3.87	3.84	3.81	3.77	3.74	3.70	3.67
7	5.59	4.74	4.35	4.12	3.97	3.87	3.79	3.73	3.68	3.64	3.57	3.51	3.44	3.41	3.38	3.34	3.30	3.27	3.23
8	5.32	4.46	4.07	3.84	3.69	3.58	3.50	3.44	3.39	3.35	3.28	3.22	3.15	3.12	3.08	3.04	3.01	2.97	2.93
9	5.12	4.26	3.86	3.63	3.48	3.37	3.29	3.23	3.18	3.14	3.07	3.01	2.94	2.90	2.86	2.83	2.79	2.75	2.71
10	4.96	4.10	3.71	3.48	3.33	3.22	3.14	3.07	3.02	2.98	2.91	2.85	2.77	2.74	2.70	2.66	2.62	2.58	2.54
11	4.84	3.98	3.59	3.36	3.20	3.09	3.01	2.95	2.90	2.85	2.79	2.72	2.65	2.61	2.57	2.53	2.49	2.45	2.40
12	4.75	3.89	3.49	3.26	3.11	3.00	2.91	2.85	2.80	2.75	2.69	2.62	2.54	2.51	2.47	2.43	2.38	2.34	2.30
13	4.67	3.81	3.41	3.18	3.03	2.92	2.83	2.77	2.71	2.67	2.60	2.53	2.46	2.42	2.38	2.34	2.30	2.25	2.21
14	4.60	3.74	3.34	3.11	2.96	2.85	2.76	2.70	2.65	2.60	2.53	2.46	2.39	2.35	2.31	2.27	2.22	2.18	2.13
15	4.54	3.68	3.29	3.06	2.90	2.79	2.71	2.64	2.59	2.54	2.48	2.40	2.33	2.29	2.25	2.20	2.16	2.11	2.07
16	4.49	3.63	3.24	3.01	2.85	2.74	2.66	2.59	2.54	2.49	2.42	2.35	2.28	2.24	2.19	2.15	2.11	2.06	2.01
17	4.45	3.59	3.20	2.96	2.81	2.70	2.61	2.55	2.49	2.45	2.38	2.31	2.23	2.19	2.15	2.10	2.06	2.01	1.96
18	4.41	3.55	3.16	2.93	2.77	2.66	2.58	2.51	2.46	2.41	2.34	2.27	2.19	2.15	2.11	2.06	2.02	1.97	1.92
19	4.38	3.52	3.13	2.90	2.74	2.63	2.54	2.48	2.42	2.38	2.31	2.23	2.16	2.11	2.07	2.03	1.98	1.93	1.88
20	4.35	3.49	3.10	2.87	2.71	2.60	2.51	2.45	2.39	2.35	2.28	2.20	2.12	2.08	2.04	1.99	1.95	1.90	1.84

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21	4.32	3.47	3.07	2.84	2.68	2.57	2.49	2.42	2.37	2.32	2.25	2.18	2.10	2.05	2.01	1.96	1.92	1.87	1.81
22	4.30	3.44	3.05	2.82	2.66	2.55	2.46	2.40	2.34	2.30	2.23	2.15	2.07	2.03	1.98	1.94	1.89	1.84	1.78
23	4.28	3.42	3.03	2.80	2.64	2.53	2.44	2.37	2.32	2.27	2.20	2.13	2.05	2.01	1.96	1.91	1.86	1.81	1.76
24	4.26	3.40	3.01	2.78	2.62	2.51	2.42	2.36	2.30	2.25	2.18	2.11	2.03	1.98	1.94	1.89	1.84	1.79	1.73
25	4.24	3.39	2.99	2.76	2.60	2.49	2.40	2.34	2.28	2.24	2.16	2.09	2.01	1.96	1.92	1.87	1.82	1.77	1.71
30	4.17	3.32	2.92	2.69	2.53	2.42	2.33	2.27	2.21	2.16	2.09	2.01	1.93	1.89	1.84	1.79	1.74	1.68	1.62
40	4.08	3.23	2.84	2.61	2.45	2.34	2.25	2.18	2.12	2.08	2.00	1.92	1.84	1.79	1.74	1.69	1.64	1.58	1.51
60	4.00	3.15	2.76	2.53	2.37	2.25	2.17	2.10	2.04	1.99	1.92	1.84	1.75	1.70	1.65	1.59	1.53	1.47	1.39
120	3.92	3.07	2.68	2.45	2.29	2.18	2.09	2.02	1.96	1.91	1.83	1.75	1.66	1.61	1.55	1.50	1.43	1.35	1.25
∞	3.84	3.00	2.60	2.37	2.21	2.10	2.01	1.94	1.88	1.83	1.75	1.67	1.57	1.52	1.46	1.39	1.32	1.22	1.00

Source: Table 5.9 was originally prepared by Merrington, M. and Thomson, C. M., *Biometrika*, 33, 73–88, 1943. Reproduced with permission from Biometrica trustees.

The *F* values may be calculated with Equation 5.45 or Equation 5.46 (Table 5.4). Distribution of the *F* values is not symmetrical (Figure 5.9). Standard *F* tables (Tables 5.8 and 5.9) are provided to give *F* values reached or exceeded with given probability. The *F* values may be used to test if the variances of two populations are the same (Table 5.4) or for the analysis of variance. MATLAB code 5.11 computes and plots cumulative probability of having values of *F* between 0 and F_α as a function of F_α.

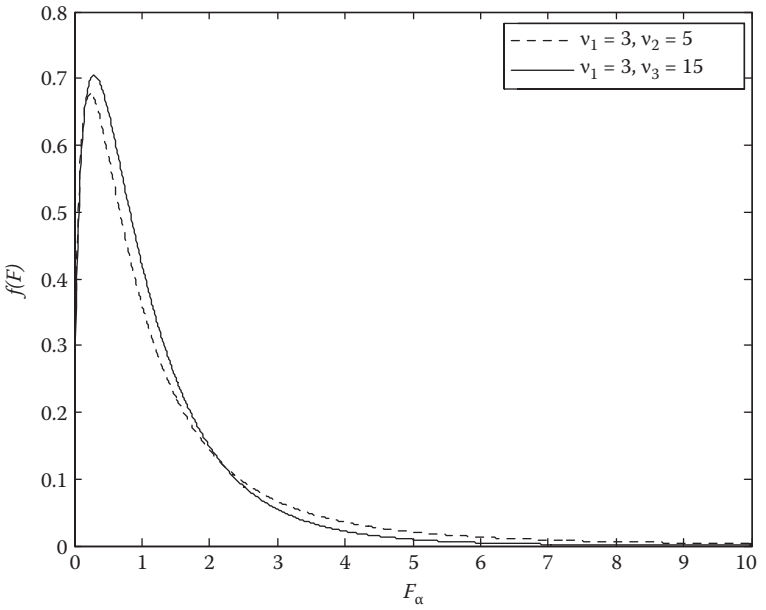


FIGURE 5.9
Cumulative probability of having values of *F* between 0 and F_α with ($\nu_1 = 3$, $\nu_2 = 5$) and ($\nu_1 = 3$, $\nu_3 = 15$).

MATLAB® CODE 5.11

Command Window:

```
clear all
close all

% enter the data
nu1=3;
nu2=5;
nu3=15;
Falpha=0:0.01:10;

% compute the probability of having values of F between 0 and Falpha
f1=fpdf(Falpha,nu1,nu2);  % f1(p) cumulative probability density
function
f2=fpdf(Falpha,nu1,nu3);  % f2(p) cumulative probability density
function
```

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```
% plot cumulative probability function of occurences of f(x,nu1,nu2)
for the given values of  Falpha
plot(Falpha,f1, ':', Falpha,f2, '-'); hold on
ylabel('f(F)')
xlabel('Falpha')
legend('nu1=3, nu2=5', 'nu1=3, nu3=15' , 'Location','NorthEast')
```

When we run the code Figure 5.9 will appear on the screen.

Example 5.14: Hypothesis Testing Concerning One Mean When the Population Standard Deviation is Known

A fruit juice producer is supposed to supply 200 g of concentrated juice in the containers. A set of 25 cans has a sample mean of 192 g. Standard deviation of the filling operation is $\sigma = 3$ g. Is the machine filling less than 200 g of concentrate into the containers?

Solution: We use z values since σ is known. The hypotheses is $\mu = 200$ g and the test is

$\mu - z_{1-\alpha/2}(\sigma/\sqrt{n}) \le \bar{x} \le \mu + z_{1-\alpha/2}(\sigma/\sqrt{n})$ (Equation 5.32 in Table 5.4) $z_{1-\alpha/2} = 2.57$ ($\alpha = 0.01$) (Table 5.5), $n = 25$ and $\sigma = 3$, after substituting the numbers in the test we will find $198.5 \le \bar{x} \le 201.5$. The experimentally determined value of the sample mean is 192 g and it is not in the given range; therefore, the hypotheses is rejected. The manufacturer is not supplying the concentrate with $\mu = 200$ g. MATLAB® code E.5.14 finds the same result.

Example 5.15: Hypothesis Testing Concerning Two Means When the Population Standard Deviations are Known

The 105 samples of a 2004 vintage wine had 0.72 g/100 ml of tartaric acid content. The 110 samples of a 2009 vintage of the same wine had 0.61 g/100 ml of tartaric acid. Standard deviation of tartaric acid contents of these samples were 0.10 g/100 ml in 2004 and 0.06 g/100 ml in 2009. Is there a significant difference between tartaric acid contents of these vintages?

Solution: The hypotheses is $\mu_A = \mu_B$, and the test is

$$-z_{1-a/2}\left(\frac{\sigma_A^2}{n_A} + \frac{\sigma_B^2}{n_B}\right)^{1/2} \le \bar{x}_A - \bar{x}_B \le z_{1-a/2}\left(\frac{\sigma_A^2}{n_A} + \frac{\sigma_B^2}{n_B}\right)^{1/2} \qquad \text{(Equation 5.35 in Table 5.4).}$$

Since the population standard deviation is known we use the z values. $z_{1-\alpha/2} = 1.88$ ($\alpha = 0.06$, Table 5.5), $\sigma_A = 0.10$ g/100 ml, $n_A = 105$, $\sigma_B = 0.06$ g/100 ml, $n_B = 110$, after substituting the numbers into the test we will get $-0.02 \le \bar{x}_A - \bar{x}_B \le 0.02$. Experimentally determined $\bar{x}_A - \bar{x}_B = 0.11$, and it is not in the limits; therefore, the hypotheses has been rejected. The population mean tartaric acid contents of the vintages are different. MATLAB® code E.5.15 finds the same results.

Example 5.16: Hypothesis Testing Concerning One and Two Means When the Population Standard Deviations are Not Known

a. The following data have been taken from two different sets of packaging equipment in a tea processing plant:

Equipment A

Number of packages	**3**	**5**	**9**	**11**	**8**	**6**	**1**
Package weight (g)	367	372	380	382	385	393	413

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MATLAB® CODE E.5.14

Command Window:

```
clear all
close all
format compact

% enter the data
mu=200; % g
xBarExp=192;
sigma=3; % population standard deviation
n=25;
alpha=0.01;

% z test
fprintf('\nHYPOTHESIS: mu=200 g\n')
H = ztest(xBarExp,mu,sigma)
% the outcome H=0 indicates that the hypothesis cannot be rejected
% the outcome H=1 indicates that the null hypothesis can be rejected

% print the results
if H==0
fprintf('\nHYPOTHESIS IS ACCEPTED mu is 200 g\n')
end

if H==1
fprintf('\nHYPOTHESIS IS REJECTED mu is not 200 g\n')
end
```

When we run the code the following lines will appear on the screen:

```
HYPOTHESIS: mu=200 g
H =
     1

HYPOTHESIS IS REJECTED mu is not 200 g
```

MATLAB® CODE E.5.15

Command Window:

```
clear all
close all

% enter the data
xBarA=0.72; % g/100 mL
sigmaA=0.10; % g/100 mL
nA=105;

xBarB=0.61; % g/100 mL
sigmaB=0.06; % g/100 mL
```

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```
nB=110;
z=1.88; % obtained from Table 5.5 for alpha=0.06

% z test
fprintf('\nHYPOTHESIS: muA=muB\n')
sigma=sqrt(((sigmaA^2)/nA)+(((sigmaB^2)/nB)));
LCL=-z*sigma;
UCL=z*sigma;
xBarDifference=xBarA-xBarB;
if (xBarDifference<LCL || xBarDifference >UCL)
    fprintf('HYPOTHESIS IS REJECTED tartaric acid contents are
different\n')
else
    fprintf('HYPOTHESIS IS ACCEPTED tartatic acid contents are the
same\n')
end
```

When we run the code the following lines will appear on the screen:

```
HYPOTHESIS: muA=muB
HYPOTHESIS IS REJECTED tartaric acid contents are different
```

Equipment B

Number of packages	**3**	**4**	**8**	**7**	**6**	**2**	**1**
Package weight (g)	380	382	390	392	394	400	401

Determine (i) mode, (ii) median, and (iii) range of the data sets.

Solution: By using Table 5.1 we can determine the following:

Equipment A: (i) Mode = 382 (value that occurs most frequently), (ii) median = 382 (when we write down the data in increasing order, it is the value that appears in the middle, i.e., the value above or below that equal number of observations fall), and (iii) range = 413 – 367 = 46 (difference between the largest and the smallest observations).

Equipment B: (i) Mode = 390, (ii) median = 392, and (iii) range = 401 – 380 = 21.

MATLAB® code 5.16.a finds the same results.

b. Grocery store representatives claimed that each of these machines were packing different amounts of tea. How would you respond to their claims after analyzing the following data?

Solution: The hypotheses is $\mu_A = \mu_B$, since the population standard deviation is not known we use the *t* values (Table 5.6) and the test is

$$-t_{1-a/2}s_p\left(\frac{1}{n_A}+\frac{1}{n_B}\right)^{1/2} \le \bar{x}_A - \bar{x}_B \le t_{1-a/2}s_p\left(\frac{1}{n_A}+\frac{1}{n_B}\right)^{1/2} \text{ (Equation 5.37 in Table 5.4).}$$

The sample means are

$$\bar{x}_A = \left((1/43)\sum_{i=1}^{43} x_{Ai}\right) = 382.2, \quad \bar{x}_B = \left((1/31)\sum_{i=1}^{31} x_{Bi}\right) = 390.2.$$

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MATLAB® CODE 5.16.a

Command Window:

```
clear all
close all

% enter the data
wA=[367 372 380 382 385 393 413]; % weights equipment A
niA=[3 5 9 11 8 6 1]; % times the same package weight observed
(equipment A)
wB=[380 382 390 392 394 400 401]; % weights equipment B
niB=[3 4 8 7 6 2 1]; % times the same package weight observed
(equipment B)

% construct the weights matrices
A=PackageMatritx(wA,niA);
B=PackageMatritx(wB,niB);

% find the medians
medianA=median(A)
medianB=median(B)

% find the modes
modeA=modes(wA,niA)
modeB=modes(wB,niB)

% find the ranges
rangeA=range(A)
rangeB=range(B)
```

M-file1

```
function AB=PackageMatritx(PackageWeight,number)
k=0;
for i=1:length(PackageWeight)
for j=1:length(number)
k=k+1;
AB(k)=PackageWeight(i);
end
end
```

M-file2

```
function modeAB=modes(wAB,niAB)
for k=1:length(wAB)
if niAB(k)==max(niAB)
m=k;
modeAB=wAB(m);
k=length(wAB);
end
end
```

When we run the code the following lines will appear on the screen:

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```
medianA =
   382

medianB =
   392

modeA =
   382

modeB =
   390

rangeA =
    46

rangeB =
    21
```

The sample variances are

$$s_A^2 = 1/(43-1)\sum_{i=1}^{43}(x_{Ai}-\bar{x}_A)^2 = 64.64 \quad \text{and} \quad s_B^2 = 1/(31-1)\sum_{i=1}^{43}(x_{Bi}-\bar{x}_B)^2 = 33.31.$$

The pooled variance (Equation 5.38 in Table 5.4) is $s_p^2 = \left(\nu_A s_A^2 + \nu_B s_B^2\right)/\left(\nu_A + \nu_B\right) = 51.58$, $s_p = 7.2$, $t_{1-\alpha/2} = 2.24$ ($\alpha = 0.05$, $\nu = \nu_A + \nu_B = 72$) after substituting the numbers into the test we will get $-3.79 \le \bar{x}_A - \bar{x}_B \le 3.79$. Experimentally determined $\bar{x}_A - \bar{x}_B = -8.2$ and it is not in the limits; therefore, the hypotheses has been rejected. The machines are packing different amounts of tea. MATLAB code E.5.16.b finds the same results.

c. Machines A and B were supposed to pack 390 g of tea (i.e., $\mu_A = 390$ g, $\mu_B = 390$ g). Are they packing the right amounts?

Solution: i) The hypotheses is $\mu_A = 390$ g, and the test is

$$\mu - t_{1-\alpha/2}\frac{s}{\sqrt{n_A}} \le \bar{x}_A \le \mu + t_{1-\alpha/2}\frac{s}{\sqrt{n_A}} \qquad \text{(Equation 5.34 in Table 5.4).}$$

We have $t_{1-\alpha/2} = 2.24$ ($\alpha = 0.025$, $\nu_A = 42$, Table 5.6), $s_A = 8.4$ and $n_A = 43$ after substituting the numbers in the test we will find $387 \le \bar{x}_A \le 393$. The experimentally determined value of the sample mean is 382.2 and it is not in the given range; therefore, the hypotheses is rejected. Equipment set A are not packing the right amount.

ii) The hypotheses is $\mu_B = 390$ g, and the test is

$$\mu - t_{1-\alpha/2}\frac{s}{\sqrt{n_B}} \le \bar{x}_B \le \mu + t_{1-\alpha/2}\frac{s}{\sqrt{n_B}} \qquad \text{(Equation 5.34 in Table 5.4).}$$

The $t_{1-\alpha/2} = 2.36$ ($\alpha = 0.05$, $\nu_B = 30$, Table 5.6), $s_B = 5.8$, and $n_B = 32$ after substituting the numbers in the test we will find $387.5 \le \bar{x}_B \le 392.5$. The experimentally determined value of the sample mean is 390.2 and it is in the given range; therefore, the hypotheses is accepted. Equipment set B are packing the right amount. MATLAB code E.5.16.c finds the same results.

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MATLAB® CODE E.5.16.b

Command Window:

```
clear all
close all

% enter the data
wA=[367 372 380 382 385 393 413]; % weights equipment A
niA=[3 5 9 11 8 6 1]; % times the same package weight observed
(equipment A)
wB=[380 382 390 392 394 400 401]; % weights equipment B
niB=[3 4 8 7 6 2 1]; % times the same package weight observed
(equipment B)
Alpha=0.05;
% construct the weights matrices
A=PackageMatritx(wA,niA);
B=PackageMatritx(wB,niB);

% t-test
HypTtest2(A,B,Alpha)
```

M-file3:

```
function HypTtest=HypTtest2(AmFile,BmFile,AlphaMfile)
fprintf('\nHYPOTHESIS: muA=muB\n')
H = ttest2(AmFile,BmFile,AlphaMfile)
% the outcome H=0 indicates that the hypothesis cannot be rejected
% the outcome H=1 indicates that the null hypothesis can be rejected

% print the results
if H==0
fprintf('\nHYPOTHESIS IS ACCEPTED population means of the data sets
are equal\n')
end

if H==1
fprintf('\nHYPOTHESIS IS REJECTED population means of the data sets
are different\n')
end
```

When we run the code the following lines will appear on the screen:

```
HYPOTHESIS: muA=muB
H =
     1
HYPOTHESIS IS REJECTED population means of the data sets are
different
```

Example 5.17: Effect of the Probability Level on the Results of the Hypothesis Testing

In a given linear wine taste scale, scores range between 80 and 100 where 80 means ordinary, 100 means perfect. The previous vintage of a wine sample was evaluated by a taste panel of 23 members. The mean taste score given by the panel members was 98 with a standard deviation of 5. A new vintage of the same wine was also tasted by the same panel, where the average taste score

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MATLAB® CODE E.5.16.c

Command Window:

```
clear all
close all

% enter the data
wA=[367 372 380 382 385 393 413]; % weights equipment A
niA=[3 5 9 11 8 6 1]; % times the same package weight observed
(equipment A)
wB=[380 382 390 392 394 400 401]; % weights equipment B
niB=[3 4 8 7 6 2 1]; % times the same package weight observed
(equipment B)
muA=390; % g
muB=390; % g

% construct the weights matrices
A=PackageMatritx(wA,niA);
B=PackageMatritx(wB,niB);

% t-test
fprintf('\nHYPOTHESIS TEST with SAMPLE SET A\n')
HypTestData(A,muA)
fprintf('\nHYPOTHESIS TEST with SAMPLE SET B\n')
HypTestData(B,muB)
```

M-file4:

```
function HypTtest=HypTestData(AB,muAB)
% t-test with sample set A
fprintf('\nHYPOTHESIS: muSample=390 g\n')
H = ttest(AB,muAB);
% the outcome H=0 indicates that the hypothesis cannot be rejected
% the outcome H=1 indicates that the null hypothesis can be rejected

% print the results
if H==0
fprintf('\nHYPOTHESIS IS ACCEPTED muSample is 390 g\n')
end

if H==1
fprintf('\nHYPOTHESIS IS REJECTED muSample is not 390 g\n')
end
```

When we run the code the following lines will appear on the screen:

```
HYPOTHESIS TEST with SAMPLE SET A
HYPOTHESIS: muSample=390 g
HYPOTHESIS IS REJECTED muSample is not 390 g

HYPOTHESIS TEST with SAMPLE SET B
HYPOTHESIS: muSample=390 g
HYPOTHESIS IS ACCEPTED muSample is 390 g
```

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was found 95 with a standard deviation of 4. Was there a significant deviation between the taste of the two wine samples? Solve the problem by using $\alpha = 0.02$ and $\alpha = 0.20$, then compare the results. (Why are the limits obtained with $\alpha = 0.02$ and $\alpha = 0.20$ different, What does it mean?).

Solution: The hypotheses is $\mu_A = \mu_B$. The pooled variance (Equation 5.38 in Table 5.4) is $s_p^2 = \left(\nu_A s_A^2 + \nu_B s_B^2\right)/\left(\nu_A + \nu_B\right) = 20.5$, $s_p = 4.53$, and the test is

$$-t_{1-a/2}s_p\left(\frac{1}{n_A}+\frac{1}{n_B}\right)^{1/2} \le \bar{x}_A - \bar{x}_B \le t_{1-a/2}s_p\left(\frac{1}{n_A}+\frac{1}{n_B}\right)^{1/2} \tag{5.37}$$

i. Choose $\alpha = 0.02$, $t_{1-\alpha/2} = 2.58$ ($\nu = \nu_A + \nu_B = 44$, Table 5.6) after substituting the numbers into the test we will get $-3.51 \le \bar{x}_A - \bar{x}_B \le 3.51$. Experimentally determined $\bar{x}_A - \bar{x}_B = 98 - 95 = 3$, and it is in the limits; therefore, the hypotheses has been accepted, the taste of the wines are not different.
ii. Choose $\alpha = 0.2$, $t_{1-\alpha/2} = 1.65$ ($\nu = \nu_A + \nu_B = 44$, Table 5.6) after substituting the numbers into the test we will get $-2.24 \le \bar{x}_A - \bar{x}_B \le 2.24$. Experimentally determined $\bar{x}_A - \bar{x}_B = 3$, and it is not in the limits; therefore, the hypotheses has been rejected, the taste of the wines are different.
iii. Choosing the level $\alpha = 0.02$ implies that if the experiments should be replicated 100 times then only 2 of them $\bar{x}_A - \bar{x}_B$ may be out of the limits, although the fact is that the samples are not actually different. The probability of making such an error is 10 times larger when $\alpha = 0.20$. The range of limits are larger with the smaller α.

MATLAB® code E.5.17 finds the same results.

MATLAB® CODE E.5.17

Command Window:

```
clear all
close all

% enter the data
nA=23; % number of the panel members in panel A
xBarA=98; % average score of panel A
sigmaA=5; % standatd deviation of the scores of panel A

nB=23; % number of the panel members in panel A
xBarB=95; % average score of panel A
sigmaB=4; % standatd deviation of the scores of panel A
alpha=[0.02 0.2];
t=[2.58 1.65]; % obtained from Table 5.6 for alpha=[0.02 0.2] and
nA+nB-2=44

% t test
for i=1:2
fprintf('\nHYPOTHESIS: muA=muB\n')
sigma=sqrt(((sigmaA^2)/nA)+(((sigmaB^2)/nB)));
LCL=-t(i)*sigma;
UCL=t(i)*sigma;
xBarDifference=xBarA-xBarB;
if (xBarDifference<LCL || xBarDifference >UCL)
    fprintf('HYPOTHESIS IS REJECTED taste of the wines are different
when alpha= %4.2f \n', alpha(i))
```

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```
else
    fprintf('HYPOTHESIS IS ACCEPTED taste of the wines are the same
when alpha=%4.2f \n', alpha(i))
end
end
```

The following lines will appear on the screen when we run the code:

```
HYPOTHESIS: muA=muB
HYPOTHESIS IS ACCEPTED taste of the wines are the same when
alpha=0.02

HYPOTHESIS: muA=muB
HYPOTHESIS IS REJECTED taste of the wines are different when alpha=
0.20
```

MATLAB® CODE E.5.18

Command Window:

```
clear all
close all

% enter the data
n=1000; % total weight of the sample
p=0.30; % probability of having meat in the sample

% compute sigma
sigma=sqrt(n*p*(1-p)); % standatd deviation of the scores of panel A
% confidence limits
LCL=n*p-3*sigma;
UCL=n*p+3*sigma;
fprintf('\nwe may expect to have %4.1f to %4.1f g ground beef in a
serving\n',LCL,UCL);
```

The following line will appear on the screen when we run the code:

```
we may expect to have 256.5 to 343.5 g ground beef in a serving
```

Example 5.18: Confidence Limits with Binomial Distribution

The recipe of canned mixed vegetables consist of 30% ground beef and 70% other ingredients. What are the confidence limits of the ground beef contents of a 1000 g can?

Solution: The total weight of the sample is $n = 1000$ g. The probability of having meat in any servings is $p = 0.30$, the standard deviation is $\sigma = \sqrt{np(1-p)} = 14.5$. The confidence limits of the meat contents of a can is $np - 3\sigma \le (np)_{exp} \le np + 3\sigma$, after substituting the numbers $256.5 \le (np)_{exp} \le 343.5$. In any can we can expect to have 256.5 to 343.5 g ground beef. MATLAB® code E.5.18 finds the same results.

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MATLAB® CODE E.5.19

Command Window:

```
clear all
close all

% enter the data
n=1e6; % total weight of the sample
x=500;
p=x/n; % probability of having meat in the sample

% compute sigma
sigma=sqrt(n*p); % standatd deviation of the scores of panel A
% confidence limits
LCL=n*p-3*sigma
UCL=n*p+3*sigma
npExp=820;
if (npExp<LCL || npExp >UCL)
    fprintf('\ningredient contributed to the unsatisfaction of the
consumers \n')
else
    fprintf('\ningredient did not contribute to the unsatisfaction
of the consumers \n')
end
```

When we run the code the following line will appear on the screen:

```
ingredient contributed to the unsatisfaction of the consumers
```

Example 5.19: Confidence Limits with Poisson Distribution

A food processing company, which returns the money of the unsatisfied consumers, produces 1,000,000 cans of soup in a year. Approximately 500 cans are expected to be returned annually. After changing one of the major ingredients, 820 cans were returned in one year. Has the ingredient contributed to the unsatisfaction of the consumers?

Solution: It is given in the problem statement that $p = 500/1{,}000{,}000 = 0.0005$ and $\lambda = np = (1{,}000{,}000)(0.0005) = 500$. Since $n > 20$ and $p < 0.05$ and constant we may use the Poisson distribution with $\sigma = \sqrt{\lambda} = 22.36$. The confidence limits are $np - 3\sigma \le (np)_{exp} \le np + 3\sigma$ or after substituting the numbers $432 \le (np)_{exp} \le 567$. The observed number of returns $(np)_{exp} = 820$ and it is not in the given limits; therefore, we may conclude that the ingredient contributed to the unsatisfaction of the consumers. MATLAB® code E.5.19 finds the same results.

Example 5.20: Testing the Validity of Normal Distribution Assumption

A cereal company started a promotion targeting the elementary school students. During the campaign, surprise toys were given in the cereal boxes. Most of these gifts were simple and inexpensive. A smaller fraction of the gifts were more attractive and sophisticated. The campaign is expected to be more successful if the gifts should be distributed normally. To check the success of the distribution process 500 different school districts were surveyed and number of the sophisticated gifts received by the school districts were determined. By using these data discuss if the sophisticated gifts are distributed normally?

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Solution: Since $n = 500$, the population mean and the population variance may be calculated as $\mu = (1/n)\sum_{i=0}^{n} x_i = 4.48$ and $\sigma^2 = (1/n)\sum_{i=1}^{n}(x_i - \mu)^2 = 4.98$, the standard deviation is $\sigma = 2.23$. The expected frequency of the distribution of the gifts may be calculated as $f_e = (1/(\sigma\sqrt{2\pi}))\exp\{-(1/2)((x-\mu)^2/\sigma^2)\}$. The expected frequency of obtaining no gifts is $f_e = 1/[2.23\sqrt{(2)(3.14)}]\ \exp\ \{-(1/2)\}[0-4.48)2.23]^2\} = 0.024$, then the expected number of the districts receiving no gifts is $(0.024)(500) = 12$. We may calculate the expected frequency and the numbers of the gifts received by each district as:

Number of Gifts Received	Experimentally Determined Number of the Districts Receiving the Gift	Expected Number of the Districts to Receive the Gift
0	18	12
1	22	26.49
2	50	48.22
3	81	71.81
4	100	87.45
5	79	87.10
6	55	70.94
7	45	47.26
8	25	25.75
9	15	11.47
10	10	4.18
TOTAL	500	492.67

$\chi^2_{\text{observed}} = \sum_{i=1}^{10}(f_o - f_e)^2/f_e = 13.65$. We have 11 terms in the equation, therefore $\nu = 11 - 1 = 10$, we choose $\alpha = 0.005$ then $\chi^2_{\text{table}} = 25.19$ (Table 5.7). Since $\chi^2_{\text{table}} > \chi^2_{\text{observed}}$, we may conclude that the variations between f_e and f_o are random and the distribution is normal. We may also use MATLAB® code E.5.20 to reconfirm the normal distribution.

MATLAB® CODE E.5.20

Command Window:

```
clear all
close all

% enter the data
nReceived= [18 22 50 81 100 79 55 45 25 15 10];

% Jarque-Bera hypothesis test for normality
fprintf('\nHYPOTHESIS: Data is distributed normally\n')
H=jbtest(nReceived); % Jarque-Bera hypothesis test for normality
% the outcome H=0 indicates that the hypothesis cannot be rejected
% the outcome H=1 indicates that the null hypothesis can be rejected

% print the results
if H==0
fprintf('\nhypothesis is accepted: GIFTS ARE NORMALLY
DISTRIBUTED\n')
end
```

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```
if H==1
fprintf('\nhypothesis is rejected, DATA IS NOT NORMALLY
DISTRIBUTED\n')
end
```

When we run the code the following lines will appear on the screen:

```
HYPOTHESIS: Data is distributed normally
hypothesis is accepted: GIFTS ARE NORMALLY DISTRIBUTED
```

Example 5.21: Confidence Limits Associated with Triangular Tasting Experiments and Testing the Validity of a Distribution Model

In a *triangular* tasting test two identical samples and one different sample are tasted by panel members, who are required to distinguish the different one. A panel of 49 individuals were given 12 replicate tasting tests and asked to identify an imitation cheese. In each set there is one imitation and two real cheese samples. The number of the times that the panel members distinguished the imitation cheese is given in the following table:

Number of Times	0	1	2	3	4	5	6	7	8	9	10	11	12
Number of the panel members	0	1	2	7	9	17	5	6	1	1	0	0	0

a. Has the imitation cheese actually been distinguished by the panel members?

Solution: The total number of the samples tasted is $n = (49)(12) = 588$. The probability of having a different sample in any trial is $p = (\text{number of different samples/total number of samples}) = 1/3$, the standard deviation is $\sigma = \sqrt{np(1-p)} = 11.4$, the test is $np - 3\sigma \le (np)_{exp} \le np + 3\sigma$, after substituting the numbers $161.8 \le (np)_{exp} \le 230.2$, the number of the correct replicates observed $= (np)_{exp} = (0)(0) + (1)(1) + (2)(2) + (3)(7) + (4)(9) + \ldots = 236$ and it is not in the given interval; therefore, the panel members actually distinguished the imitation cheese. MATLAB® code E.5.21.a finds the same results.

MATLAB® CODE E.5.21.a

Command Window:

```
clear all
close all

% enter the data
p=1/3; % probability of having meat in the sample
n=49*12; % (number of the panellists)*(number of tastings done by
each panellist )
Panellists=[0 1 2 7 9 17 5 6 1 1 0 0 0]; % number of the panellists
who made the distinction
ni=[0 1 2 3 4 5 6 7 8 9 10 11 12]; % number of times

% construct the npExp matrice (total number of times the distinction
has been made
npExp=sum(Panellists.*ni)

% compute sigma
```

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```
sigma=sqrt(n*p*(1-p)); % standatd deviation of the scores of panel A
% confidence limits
LCL=n*p-3*sigma
UCL=n*p+3*sigma
if (npExp<LCL || npExp >UCL)
    fprintf('\npanellists distinguished the imitation cheese \n')
else
    fprintf('\n panellists did not distinguished the imitation
cheese \n')
end
```

When we run the code the following lines will appear on the screen:

```
npExp =
   236

LCL =
  161.7071

UCL =
  230.2929

panellists distinguished the imitation cheese
```

b. Is the assumption of binomial distribution appropriate?

Solution: Calculate the expected number of panel members that distinguished the imitation cheese 0, 1, 2, ..., 11, 12 times. The binomial formula is $f(x,n,p) = (n!/(x!(n–x)!))p^x(1–p)^{(n–x)}$ with $n = 12$ (number of replications) and $p = 1/3$ (probability of guessing the imitation cheese in any trial). The probability of one person detecting the imitation cheese exactly 0 times in 12 trials = $f(0,12,1/3) = (12!(0!(12–0)!))(1/3)^0(1–(1/3))^{(12–0)} = 0.0079$. The probability of 49 people detecting the imitation cheese exactly 0 times in 12 trials = (0.0079)(49) = 0.4. The same procedure may be repeated for the other occasions.

Number of Times the Imitation Cheese is Distinguished	Number of the Panel Members that made the Distinction	Expected Number of the Panel Members Making the Distinction
0	0	0.4
1	1	2.3
2	2	6.3
3	7	10.4
4	9	11.6
5	17	9.3
6	5	5.4
7	6	2.4
8	1	0.7
9	1	0.2
10	0	0
11	0	0
12	0	0
TOTAL	49	49

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$$\chi^2_{\text{observed}} = \sum_{i=1}^{12} \frac{(f_0 - f_e)^2}{f_e} = 20.88 \qquad \text{(Table 5.4).}$$

We have 13 terms in the equation, therefore $\nu = 13 - 1 = 12$, we choose $p = 0.01$ then $\chi^2_{\text{table}} = 26.22$ (Table 5.7). Since $\chi^2_{\text{table}} > \chi^2_{\text{observed}}$, we may conclude that the assumption was appropriate. MATLAB code E.5.21.b finds the same results.

MATLAB® CODE E.5.21.b

Command Window:

```
clear all
close all

% enter the data
p=1/3; % probability of having meat in the sample
n=49*12; % (number of the panellists)*(number of tastings done by
each panellist )
nPanellistsObserved=[0 1 2 7 9 17 5 6 1 1 0 0 0]; % number of the
panellists who made the distinction
ni=[0 1 2 3 4 5 6 7 8 9 10 11 12]; % number of times
Chi2Table=26.22

% compute the expected number of the panellists who may make the
distinction
nPanellistsExpected=49*binopdf(ni,12,p);

 % compute the observed chi square
Chi2Observed=sum(((nPanellistsObserved-nPanellistsExpected).^2)./
nPanellistsExpected)

% Chi square test
if Chi2Table> Chi2Observed
    fprintf('\n Chi2Table> Chi2Observed: the binomial distribution
assumption was appropriate \n')
else
    fprintf('\n Chi2Table =or < Chi2Observed the binomial
distribution assumption was not appropriate \n')
end
```

When we run the code the following lines will appear on the screen:

```
Chi2Table =
   26.2200

Chi2Observed =
   22.1754

 Chi2Table> Chi2Observed: the binomial distribution assumption was
appropriate
```

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Example 5.22: Confidence Limits Associated with Duo-Trio Tasting Experiments and Testing the Validity of a Distribution Model

In *duo-trio* tasting test a standard is presented to a panel, then they are asked to taste two coded samples (one of them is the same as the standard, the other is different), and find the identical one. A food producer developed an inexpensive ingredient, and was concerned about the consumer response to the new formulation. With a taste panel of 70 individuals eight replica experiments were performed, and the following results were obtained:

Number of Times	0	1	2	3	4	5	6	7	8
Number of the panelists	1	2	5	10	15	22	11	4	0

a. Has the additive affected the taste of the product?

Solution: The total number of the samples tasted is $n = (70)(8) = 560$. The probability of having a different sample in any trial is $p = (\text{number of different samples/total number of samples}) = 1/2$, the standard deviation is $\sigma = \sqrt{np(1-p)} = 11.8$, the test is $np - 3 \le np_{exp} \le np + 3\sigma$ after substituting the numbers $245 \le np_{exp} \le 315$, the number of the correct replicates observed $= (np)_{exp} = (0)(2) + (1)(2) + (2)(5) + \ldots = 306$ and it is in the given interval; therefore, the additive did not actually affect the taste of the product. MATLAB® code E.5.22.a finds the same results.

MATLAB® CODE E.5.22.a

Command Window:

```
clear all
close all

% enter the data
p=1/2; % probability of having meat in the sample
n=70*8; % (number of the panellists)*(number of tastings done by
each panellist )
Panellists=[1 2 5 10 15 22 11 4 0]; % number of the panellists who
made the distinction
ni=[0 1 2 3 4 5 6 7 8]; % number of times

% construct the npExp matrice (total number of times the distinction
has been made
npExp=sum(Panellists.*ni)

% compute sigma
sigma=sqrt(n*p*(1-p)); % standatd deviation of the scores of panel A
% confidence limits
LCL=n*p-3*sigma
UCL=n*p+3*sigma
if (npExp<LCL || npExp >UCL)
    fprintf('\nthe additive affected the taste of the product \n')
else
    fprintf('\n the additive did not affect the taste of the
product\n')
end
```

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When we run the code the following lines will appear in the screen:

```
npExp =
    306

LCL =
  244.5035

UCL =
  315.4965

 the additive did not affect the taste of the product
```

b. Is the assumption of binomial distribution appropriate?

Solution: Calculate the expected number of panel members that distinguished the food with the inexpensive additive 0, 1, 2, ..., 7, 8 times. The binomial formula is $f(x,n,p) = n!/x!(n-x)!p^x(1-p)^{(n-x)}$ with $n = 8$ = number of replications and $p = ½$ = probability of guessing the right sample in any trial. The probability of one person detecting the inexpensive additive exactly 0 times in eight trials = $f(0,8,0.5) = 8!/0!(8)!(0.5)^x(1-0.5)^{(8-0)} = 0.0039$. The probability of 70 people detecting the inexpensive additive exactly 0 times in eight trials = (0.0039)(70) = 0.27. The same procedure may be repeated for the other occasions.

Number of Times the Inexpensive Additive was Distinguished	Number of the Panel Members that made the Distinction	Expected Number of Panel Members to make the Distinction
0	1	0.27
1	2	2.19
2	5	7.66
3	10	15.31
4	15	19.14
5	22	15.31
6	11	7.66
7	4	2.19
8	0	0.27
TOTAL	70	70

$$\chi^2_{\text{observed}} = \sum_{i=1}^{8} \frac{(f_0 - f_e)^2}{f_e} = 11.78 \qquad \text{(Table 5.4)}$$

We have nine terms in the equation, therefore $\nu = 9 - 1 = 8$, we choose $p = 0.01$ then $\chi^2_{\text{table}} = 20.09$ (Table 5.7). Since $\chi^2_{\text{table}} > \chi^2_{\text{observed}}$, we may conclude that the assumption was appropriate. MATLAB code E.5.22.b finds the same results.

Example 5.23: Probability of Obtaining the Required Value of a Sample Standard Deviation

a. A food processing company wants to keep a sample standard deviation of the packages small to maintain uniform shipments. Population standard deviation of the product is 1.26 g.

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MATLAB® CODE E.5.22.b

Command Window:

```
clear all
close all

% enter the data
p=1/2; % probability of having meat in the sample
n=49*12; % (number of the panellists)*(number of tastings done by each
panellist )
nPanellistsObserved=[1 2 5 10 15 22 11 4 0]; % number of the panellists
who made the distinction
ni=[0 1 2 3 4 5 6 7 8]; % number of times
Chi2Table=20.09

% compute the expected number of the panellists who may make the
distinction
nPanellistsExpected=70*binopdf(ni,8,p);

 % compute the observed chi square
Chi2Observed=sum(((nPanellistsObserved-nPanellistsExpected).^2)./
nPanellistsExpected)

% Chi square test
if Chi2Table> Chi2Observed
    fprintf('\n Chi2Table> Chi2Observed: the binomial distribution
assumption was appropriate \n')
else
    fprintf('\n Chi2Table =or < Chi2Observed the binomial distribution
assumption was not appropriate \n')
end
```

When we run the code the following lines will appear on the screen:

```
Chi2Table =
   20.0900

Chi2Observed =
   11.7633

 Chi2Table> Chi2Observed: the binomial distribution assumption was
appropriate
```

Assume that the samples were taken randomly from a normally distributed population and calculate the probability of having a shipment of 20 packages with more than 1.7 of the sample standard deviation.

Solution: It is given in the problem statement that $n = 20$, $s = 1.7$, and $\sigma = 1.26$. After substituting the numbers $\chi^2 = [(n-1)s^2]/\sigma^2 = 34.6$. With $\nu = 20 - 1 = 19$, and $\chi^2 = 34.6$, we determine with interpolation from the χ^2 table (Table 5.7) that $\alpha = 0.018$, implying that there is 1.8% probability for a shipment with $s \geq 1.7$.

b. Calculate the probability of having a sample standard deviation of more than 1.7 in a shipment of 15 packages in the previous example.

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Solution: It is given in the problem statement that $n = 15$, $s = 1.7$, and $\sigma = 1.26$. After substituting the numbers $\chi^2 = [(n-1)s^2]/\sigma^2 = 25.5$. With $\nu = 14$ and $\chi^2 = 25.5$, we determine with interpolation from the χ^2 table (Table 5.7) that $\alpha = 0.038$, implying that there is 3.8% probability for a shipment with $s \geq 1.7$. It should be noticed that the probability of the shipment of the packages with $s \geq 1.7$ increases as the sample size decreases.

Example 5.24: Confidence Limits of Population Means and Standard Deviations

A Turkish newspaper made a survey concerning the actual volumes of the so called one liter fruit juice and carbonated beverages. After measuring one box or bottle of each of the given brand names they published the following data (Hürriyet, March 23, 1995; page 9):

Fruit Juice	Actual Volume Measured (mL)	Carbonated Beverages	Actual Volume Measured (mL)
Tamek (sour cherry)	1000	Coca Cola	1025
Aroma (orange)	1000	Pepsi Cola	1025
Dimes (orange)	1000	Uludag	950
Tamek (peach)	1025	Seven-Up	1000
Meysu (apricot)	1010	Çamlica (lemon)	1000
Tikvesli (apple)	1030	Çamlica (orange)	1000
Cappy (apricot)	1000	Yedigün (orange)	1000
Aroma (apricot)	1000	Schweppes (tangerine)	1000
		Fanta (orange)	1025

All the juices and the carbonated beverages were reported to be purchased from the same market; therefore, we may assume that they were subjected to the same treatment during storage and handling. Although the measuring volume of a single container is not sufficient to make any judgment concerning any brand names, the data may be regarded as stratified samples and used to make the following analysis.

a. Determine the confidence limits of μ_{juice}, $\mu_{beverage}$, σ_{juice}, $\sigma_{beverage}$.

Solution: The sample means and standard deviations are

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i, \tag{5.10}$$

$$s^2 = \frac{1}{n-1}\sum (x_i - \bar{x})^2. \tag{5.13}$$

After substituting the numbers in Equations 5.10 and 5.13 we will obtain $\bar{x}_{juice} = 1008.1\,\text{mL}$, $s_{juice} = 12.5$ mL, $\bar{x}_{beverage} = 1002.8$ mL, $s_{beverage} = 12.5$ mL,confidence limits of μ:

$$\bar{x} - t\frac{s}{\sqrt{n}} \leq \mu \leq \bar{x} + t\frac{s}{\sqrt{n}}, \tag{5.26}$$

confidence limits of σ^2:

$$\frac{s^2\nu}{\chi^2_\beta} \leq \sigma^2 \leq \frac{s^2\nu}{\chi^2_\alpha}. \tag{5.30}$$

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We have $t_{1-\alpha/2} = 3.50$ ($\nu_{juice} = 7$, $\alpha = 0.02$, Table 5.6) for the fruit juices and $t_{1-\alpha/2} = 3.36$ ($\nu_{beverage} = 8$, $\alpha = 0.02$, Table 5.6) for the beverages. The chi-square values are $\chi^2_\beta = 16.01$ with ($\beta = 0.025$ and $\nu = 7$, Table 5.7) and $\chi^2_\beta = 1.69$ with ($\gamma = 0.975$ and $\nu = 7$) for the fruit juice and $\chi^2_\beta = 17.54$ with ($\beta = 0.025$ and $\nu = 8$, Table 5.7) and $\chi^2_\gamma = 2.18$ with ($\gamma = 0.975$ and $\nu = 8$) for the beverage. After substituting the numbers in Equations 5.26 and 5.30 we will obtain the confidence limits as $992.6 \le \mu_{juice} \le 1023.6$, $8.3 \le \sigma_{juice} \le 25.4$, $976.9 \le \mu_{beverage} \le 1028.7$ and $15.7 \le \sigma_{beverage} \le 44.4$. MATLAB® code E.5.24.a returns $100(1 - \alpha)\%$ confidence intervals for the parameter estimates.

MATLAB® CODE E.5.24.a

Command Window:

```
clear all
close all
format compact
format short g

% enter the data
Vjuice=[1000 1000 1000 1025 1010 1030 1000 1000];
Vbeverage=[1025 1025 950 1000 1000 1000 1000 1000 1025];
alpha=0.02;

%  determine the confidence intervals
[xBarJuice,sigmaJuice,muJuiceCI,sigmaJuiceCI] = normfit(Vjuice,alpha)
[xBarBeverage,sigmaBeverage,muBeverageCI,sigmaBeverageCI] =
normfit(Vbeverage,alpha)

% muJuiceCI=confidence interval of  muJuice
% sigmaJuiceCI=confidence interval of  sigmaJuice
% muBeverageCI=confidence interval of  muBeverage
% sigmaBeverageCI=confidence interval of  sigmaBeverage
```

When we run the code the following lines will appear on the screen:

```
xBarJuice =
       1008.1
sigmaJuice =
       12.518
muJuiceCI =
       994.86
       1021.4
sigmaJuiceCI =
       7.7052
       29.753
xBarBeverage =
       1002.8
sigmaBeverage =
       23.199
muBeverageCI =
       980.38
       1025.2
sigmaBeverageCI =
       14.639
       51.137
```

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b. Determine if $\mu_{juice} = \mu_{beverage}$.

Solution: The hypothesis is $\mu_{juice} = \mu_{beverage}$ and the test is

$$-t_{1-a/2}s_p\left(\frac{1}{n_A}+\frac{1}{n_B}\right)^{1/2} \le \bar{x}_A - \bar{x}_B \le t_{1-a/2}s_p\left(\frac{1}{n_A}+\frac{1}{n_B}\right)^{1/2}, \tag{5.37}$$

$$\text{where} \quad s_p^2 = \left(\nu_A s_A^2 + \nu_B s_B^2\right)/\left(\nu_A + \nu_B\right) = 360, \tag{5.38}$$

$t_{1-\alpha/2} = 2.13$ ($\nu = \nu_A + \nu_B = 15$, $\alpha = 0.10$, Table 5.6). After substituting the numbers in Equation 5.37 we will obtain: $-9.94 \le \bar{x}_{juice} - \bar{x}_{beverage} \le 9.94$, since $\bar{x}_{juice} - \bar{x}_{beverage} = 5.3$ mL and it is within the given limits, we may conclude that $\mu_{juice} = \mu_{beverage}$. MATLAB code E.5.24.b finds the same results.

c. Determine if $\sigma_{juice} = \sigma_{beverage}$.

Solution: The hypothesis is $\sigma_{juice} = \sigma_{beverage}$, and the test is $1/F_{\alpha/2}(\nu_{juice}, \nu_{beverage}) \le s_{juice}^2/s_{beverage}^2 \le F_{\alpha/2}(\nu_{juice}, \nu_{beverage})$ (Equation 5.44 in Table 5.4). $F_{table} = 6.18$ ($\alpha = 0.02$, $\nu_{juice} = 7$, $\nu_{beverage} = 8$, Table 5.8), after substituting F_{table} in the test: $0.161 \le \left(s_{juice}^2/s_{beverage}^2\right)_{exp} \le 6.18$, since the $\left(s_{juice}^2/s_{beverage}^2\right)_{exp} = 0.29$ is within the given limits, we may conclude that $\sigma_{juice} = \sigma_{beverage}$. MATLAB code E.5.24.c finds the same results.

d. Are these distribution curves similar?

Solution: Since both $\mu_{juice} = \mu_{beverage}$ and $\sigma_{juice} = \sigma_{beverage}$ we may conclude that the relative frequency versus the volume distribution curves of the juice and the beverages are the same.

e. What are the smallest fruit juice and beverage volumes possible in the containers according to this data?

Solution: Figure 5.3 indicates that: $\mu - 3\sigma \le x \le \mu + 3\sigma$ $p = 99.73\%$). After substituting the lower confidence limits of μ and the upper confidence limits of σ in this equation we will obtain $916.4 \le x_{juice} \le 1053.1$ and $843.7 \le x_{juice} \le 1110.1$, implying that the smallest juice and the beverage volumes available in the market would be 916.4 mL and 843.7 mL, respectively.

MATLAB® CODE E.5.24.b

Command Window:

```
clear all
close all
format compact

% enter the data
Vjuice=[1000 1000 1000 1025 1010 1030 1000 1000];
Vbeverage=[1025 1025 950 1000 1000 1000 1000 1000 1025];
Alpha=0.10;

% t-test
HypTtest2(Vjuice,Vbeverage,Alpha); % (same as M-file3; Example 5.16)
```

When we run the code the following lines will appear on the screen:

```
HYPOTHESIS: muA=muB
H =
     0
HYPOTHESIS IS ACCEPTED population means of the data sets are equal
```

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MATLAB® CODE E.5.24.c

Command Window:

```
clear all
close all

format compact

% enter the data
Vjuice=[1000 1000 1000 1025 1010 1030 1000 1000];
Vbeverage=[1025 1025 950 1000 1000 1000 1000 1000 1025];
alpha=0.10;

% F-test
fprintf('\nHYPOTHESIS: sigmaA=sigmaB\n')
H = vartest2(Vjuice,Vbeverage,alpha)
% the outcome H=0 indicates that the hypothesis cannot be rejected
% the outcome H=1 indicates that the null hypothesis can be rejected

% print the results
if H==0
fprintf('HYPOTHESIS IS ACCEPTED variances of the data sets are
equal\n')
end

if H==1
fprintf('HYPOTHESIS IS REJECTED variances of the data sets are
different\n')
end
```

When we run the code the following lines will appear on the screen:

```
HYPOTHESIS: sigmaA=sigmaB
H =
     0
HYPOTHESIS IS ACCEPTED variances of the data sets are equal
```

Example 5.25: One Way Analysis of Variance to Test Consumer Preference of Different Cake Formulations

The cost of cake with formulations A and B is the same, but substantially inexpensive with C. The consumer preference of these formulations was assessed with test scores between + 2 (the highest preference) and –2 (strongest rejection). The test scores for each cake are listed as n_A, n_B, and n_C. Is the consumer preference of these formulations the same?

SCORE	n_A	n_B	n_C
+ 2	20	40	5
+ 1	75	70	40
0	35	20	70
–1	17	14	25
–2	3	6	10

MATLAB® function anova1 (anova one) may be used for the solution as depicted in the code E.5.25.

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MATLAB® CODE E.5.25

Command Window:

```
clear all
close all
format short g
format compact

% enter the data
x=[2 20 40 5;1 75 70 40;0 35 20 70;-1 17 14 25;-2 3 6 10];

% (anova one means one way of analysis of variance)
p = 100*anova1(x,[ ], 'off'); % p=probability of having the rows of
matrix x be the same

% print the results
fprintf('the formulations may be assumed to be the same with only
%3.1f  %% probability\n', p)
```

When we run the code the following line will appear on the screen:

```
the formulations may be assumed to be the same with only 13.6  %
probability
```

Example 5.26: Two Way Analysis of Variance to Check the Difference Between the Scores of the Different Panel Members and the Difference in the Scatter of the Test Scores

Three different sets (A, B, C) of fermented olive samples were tasted by 12 panelists. They scored (x) the samples between zero to five according to their bitterness, where zero means acceptable and five means too bitter. Is there an actual difference in bitterness of the olive samples? Is there an actual difference between the scores of the different panel members? Is there an actual difference in the scatter of the test scores of the samples A and B?

Panelist	x_A	x_B	x_C
1	3	0	1
2	2	2	2
3	3	1	2
4	1	1	0
5	3	1	3
6	2	1	1
7	3	2	2
8	2	0	1
9	3	1	2
10	4	2	3
11	1	1	0
12	2	2	2

MATLAB® function anova1 may be used for the solution as shown in code E.5.26.

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MATLAB® CODE E.5.26

Command Window:

```
clear all
close all
format compact

% enter the data
x=[3 0 1;2 2 2;3 1 2;1 1 0;3 1 3;2 1 1;3 2 2;2 0 1;3 1 2;4 2 3;1 1
0;2 2 2];
[p Table]=anova2(x,1, 'off')
```

When we run the code the following lines will appear on the screen:

```
p =
   0.00019456      0.00216
Table =
    'Source'      'SS'       'df'      'MS'       'F'         'Prob>F'
    'Columns'    [9.7222]    [ 2]    [4.8611]    [12.919]   [0.00019456]
    'Rows'       [17.222]    [11]    [1.5657]    [4.1611]   [0.00216]
    'Error'      [8.2778]    [22]    [0.37626]      []          []
    'Total'      [35.222]    [35]       []          []          []
```

We may interpret the results as follows:

- The first column of the matrix (source) shows the source of the variability
- The second column of the matrix shows the Sum of Squares (SS) due to each source
- The third column of the matrix shows the degrees of freedom (df) associated with each source
- The fourth column of the matrix shows the Mean Squares (MS), which is the ratio SS/df
- The fifth column of the matrix shows the F statistics, which is the ratio of the mean squares

p(1)=0.00019456 shows the probability for all the column-samples are drawn from the same population

p(2)=0.00216 shows the probability of all the row-samples are drawn from the same population

A sufficiently small p(1)-value suggests that at least one column-sample mean is significantly different than the other row-sample means

A sufficiently small p(2)-value suggests that at least one row-sample mean is significantly different than the other row-sample means

It is common to declare a result significant if the p-value is less than 0.05 or 0.01. Since both $p(1)<0.05$ and $p(2)<0.05$ significant difference both in the taste of the olives and in the scores of the panellists may be claimed

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5.3 Quality Control Charts for Measurements

There is always a certain amount of variability in any production process. It is mostly random and cannot be completely eliminated. A manufacturing process is called under *statistical control* when the variability is confined in the *random variability limits*. If the process variability goes out of these limits, there should be something wrong with the process and corrective action is needed (Figure 5.10).

While constructing the statistical quality control charts we are actually preparing the graphical representation of the confidence limits, presented in the previous discussion. When we consider the analogy of the two concepts CL, UCL, and LCL corresponds to the population mean, upper confidence limit and the lower confidence limit, respectively. The quality factor may be evaluated either by measurements or by the counts of the nonconfirming units (i.e., attributes). Quality control charts are based on different statistical distribution models for each case.

Quality control techniques are generally applied to commodities consisting of a large number of individuals. It is not usually feasible to measure the quality factor of each item, therefore the tests are applied on the samples. The samples may be destroyed (i.e., pressed or ground and the measurements are made with the juice or powder). The sample size is usually chosen much smaller than the total size of the population to reduce the cost of quality control. The Shewhart control charts consist of means and range charts and are used in quality control with measured properties. The mean chart aims to confine the variation of the sample means between the predetermined acceptable limits. The range chart aims to limit the range within individual samples. The mean of the replicate measurements may be calculated as

$$\bar{x} = \frac{1}{n}\sum_{i=1}^{n} x_i. \tag{5.10}$$

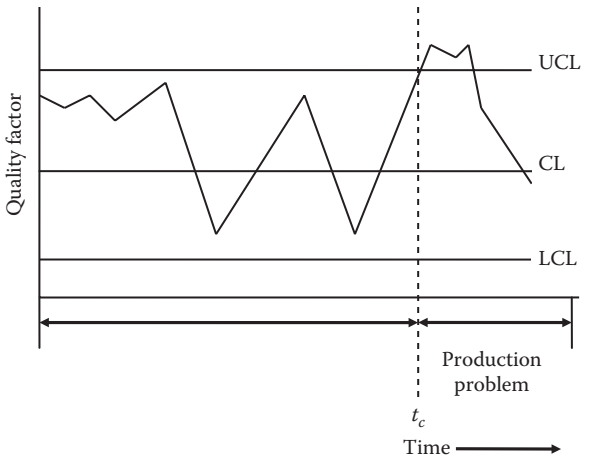


FIGURE 5.10
Variations in a quality factor during processing. The process goes out of statistical control at time $t = t_c$.

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Where $\bar{x}$ is the sample mean, x_i's are the values of the individual items constituting the sample, and n is the number of the items in the sample set. The mean charts are constructed to control the means of the replicate samples within the required UCL and LCL. The range of a sample is defined as

$$R_i = x_{i,\max} - x_{i,\min}, \tag{5.48}$$

where $x_{i,\max}$ and $x_{i,\min}$ corresponds to the maximum and the minimum measurements of the quality factor in the ith sample set. The mean value of the ranges may be calculated as

$$\bar{R} = \frac{1}{k}\sum_{i=1}^{k} R_i, \tag{5.49}$$

where k is the number of the sample sets. In such a quality control plan the central line (CL_x) is

$$CL_x = \frac{1}{k}\sum_{i=1}^{k} \bar{x}_i. \tag{5.50}$$

The upper (UCL_x) and lower (LCL_x) control limits of the mean chart may be calculated as

$$UCL_x = CL_x + \frac{3\sigma}{\sqrt{n}} \tag{5.51}$$

and

$$LCL_x = CL_x - \frac{3\sigma}{\sqrt{n}}. \tag{5.52}$$

If σ is not known it may be estimated as

$$\sigma = \frac{\bar{R}}{d_2}, \tag{5.53}$$

values of d_2 are given in Table 5.10. After substituting Equation 5.53 in Equations 5.51 and 5.52:

$$UCL_x = CL_x + \frac{3\bar{R}}{d_2\sqrt{n}}, \tag{5.54}$$

$$LCL_x = CL_x - \frac{3\bar{R}}{d_2\sqrt{n}}. \tag{5.55}$$

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The range charts are constructed to assure that the range (i.e., the variance) of the individual samples are confined within predetermined limits. The central line (CL_R) and the upper (UCL_R) and lower (LCL_R) control limits of the range chart may be calculated as

$$CL_R = \bar{R}, \tag{5.56}$$

$$UCL_R = \bar{R} + 3d_3\sigma, \tag{5.57}$$

$$LCL_R = \bar{R} - 3d_3\sigma. \tag{5.58}$$

After substituting the equivalent of $\bar{R}$ from Equation 5.53 and letting $D_1 = d_2 - 3d_3$ and $D_2 = d_2 + 3d_3$ we may obtain

$$UCL_R = D_2\sigma, \tag{5.59}$$

$$LCL_R = D_1\sigma. \tag{5.60}$$

When σ is not known, its value may be estimated from Equation 5.53 and substituted in Equations 5.59 and 5.60 as

$$UCL_R = D_4\bar{R}, \tag{5.61}$$

$$LCL_R = D_3\bar{R}, \tag{5.62}$$

where $D_3 = D_1/d_2$ and $D_4 = D_2/d_2$. Equations 5.61 and 5.62 may be used when σ is not known. Values of d_3, D_1, D_2, D_3, and D_4 are given in Table 5.10.

TABLE 5.10

Control Chart Constants

n	d_2	D_1	D_2	D_3	D_4
2	1.128	0	3.686	0	3.267
3	1.693	0	4.358	0	2.575
4	2.059	0	4.698	0	2.282
5	2.326	0	4.918	0	2.115
6	2.534	0	5.078	0	2.004
7	2.704	0.205	5.203	0.076	1.924
8	2.847	0.387	5.307	0.136	1.864
9	2.970	0.546	5.394	0.184	1.816
10	3.078	0.687	5.496	0.223	1.777
11	3.173	0.812	5.534	0.256	1.744
12	3.258	0.924	5.592	0.284	1.716
13	3.336	1.026	5.646	0.308	1.692
14	3.407	1.121	5.693	0.329	1.671
15	3.472	1.207	5.737	0.348	1.652

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In any statistical quality control plan, the range and the mean of the samples try to be maintained within the predetermined control limits. The operators warn that violation of these limits will deteriorate the quality if the process conditions should not be corrected; the operators then may readjust the process parameters to prevent quality loss.

The central limit theorem states that regardless of the distribution behavior of the individual values around the population mean, the sampling distribution of the mean will approach normality as sample size increases (i.e., $n \geq 4$). Therefore the mean and range charts may be used to control a process even when the distribution of individual measurements around the population mean are not Gaussian.

Example 5.27: The Mean and the Range Charts for a Packaging Process

Five consecutive packages were taken from a production line and weighed for 10 days while a filling machine was operating. Sample weights were reported in grams as

X_A	X_B	X_C	X_D	X_E	X_F	X_G	X_H	X_I	X_J
103	104	102	103	102	101	103	104	102	100
101	103	102	102	101	97	104	106	104	102
104	105	104	99	104	100	102	102	99	98
100	99	101	102	101	102	101	103	102	102
99	103	102	98	100	100	102	99	102	102

Prepare control charts for means and ranges.

Solution: The sample means and the ranges were calculated as $\bar{x} = (1/n)\sum_i^n x_i$ and $R_i = x_{i,\max} - x_{i,\min}$

	A	B	C	D	E	F	G	H	I	J
$\bar{x}$	101.4	102.8	102.2	100.8	101.6	100.0	102.4	102.8	101.8	100.8
R	5	6	3	5	4	5	3	7	5	4

These data may be used to calculate

$$\mathrm{CL}_x = \frac{1}{k}\sum_{i=1}^{n} \bar{x} = 101.7 \quad \text{and} \quad \bar{R} = \frac{1}{k}\sum_{i=1}^{n} R_i = 4.7.$$

Since σ is not known, we may calculate UCL_x, LCL_x, UCL_R, and LCL_R with $n = 5$, $d_2 = 2.326$, $D_3 = 0$, and $D_4 = 2.115$ as $\mathrm{UCL}_x = \mathrm{CL}_x + 3\bar{R}/d_2\sqrt{n} = 104.4$, $\mathrm{LCL}_x = \mathrm{CL}_x - 3\bar{R}/d_2\sqrt{n} = 98.9$, $\mathrm{LCL}_R = D_3\bar{R} = 0$, and $\mathrm{UCL}_R = D_4\bar{R} = 9.9$.

MATLAB® code.5.27 shows the details of the computations.

b. Determine the control chart limits if the minimum sample mean fill is required to be 100 g.

Solution: $\mathrm{LCL}_x = 100$ g. Equation 5.55 requires $\mathrm{CL}_x = \mathrm{LCL}_x + (3\bar{R}/d_2\sqrt{n}) = 102.7$, therefore $\mathrm{UCL}_x = \mathrm{CL}_x + (3\bar{R}/d_2\sqrt{n}) = 105.4$. The range chart will remain the same.

c. Readjust the control limits if only 10% of the average package weights are tolerated to be less than 100 g.

Solution: Standard normal variable is $z_{0.10} = \left(\bar{x} - CL_x\right)/\left(\sigma/\sqrt{n}\right)$. $Z_{0.10} = -z_{0.90} = -1.29$ (Table 5.5), $\bar{x} = 100$, $n = 5$ and $\sigma = \bar{R}/d_2 = 2.02$. After filling the numbers in the above equation $-1.29 = \left(100 - \mathrm{CL}_x\right)/\left(2.02/\sqrt{5}\right)$, $\mathrm{CL}_x = 101.2$, consequently $\mathrm{UCL}_x = \mathrm{CL}_x + (3\bar{R}/d_2\sqrt{n}) = 103.9$ and $\mathrm{LCL}_x = \mathrm{CL}_x - (3\bar{R}/d_2\sqrt{n}) = 98.5$. The range chart will remain the same.

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MATLAB® CODE E.5.27

Command Window:

```
clear all
close all

% enter the data
x=[103 101 104 100 99 ; 104 103 105 99 103 ; 102 102 104 101 102 ;
103 102 99 102 98 ; 102 101 104 101 100 ; 101 97 100 102 100 ; 103
104 102 101 102 ; 104 106 102 103 99 ; 102 104 99 102 102 ; 100 102
98 102 102];
sampleno=[1:1:10];

% calculate the means and the ranges
for i=1:length(x)
    xmean(i)=mean(x(i))
    R(i) = max(x(i,:))-min(x(i,:));
end
n=5;
d2=2.326;
Rbar=sum(R)/length(R)
for i=1:length(x)
CLx(i)= mean(xmean)
UCLx(i)=CLx(i)+3*Rbar/(d2*n^(0.5))
LCLx(i)=CLx(i)-3*Rbar/(d2*n^(0.5))
end
D3=0;
D4=2.115;
for i=1:length(x)
RBAR(i)= Rbar
LCLR(i)=D3*Rbar
UCLR(i)=D4*Rbar
end
% plot the means chart
figure
plot(sampleno,UCLx, 'k-');
hold on
plot(sampleno,CLx, 'k-');
hold on
plot(sampleno,LCLx, 'k-')
hold on
plot(sampleno,xmean)
xlabel('sample number')
ylabel('xbar')
legend('CLx','LCLx','UCLx')

% plot the R-chart
figure
plot(sampleno,LCLR, 'k-')
hold on
plot(sampleno,RBAR, 'k-')
hold on
plot(sampleno,UCLR, 'k-')
hold on
```

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```
plot(sampleno,R)
xlabel('sample number')
ylabel('R')
legend('CLR','LCLR','UCLR')
```

When we run the code Figures E.5.27.1 and E.5.27.2 will appear on the screen.

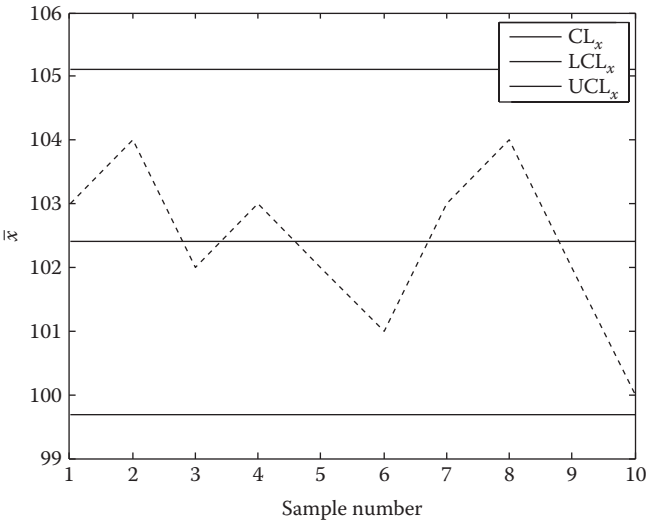


FIGURE E.5.27.1
The means chart for the weights of the packages.

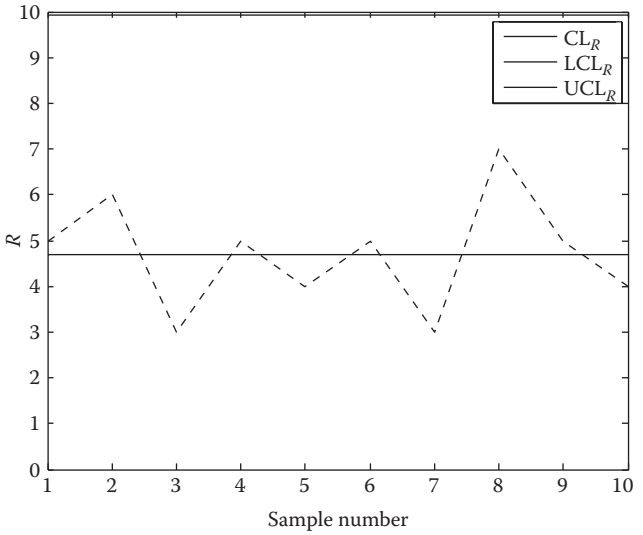


FIGURE E.5.27.2
The range chart for the weights of the packages.

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Equations 5.50 through 5.62 are used in the processes where the quality factors are maintained within the prespecified constant limits, and are not suitable for use in quality control of some foods (i.e., apricots, apples, and eggs) in storage where deterioration is inevitable and acceptable at reasonably slow rates (Kahraman–Dogan, Bayindirli, and Özilgen 1994; Sumnu, Bayindirli, and Özilgen 1994a, 1994b). The central line of the mean and the range charts may be determined as

$$CL_x = CL_{x0} - \alpha t, \tag{5.63}$$

and

$$CL_R = CL_{R0} - \beta t, \tag{5.64}$$

where CL_x and CL_R represents the fitted sample means and the ranges, respectively. CL_{x0} and CL_{R0} are the initial average weight and the range of the sample, α and β are the slopes. Equations 5.63 and 5.64 may be determined with linear regression. Equation 5.56 may be substituted for CL_x and Equation 5.64 for CL_R in Equations 5.54 through 5.62 to construct the means and the range charts for the processes with time dependent CL_x and CL_R.

Example 5.28: Means and the Range Charts for Storage of Eggs

Variation of the mean and range of internal quality of untreated eggs in storage were evaluated in Haugh Units (HU) as $CL_x = 76.7 - 1.15t$ and $CL_R = 12.7$ (Kahraman-Dogan, Bayindirli, and Özilgen 1994). By using the following sample mean and ranges ($n = 3$) determine if the process was under statistical control?

***t* (days)**	**0**	**3**	**6**	**10**	**20**	**25**	**28**	**31**	**38**	**45**
$\bar{x}$ (HU)	89.4	73.4	67.7	66.8	43.2	38.3	40.4	38.3	36.4	37.1
R (HU)	4.6	23.7	24.4	20.0	3.5	7.6	7.7	4.8	17.2	9.3

Solution: After substituting $CL_x = 76.7 - 1.15t$ and $\bar{R} = CL_R = 12.7$ in Equations 5.54, 5.55, 5.61, and 5.62 with $d_2 = 1.693$, $D_3 = 0$ and $D_4 = 2.575$ we will obtain $LCL_x = 63.7 - 1.15t$, $UCL_x = 89.7 - 1.15t$, $LCL_R = 0$ and $UCL_R = 32.7$. The control charts are shown in Figures E.5.28.1 and E.5.28.2. Since all the measurements are confined within the limits we may conclude that the process is under statistical control. Details of the computations are given in MATLAB® code E.5.28.

In most processes, USL (upper specification limit) and LSL (the lower specification limit) are different than control limits. Usually LCL_x ($LCL_x > LSL$) CL_x and UCL_x ($UCL_x < USL$) are established to assure a tolerance band for process fluctuations. When the control limits are constant, *process capability index* C_{pk} measures centering of the data in the control charts and defined as the smallest of

$$C_{pk} = \frac{CL - LSL}{3\sigma}, \tag{5.65}$$

and

$$C_{pk} = \frac{USL - CL}{3\sigma}. \tag{5.66}$$

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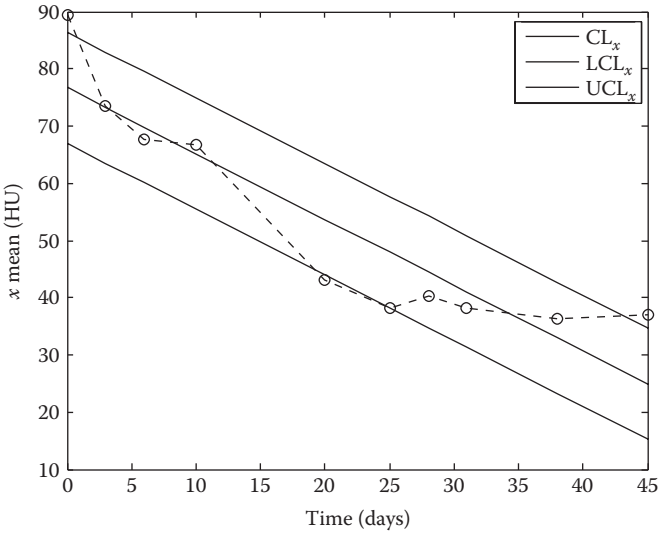


FIGURE 5.28.1
The means chart for the Haugh units. (From Kahraman-Dogan, H., Bayindirli, L., and Özilgen, M., *Journal of Food Quality,* 17, 495–501, 1994.)

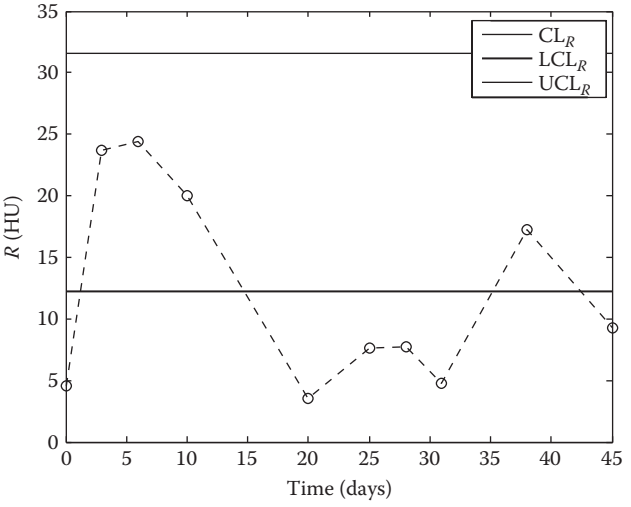


FIGURE 5.28.2
The range chart for the Haugh Units. (From Kahraman-Dogan, H., Bayindirli, L., and Özilgen, M., *Journal of Food Quality,* 17, 495–501, 1994.)

The C_{pk} as defined in Equations 5.65 and 5.66 measures the distance between the process mean and LSL or USL and expresses this as a ratio of half of the width of the normal distribution curve (Oakland and Followell 2003). A C_{pk} of 1 or less means that the width of the distribution curve and its centering is such that it infringes the tolerance limit and the process needs improvement.

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MATLAB® CODE E.5.28

Command Window:

```
clear all
close all

% data input
t=[0 3 6 10 20 25 28 31 38 45];
xmean=[89.4 73.4 67.7 66.8 43.2 38.3 40.4 38.3 36.4 37.1];
R=[4.6 23.7 24.4 20 3.5 7.6 7.7 4.8 17.2 9.3];
Rmean=mean(R);
d2=1.693;
n=length(t);
% Preparation of the means chart
CLx=76.7-1.15*t;
figure
plot(t,CLx,'r')
hold on
LCLx=CLx-3*Rmean/(d2*(5^0.5));
plot(t,LCLx,'-')
    hold on
UCLx=CLx+3*Rmean/(d2*(5^0.5));
    plot(t,UCLx,'m')
hold on
plot(t,xmean,'o')
xlabel('time (days)')
ylabel('xmean (HU)')
legend('CLx','LCLx','UCLx')
% Preparation of the range chart
D3=0;
D4=2.575;
for i=1:10
     LCLR(i)=D3*Rmean;
     UCLR(i)=D4*Rmean;
     CLR(i)=Rmean;
 end
figure
plot(t,UCLR, 'm')
hold on
plot(t,CLR)
hold on
plot(t,LCLR)
hold on
plot(t,R,'o')
xlabel('time (days)')
ylabel('R (HU)')
legend('CLR','LCLR','UCLR')
```

When we run the code Figures E.5.28.1 and E.5.28.2 will appear on the screen.

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Example 5.29: Process Capability Index as a Measure of the Goodness of the Quality Control Charts

a. A set of packaging equipment operates with the following CL_x and σ at different settings. If USL and the LSL of the packages are 505 and 495 g, respectively, which one of the settings should be preferred?

Setting	CL_x (g)	σ (g)
I	498	1.2
II	500	2.0
III	501	0.5

Solution: The process capability index is defined as the smaller one of $C_{pk} = CL_x–LSL/3\sigma$ and $C_{pk} = USL–CL_x/3\sigma$ calculated as

Setting	I	II	III
C_{pk}	0.83	0.83	2.67

Settings I and II yields $C_{pk} = 0.83$, implying that the data are badly scattered and the process does not satisfy the required standards. Having $C_{pk} = 2.67$ with settings III shows that the data are scattered among the process limits satisfactorily.

Details of the computations are given in MATLAB® codes E.5.29.a and E.5.29.b.

MATLAB® CODE E.5.29.a

Command Window:

```
clear all
close all
format compact

USL=505;
LSL=495;
CLx=[498 500 501];
sigma=[1.2 2.0 0.5];

% compute the Cpk values
Cpk1=(CLx-ones(1,3)*LSL)./(sigma*3);
Cpk2=(ones(1,3)*USL-CLx)./(sigma*3);
Cpk=[Cpk1;Cpk2];
Cp(1)=min(Cpk(:,1));
Cp(2)=min(Cpk(:,2));
Cp(3)=min(Cpk(:,3));

% the best process is the one with the largest Cpk
CpMax=max(Cp);
for i=1:3
if Cp(i)==CpMax
N=i;
end
end
```

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```
fprintf('\nprocess with settings %1i is the best with Cpk= %2.1f\
n',N, CpMax);
```

When we run the code the following line will appear on the screen:

```
process with settings 3 is the best with Cpk= 2.7
```

MATLAB® CODE E.5.29.b

Command Window:

```
clear all
close all
format compact

% input the data
USL=505;
LSL=495;
CLx=[498 500 501];
sigma=[1.2 2.0 0.5];
n=5;

% compute the z values corresponding to the USL and LSL
z1=(USL-CLx(1,3))/(sigma(1,3)/(n^0.5));
z2=(LSL-CLx(1,3))/(sigma(1,3)/(n^0.5));

% compute the probabilities corresponding to USL and LSL
p1=normpdf(z1)*100;
p2=normpdf(z2)*100;
fprintf('\nprobability of violating the USL is %2.1f%%\n',p1);
fprintf('\nprobability of violating the LSL is %2.1f%%\n',p2);
```

When we run the code the following lines will appear on the screen:

```
probability of violating the USL is 0.0%

probability of violating the LSL is 0.0%
```

b. What is the probability of exceeding the USL and the LSL with settings III with sample size = 5?

Solution: Standard normal variable is

$$z = \frac{\text{USL} - \text{CL}_x}{\sigma/\sqrt{n}} = 16 \quad \text{or} \quad z = \frac{\text{LSL} - \text{CL}_x}{\sigma/\sqrt{n}} = -12$$

indicating that the probability of violating USL or LSL with random process fluctuations is practically zero.

It was shown in Example 5.2 that by taking the logarithm of a variable it was possible to convert a population from nonnormal to normal distribution. There are also a number of other conversion methods as depicted in Table 5.11.

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TABLE 5.11

The Common Transformation Techniques from Nonnormal to Normal Distribution and the Associated Standard Variable and control Limits ($p = 0.9973$)

Transformation	Transformed Variable	Standard Variable	LCL_x and UCL_x
Natural logarithm	$y_i = \ln(x_i - \theta)$ where $(\theta < x_{min})$	$z = \dfrac{\ln(x-\theta) - \bar{y}}{\theta_y}$	$UCL_x = \theta + \exp(\bar{y} + 3\sigma_y)$ $LCL_x = \theta - \exp(\bar{y} + 3\sigma_y)$
Square root	$y_i = \sqrt{(x_i - \theta)}$ where $\theta \le x_{min}$	$z = \dfrac{\ln\sqrt{x-\theta} - \bar{y}}{\theta_y}$	$UCL_x = \theta + (\bar{y} + 3\sigma_y)^2$ $LCL_x = \theta - (\bar{y} - 3\sigma_y)^2$
arcsine	$y_i = \arcsin\left[\sqrt{\dfrac{x_i}{\theta}}\right]$ where $\theta \le x_{min}$	$z = \dfrac{\arcsin\left[\sqrt{\dfrac{x_i}{\theta}}\right] - \bar{y}}{\theta_y}$	$UCL_x = \theta \sin(\bar{y} + 3\sigma_y)^2$ $LCL_x = \theta \sin(\bar{y} - 3\sigma_y)^2$

Source: Jacobs, D. C., *Chemical Engineering Progress,* 86, no. 11, 19–27, 1990.

Notes: Where x_i = nonnormal parameter, y_i = normally distributed parameter, x_{min} = minimum attainable value of x_i in the data set, x_{max} = maximum attainable value of x_i in the data set, θ = threshold parameter, $\bar{y}$ = average of the values of y and σ_y = standard deviation of the y values.

Example 5.30: Quality Control Charts for Alcohol Content of Bottled Beer

In a case study sample means of the alcohol content $\bar{x}_i$ in bottled beer were reported to be nonnormally distributed around μ, therefore the conventional control charts were not satisfactory and natural logarithmic transformation is applied (Özilgen 1998) as $y_i = \ln(x_i - \theta)$ (where $\theta = 0.5$). Table E.5.30 gives the original alcohol measurements (x_i). The data are introduced into MATLAB® code as a matrix, then transformed into y's and R_y's are calculated by the code. We need to prepare the means and range control charts for the process.

The equations needed are

$$CL_y = \bar{y} = \frac{1}{k}\sum_{i=1}^{n} y_i, \quad \sigma_y = \sqrt{\frac{1}{k-1}\sum_{i=1}^{k}(y_i - \bar{y})^2}, \quad LCL_y = \bar{y} - 3\sigma_y, \quad UCL_x = CL_y + 3\sigma_y$$

and

$$\bar{R}_x = (1/k)\sum_{i=1}^{k} R_i.$$

The MATLAB code shows the details to calculate CL_y, LCL_y, UCL_y, CL_R, LCL_R, UCL_R and prepare the means and the range (Shewhart) charts.

The EWMA (Exponentially Weighted Moving Average) charts are used as an alternative to the Shewhart charts (Singh 2006). Where sample means (i.e., $\bar{x}_i$'s) are transformed into $\mathcal{Z}_i$'s:

$$\mathcal{Z}_i = \lambda \bar{x}_i + (1-\lambda)\mathcal{Z}_{i-1}.$$

The parameter λ is a constant (generally $0 < \lambda \le 1$). The EWMA charts detect the small shifts much faster than Shewhart charts, if the shift is in the range of 0.5–2σ. But they are slower in detecting large shifts in the process mean. It is recommended using small values of λ (such as 0.2) to detect

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TABLE E.5.30

The Alcohol Content Measurements

Sample	x_i (%)	Sample	x_i (%)	Sample	x_i (%)
1	4.3, 4.3, 4.2	10	4.0, 4.0, 4.0	19	4.4, 4.3, 4.3
2	4.3, 4.3, 4.4	11	4.1, 4.1, 4.0	20	4.3, 4.3, 4.4
3	4.7, 4.7, 4.7	12	3.9, 3.8, 4.2	21	4.1, 4.1, 4.0
4	4.6, 4.5, 4.6	13	4.3, 4.0, 4.2	22	3.9, 3.9, 4.0
5	4.4, 4.6, 4.4	14	4.1, 4.1, 4.0	23	4.1, 4.0, 4.1
6	4.2, 4.4, 4.3	15	4.0, 4.2, 4.2	24	3.9, 3.9, 4.0
7	4.8, 4.8, 4.6	16	4.0, 4.1, 4.1	25	4.1, 4.1, 4.1
8	4.3, 4.4, 4.6	17	3.9, 3.9, 3.9	26	3.7, 3.8, 3.8
9	4.1, 4.3, 4.3	18	4.0, 3.9, 3.9		

small shifts, and larger values of λ (i.e., $0.2 \le \lambda \le 0.4$) for larger shifts. EWMA charts are also preferred when the sample size $n = 1$ (Singh 2006).

The EWMA variable $\mathcal{Z}_i$ may also be calculated as

$$\mathcal{Z}_i = \lambda\bar{x}_i + \lambda(1-\lambda)\bar{x}_{i-1} + (1-\lambda)^2\mathcal{Z}_{i-2} = \lambda\sum_{j=0}^{i-1}(i-\lambda)^j\bar{x}_{i-j} + (i-\lambda)^j\mathcal{Z}_{i-j},$$

where the weights, $\lambda\sum_{j=0}^{i-1}(i-\lambda)^j$, decrease geometrically with j, therefore EWMA is also called the geometric moving average (GMA). The central line of the EWMA charts are the same as those of the Shewhart charts (i.e., CL = μ). The upper control limit (UCL) and the lower control limit (LCL) varies with λ:

$$\text{UCL} = \text{CL} + L\sigma\sqrt{\frac{\lambda\left[1-(1-\lambda)^{2i}\right]}{2-\lambda}} \quad \text{and} \quad \text{LCL} = \text{CL} - L\sigma\sqrt{\frac{\lambda\left[1-(1-\lambda)^{2i}\right]}{2-\lambda}}.$$

MATLAB code E.5.30 and Figure E.5.30.2 describes the construction of the EWMA chart and variation of the UCL and the LCL with parameter λ.

Example 5.31: Analysis of the Sourdough Bread-Making Process (Durukan, Özilgen, and Özilgen 1992)

In a typical sourdough bread-making process (Figure E.5.31.1) dough is cut into small portions with the divider, then these portions are put into a spherical shape in the rounder. The dough undergoes the fermentation process in the resting chamber. The loaves are given their final elongated shape in the long molder. The loaves are fermented further in the final proofer and baked in the oven. The hot bread is cooled for about 5 hours before being distributed to the markets.

The distribution of the relative frequency of the dough portion and the loaf weights at the sampling locations A–E indicated two superimposed populations (Figure E.5.31.2). The first population was initiated by the dough portions with exactly 400 g weight, the remaining dough portions initiated the second population. There were four knives in the divider and apparently one of them was malfunctioning. Since the malfunctioning did not cause considerable commercial effect on the operation of the plant it was not replaced, but created the superimposed populations.

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MATLAB® CODE E.5.30

Command Window:

```
clear all;
close all;
clc;
format short g

% The Means and the Range (Shewhart) charts.

x = [4.3 4.3 4.2;4.3 4.3 4.4;4.7 4.7 4.7;4.6 4.5 4.6;4.4 4.6 4.4;4.2
4.4 4.3;4.8 4.8 4.6;...
    4.3 4.4 4.6;4.1 4.3 4.3;4.0 4.0 4.0;4.1 4.1 4.0;3.9 3.8 4.2;4.3
4.0 4.2;4.1 4.1 4.0;...
    4.0 4.2 4.2;4.0 4.1 4.1;3.9 3.9 3.9;4.0 3.9 3.9;4.4 4.3 4.3;4.3
4.3 4.4;4.1 4.1 4.0;...
    3.9 3.9 4.0;4.1 4.0 4.1;3.9 3.9 4.0;4.1 4.1 4.1;3.7 3.8 3.8];

theta = 0.5;
y = log(x - theta);

for i=1:length(x)
    R(i) = max(x(i,:))-min(x(i,:));
end
R=R';

meanx = mean(x,2);
xmean = mean(meanx);
yi_mean = mean(y,2);

k = 26;

y_mean = sum(yi_mean)/k;
mue_y = y_mean;

variance = sqrt((sum((yi_mean-y_mean).^2))/(k-1));

% LCLy = theta + exp(y_mean-(3*variance))
% UCLy = theta + exp(y_mean+(3*variance))
LCLy = y_mean-(3*variance); %corrected version
UCLy = y_mean+(3*variance); %corrected version

Ry_mean = (1/k)*sum(R);

CLR = Ry_mean;
CLy = mue_y; %mue_y = y_mean = sum(yi_mean)/26

D3 = 0;
LCLR = D3 * Ry_mean;

D4 = 2.575;
UCLR = D4 * Ry_mean;

t=1:26;
figure
```

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```
% Figure E.5.30.1
subplot(2,1,1)
%since UCLy, CLy and LCLy are just one data, I multiply them with
ones
%array that is 26 long to be able to draw them on the same plot.
plot(t,yi_mean,'ok',t,ones(1,26)*UCLy,'-.k',t,ones(1,26)*CLy,'--
k',t,ones(1,26)*LCLy,'-k')
axis([0 30 1 1.6])
ylabel('Sample Means of Alcohol')
legend('Mean Yi','UCLy','CLy','LCLy')

subplot(2,1,2)
plot(t,R,'ok',t,ones(1,26)*UCLR,'-.k',t,ones(1,26)*CLR,'--
k',t,ones(1,26)*LCLR,'-k')
axis([0 30 -0.05 0.4])
xlabel('Sample Sets')
legend('R','UCLR','CLR','LCLR')

%  EWMA CHART

z_1(1) = y_mean;
z_2(1) = y_mean;
z_3(1) = y_mean;

lambda1 = 0.3;
lambda2 = 0.7;
lambda3 = 0.9;

for i=2:k;
z_1(i) = lambda1 * yi_mean(i) + (1-lambda1) * z_1(i-1);
z_2(i) = lambda2 * yi_mean(i) + (1-lambda2) * z_2(i-1);
z_3(i) = lambda3 * yi_mean(i) + (1-lambda3) * z_3(i-1);
end

for i=1:k
    UCL_y1(i) = y_mean + 3* variance * sqrt ((lambda1 * (1-(1-
lambda1)^(2*i)))/(2-lambda1));
    LCL_y1(i) = y_mean - 3* variance * sqrt ((lambda1 * (1-(1-
lambda1)^(2*i)))/(2-lambda1));

    UCL_y2(i) = y_mean + 3* variance * sqrt ((lambda2 * (1-(1-
lambda2)^(2*i)))/(2-lambda2));
    LCL_y2(i) = y_mean - 3* variance * sqrt ((lambda2 * (1-(1-
lambda2)^(2*i)))/(2-lambda2));

    UCL_y3(i) = y_mean + 3* variance * sqrt ((lambda3 * (1-(1-
lambda3)^(2*i)))/(2-lambda3));
    LCL_y3(i) = y_mean - 3* variance * sqrt ((lambda3 * (1-(1-
lambda3)^(2*i)))/(2-lambda3));
end

z_1=z_1';
z_2=z_2';
z_3=z_3';
UCL_y1=UCL_y1';
LCL_y1=LCL_y1';
```

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```
UCL_y2=UCL_y2';
LCL_y2=LCL_y2';
UCL_y3=UCL_y3';
LCL_y3=LCL_y3';

%  Figure E.5.30.2
figure
subplot(3,1,1)
%  since CLy is just one data, I multiplied it with ones
%  array that is 26 long to be able to draw them on the same plot.
plot(t,UCL_y1,'-.k',t,LCL_y1,'--k',t,ones(1,26)*CLy,'-k',t,z_1,'ok')
legend('UCL_y','LCL_y','CLy')
title(['\lambda=',num2str(lambda1)])

subplot(3,1,2)
plot(t,UCL_y2,'-.k',t,LCL_y2,'--k',t,ones(1,26)*CLy,'-k',t,z_1,'ok')
legend('UCL_y','LCL_y','CLy')
ylabel('Sample Means of Alcohol')
title(['\lambda=',num2str(lambda2)])

subplot(3,1,3)
plot(t,UCL_y3,'-.k',t,LCL_y3,'--k',t,ones(1,26)*CLy,'-k',t,z_1,'ok')
xlabel('Sample Sets')
legend('UCL_y','LCL_y','CLy')
title(['\lambda=',num2str(lambda3)])
```

When we run the code Figures E.5.30.1 and E.5.30.2 will appear on the screen.

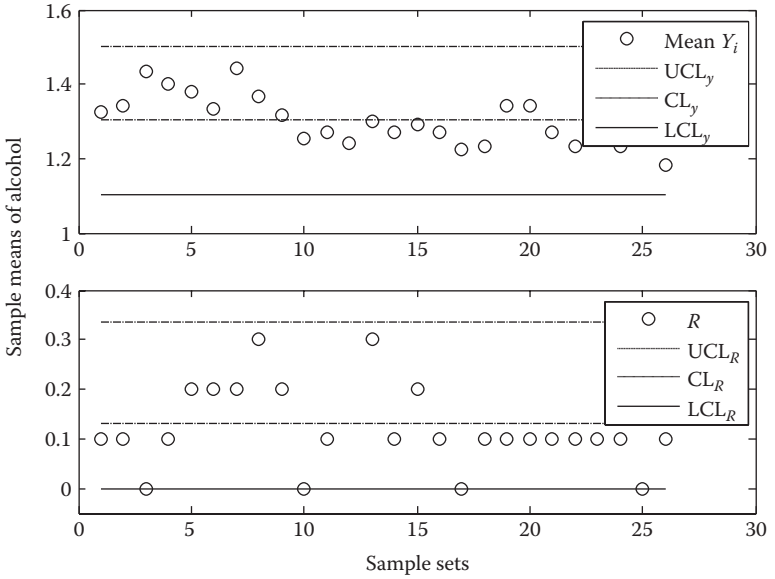


FIGURE E.5.30.1
The means and the range (Shewhart) charts for the percentage of alcohol in the bottled beer.

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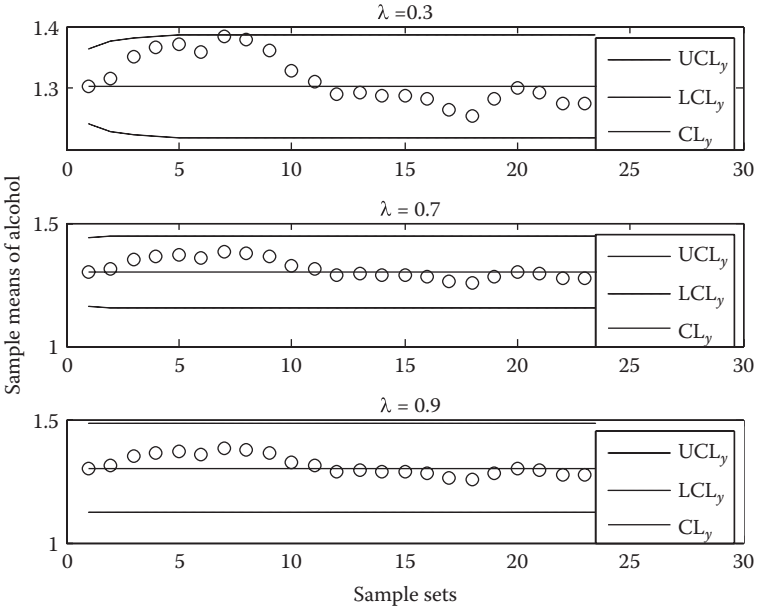


FIGURE E.5.30.2
Variation of the UCL and the LCL of the EWMA charts with parameter λ (λ = 0.1 at the top, λ = 0.5 in the middle, and λ = 1.0 in the last figure).

Each sample contained 15 dough portions (or loaves). Measurements of the each sample set were separated intuitively into two groups. Each group was supposed to be homogeneous throughout an experiment. Homogeneity of these groups were confirmed with the Bartlett's test. Each group of data was confirmed to have the same population variance by using the *F*-test (Table 5.4). Bartlett's test for homogeneity of variances is based on the χ^2 test similar to the discussion in Section 5.2 (Statistical Process Analysis) (i.e., if $\chi^2_{\text{table}} \geq \chi^2_{\text{calculated}}$ we may conclude that the variances of the k sample sets are homogeneous). Parameter $\chi^2_{\text{calculated}}$ was defined by Sokal and Rohlf (1981) as

$$\chi^2_{\text{calculated}} = \frac{\left[\sum_{i=1}^{k} \nu_i\right] \ln\left(s_p^2\right) - \left[\sum_{i=1}^{k} \ln\left(s_p^2\right)\right]}{C}, \tag{E.5.31.1}$$

where k is the number of the sample sets, s_p^2 and C are the generalized pooled variance and correction factors:

$$s_p^2 = \left[\sum_{i=1}^{k} \nu_i s_i^2\right] / \left[\sum_{i=1}^{k} \nu_i\right], \tag{E.5.31.2}$$

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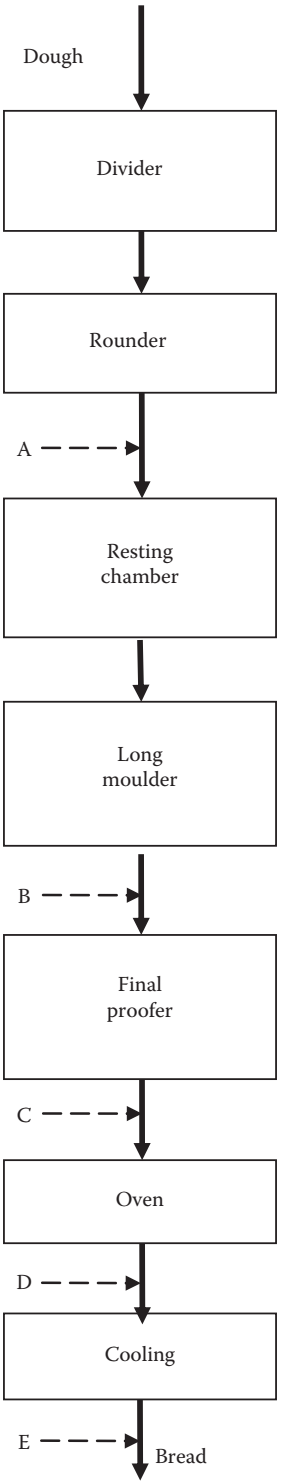


FIGURE E.5.31.1
Sampling locations (A, B, C, D, E) in the sourdough bread-making process.

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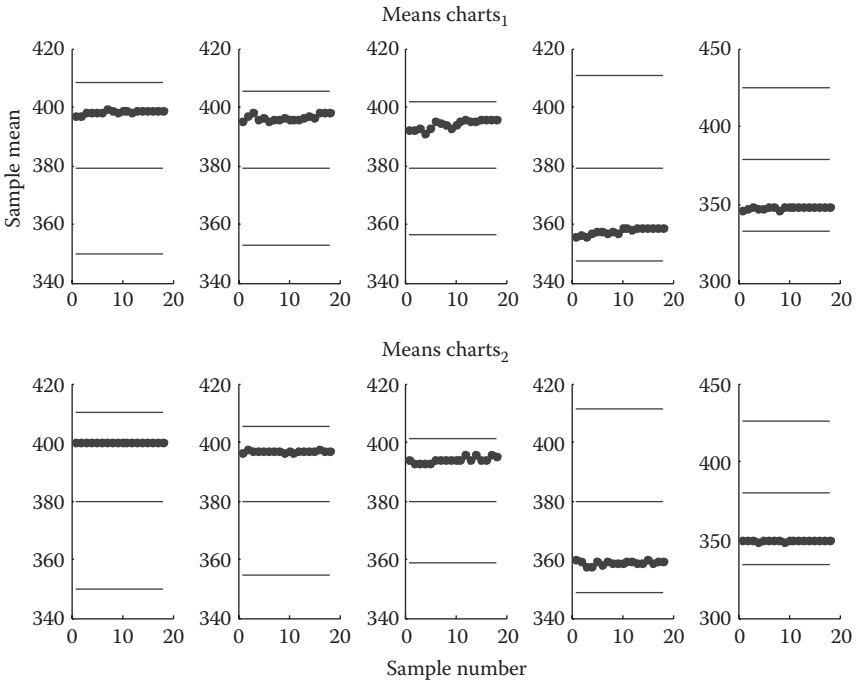


FIGURE E.5.31.2
The means charts for the samples taken at locations A–E. The charts appearing at the bottom are pertaining to the 400 g dough portions. The charts appearing at the top are pertaining to the remaining dough portions. (Adapted from Durukan, A., Özilgen, S., and Özilgen, M., *Process Control and Quality*, 2, 327–33, 1992.)

TABLE E.5.31

Equations for the Central, Upper, and Lower Control Limits for the Means and the Range Charts

	LCL	CL	UCL
Means chart	$LCL_{\bar{x}} = \mu - 3\sigma_{\bar{x}}$	$CL = \mu$	$UCL_{\bar{x}} = \mu + 3\sigma_{\bar{x}}$
Range chart	$LCL_R = \bar{R} - 3\sigma_{\bar{R}}$	$CL = \bar{R}$	$UCL_R = \bar{R} + 3\sigma_{\bar{R}}$

Note: Where $\sigma_{\bar{x}} = \sqrt{(1/k-1)\sum_{i=1}^{k}(\bar{x}_i - \mu)^2}$ and $\sigma_R = \sqrt{(1/k-1)\sum_{i=1}^{k}(R_i - \bar{R})^2}$.

and

$$C = 1 + \frac{1}{3(k+1)}\left[\sum_{i=1}^{k}\frac{1}{\nu_i} - \frac{1}{\sum_{i=1}^{k}\nu_i}\right]. \tag{E.5.31.3}$$

Equations for the central, upper, and lower control lines of the means and the range charts are calculated for each group separately with the formulas given in Table E.5.31. The data have been compared with the control limits in Figure E.5.31.3.

MATLAB® code E.5.31 gives the details of the computations.

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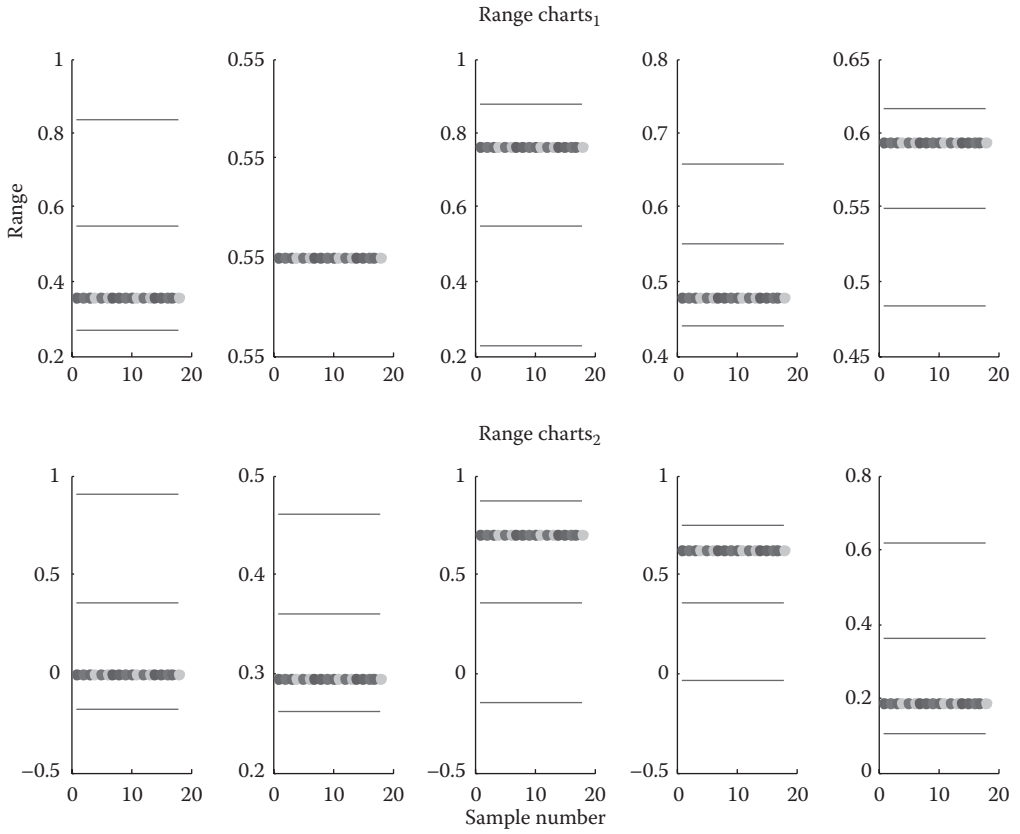


FIGURE E.5.31.3
The range charts for the samples taken at locations A–E. The charts appearing at the bottom are pertaining to the 400 g dough portions. The charts appearing at the top are pertaining to the remaining dough portions. (Adapted from Durukan, A., Özilgen, S., and Özilgen, M., *Process Control and Quality,* 2, 327–33, 1992.)

MATLAB® CODE E.5.31

Command Window:

```
clear all;
close all;

% enter the data
A1=[400 400 400 400 400 400 400 400 400 400 400 400 400 400 400 400
400 400];
A2=[396.9 397 398 398.3 398.2 398.2 399.2 398.9 398.1 399 398.9
398.2 398.9 398.8 398.9 399 398.9 399];
B1=[396.7 397.5 397 397 396.8 396.9 397 396.9 396.2 396.8 396.7 397
397 396.9 396.9 397.9 397.2 397.2];
B2=[395.1 396.8 398 395.9 396.2 395.2 395.7 396 396.2 396 396 396
396.2 396.8 396.6 398 398 398];
C1=[394 393 392.8 393 392.8 394 394.1 394 393.9 393.8 394.2 395.8
394.2 395.8 394.2 394 395.7 395];
```

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```
C2=[392 392.1 392.8 391 393 395 394.9 394 393 394 395 396 395 395
396 396 395.8 395.8];
D1=[359.9 359.5 357.4 357.8 359.5 358 359.5 359 359 359 359.4 359.2
359 359 359.8 359 359.3 359.7];
D2=[356 356.4 356 357 357.9 357.5 357.2 357.9 357.2 359 358.6 358
359 359 359 359 359 359];
E1=[349.9 349.9 349.4 349 349.9 349.7 349.5 349.5 349 349.5 349.5
349.5 349.5 349.5 349.5 349.5 349.5 349.7];
E2=[346.7 347.6 348.5 347.6 348 349.2 348.5 346.7 348.7 349.2 348.5
349.2 349.2 349.2 349.2 349.2 349.2 349.2];

table1=[A1' B1' C1' D1' E1'];
table2=[A2' B2' C2' D2' E2'];
s=[1:18];

% range charts
for j=1:5
    for i=2:18
    if abs(table1(i-1,j))>=abs(table1(i,j))
        table1max(i-1,j)=table1(i-1,j);
    else
       table1max(i-1,j)=table1(i,j);
    end
    if abs(table1(i-1,j))>=abs(table1(i,j))
        table1min(i-1,j)=table1(i,j);
    else
       table1min(i-1,j)=table1(i-1,j);
    end
    R(i-1,j)=table1max(i-1,j)-table1min(i-1,j);

    if abs(table2(i-1,j))>=abs(table2(i,j))
        table2max(i-1,j)=table2(i-1,j);
    else
       table2max(i-1,j)=table2(i,j);
    end
    if abs(table2(i-1,j))>=abs(table2(i,j))
        table2min(i-1,j)=table2(i,j);
    else
       table2min(i-1,j)=table2(i-1,j);
    end
    R2(i-1,j)=table2max(i-1,j)-table2min(i-1,j);
    end
end

Rx=sum(R,1)./18; % first range charts
Ravg=sum(Rx)/5;
sdR=sqrt(((Rx-Ravg).*(Rx-Ravg))./4);

CL_R=Ravg;
UCL_R=Ravg+3*sdR;
LCL_R=Ravg-3*sdR;

Rx2=sum(R2,1)./18; % second range charts
Ravg2=sum(Rx2)/5;
sdR2=sqrt(((Rx2-Ravg2).*(Rx2-Ravg2))./4);
```

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```
CL_R2=Ravg2;
UCL_R2=Ravg2+3*sdR2;
LCL_R2=Ravg2-3*sdR2;

% means charts

avg=sum(table1,1)./18; % first means charts
nu=sum(avg)/5;
sd=sqrt(((avg-nu).*(avg-nu))./4);

CL=nu;
UCL=nu+3*sd;
LCL=nu-3*sd;

avg2=sum(table2,1)./18; % second means charts
nu2=sum(avg2)/5;
sd2=sqrt(((avg2-nu2).*(avg2-nu2))./4);

CL2=nu2;
UCL2=nu2+3*sd2;
LCL2=nu2-3*sd2;

y=ones(1,18);

for i=1:5

figure(1)
if i==4
    title('Means Charts_1')
end
subplot(2,5,i+5),line(s,CL*y)
hold on
line(s,UCL(i)*y)
hold on
line(s,LCL(i)*y)
hold all
plot(s,transpose(table1(:,i)),'.')
if i==3
    xlabel('sample number')
end

if i==3
    title('Means Charts_2')
end
subplot(2,5,i),line(s,CL2*y)
hold on
line(s,UCL2(i)*y)
hold on
line(s,LCL2(i)*y)
hold on
plot(s,transpose(table2(:,i)),'.')
if i==1
    ylabel('sample mean')
end
```

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```
figure(2)
if i==4
    title('Range Charts_1')
end
subplot(2,5,i+5),line(s,CL_R*y)
hold on
line(s,UCL_R(i)*y)
hold on
line(s,LCL_R(i)*y)
hold all
plot(s,transpose(Rx(:,i)),'.')
if i==3
    xlabel('sample number')
end

if i==3
    title('Range Charts_2')
end
subplot(2,5,i),line(s,CL_R2*y)
hold on
line(s,UCL_R2(i)*y)
hold on
line(s,LCL_R2(i)*y)
hold on
plot(s,transpose(Rx2(:,i)),'.')
if i==1
    ylabel('range')
end

end
```

When we run the code Figures E.5.31.2 and E.5.31.3 will appear on the screen.

5.4 Quality Control Charts for Attributes

Attributes are the characteristics used for quality control when actual measurements of the quality factors are not available. In quality control with attributes, simpler methods (i.e., visual observation of the defects, etc.) may substitute for the measurements. Each unit in a sample set is characterized on the basis of either *confirming* or *nonconfirming* the required standards. Quality control with attributes saves time and money when used effectively. Weighing apples one by one is a way of obtaining the measurements to construct the quality control charts. The same purpose may be achieved if apples should be rolled over a slanted surface with constant diameter holes. Apples larger than the hole size are the confirming ones and will remain on the top while the others (i.e., nonconfirming small apples) are collected under the separator. This procedure helps to obtain the counts of the nonconfirming apples rapidly. The latter procedure may be preferred to the former because it needs less labor and costs less. The counts of the nonconfirming units in a sample set of constant size are used to construct the *np charts* following the normal curve approximation of the binomial distribution model. The mean and the standard deviation of binomial distribution are (Table 5.1):

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$$\mu = np \tag{5.4}$$

and

$$\sigma = \sqrt{np(1-p)}. \tag{5.5}$$

Confidence limits under these conditions may be expressed as (Table 5.3):

$$np - 3\sqrt{np(1-p)} \le (np)_{\exp} \le np + 3\sqrt{np(1-p)}. \tag{5.28}$$

Implying that if $(np)_{\exp}$ is a member of the distribution curve with given values of μ and σ, it will fall between these limits in 99.73% of all occasions. The *np* chart is actually a graphical representation of the confidence limits with

$$\mathrm{CL} = np, \tag{5.67}$$

$$\mathrm{LCL} = np - 3\sqrt{np(1-p)}, \tag{5.68}$$

and

$$\mathrm{UCL} = np + 3\sqrt{np(1-p)}. \tag{5.69}$$

Parameter p is the probability of having nonconfirming units in a sample set of n units. It may be estimated from the experimental data:

$$p = \frac{1}{k}\sum_{i=1}^{k} p_i, \tag{5.70}$$

where k is the number of the sample sets and p_i is the fraction of the nonconfirming units in i^{th} sample set.

When the fractions of the defectives, instead of their counts, are determined with constant sample size n, the *p chart* may be prepared. Control chart parameters of the *p chart with constant n* may be obtained after dividing Equations 5.67–5.69 into n:

$$\mathrm{CL} = p, \tag{5.71}$$

$$\mathrm{LCL} = p - 3\left(\sqrt{\frac{p(1-p)}{n}}\right), \tag{5.72}$$

and

$$\mathrm{UCL} = p + 3\left(\sqrt{\frac{p(1-p)}{n}}\right). \tag{5.73}$$

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Example 5.32: The *np* and *p* Charts for Quality Control of the Confectionery Products

In a confectionery process, 200 bars were sampled after coating for 10 days and the following number (np_i) and fraction (p_i) of defectives were found:

Day	np_i	p_i
1	5	0.025
2	4	0.020
3	4	0.020
4	7	0.035
5	3	0.015
6	2	0.010
7	6	0.030
8	4	0.020
9	6	0.030
10	7	0.035

a. Construct the *np* chart for maintaining the present level of operation.

Solution: $k = 10$ and $\underline{p} = (1/k)\sum_{i=1}^{n} p_i = 0.024$. The control line parameters are CL = np = 4.8, $\text{LCL} = np - 3\sqrt{np(1-p)} = -1.69$, $\text{UCL} = np + 3\sqrt{np(1-p)} = 11.3$. Since it is not possible to have a negative number of defective bars, a lower control limit will be reestablished as LCL = 0. The control chart is given in Figure E.5.32.1.

b. Construct a *p* chart with the same data.

Solution: The *p* chart control parameters are CL = p = 0.024,

$$\text{LCL} = p - 3\sqrt{p\frac{(1-p)}{n}} = -0.008.$$

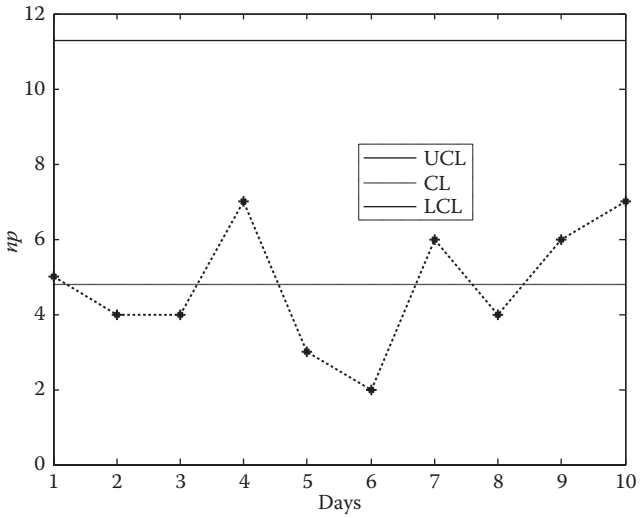


FIGURE E.5.32.1
The *np* chart to maintain the present level of the operation.

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Since it is not possible to have a negative fraction of defective bars, a lower control limit will be reestablished as LCL = 0 and

$$\text{UCL} = p + 3\sqrt{p\frac{(1-p)}{n}} = 0.056.$$

Comparison of the data with the control limits is given in Figure E.5.32.2.

Equations 5.55 through 5.57 may also be used with variable size samples (n is not constant). In this case p may be evaluated as

$$p = \frac{\sum_{i=1}^{k} p_i n_i}{\sum_{i=1}^{k} n_i}, \tag{5.74}$$

where n_i is the size and p_i is the fraction of the nonconfirming units in ith sample set. Several control limits LCL and UCL are determined for a whole range of sample sizes and the appropriate ones are used with each n.

MATLAB® code E.5.32 constructs the control charts.

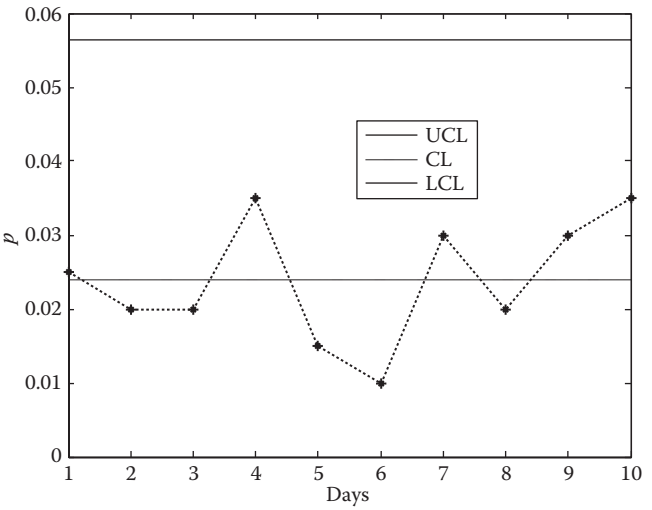


FIGURE E.5.32.2
The p chart to maintain the present level of the operation.

MATLAB® CODE E.5.32

Command Window:

```
clear all;
close all;

%  np chart
n=200;
```

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```
k=10;
p=[0.025 0.020 0.020 0.035 0.015 0.010 0.030 0.020 0.030 0.035];
pAverage=sum(p)/sum(k); % average probability of defects

% CONSTRUCT THE np CHART
j=1;
 while j<11;
    CL(j)=n*pAverage; % central line vector
    LCL(j)=(n*pAverage)-3*((n*pAverage*(1-pAverage))^(0.5)); % lower
control limit vector
       if LCL(j)<0
           LCL(j)=0;
         end
    UCL(j)=(n*pAverage)+3*((n*pAverage*(1-pAverage))^(0.5)); % upper
control limit vector
    j=j+1;
end

% compute np values
np=n.*p;

% construct time vector
t=1:10;

% plot the np chart
plot(t,UCL,'-', t,CL,'--', t,LCL,'-', t,np,'*:') ; hold on
legend('UCL','CL','LCL', 'Location', 'Best')
xlabel('days')
ylabel('np')

% CONSTRUCT THE p CHART
CL2(1:10)=pAverage; % central line vector
LCL2(1:10)=pAverage-3*((pAverage*(1-pAverage)/n)^0.5); % lower
control limit vector

for j=1:10
      if LCL2(j)<0 % lower control limit can not be negative
           LCL2(j)=0;
      end
end

UCL2(1:10)=pAverage+3*((pAverage*(1-pAverage)/n)^0.5); % lower
control limit vector

% plot the p chart
figure
plot(t,UCL2,'-', t,CL2,'--', t,LCL2,'-', t,p,'*:') ; hold on
legend('UCL','CL','LCL', 'Location', 'Best')
xlabel('days')
ylabel('p')
```

When we run the code we will obtain the np and p charts.

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Example 5.33: The *p* Charts with Variable Sample Size

Prior to packaging broiler drum sticks, quality control makes sure an acceptable level of feathers have been removed. The following samples with the given number of defectives were accounted for during 1 week of operation:

	Sample Size (n)	Number of Defectives (np)
Monday	175	5
Tuesday	150	7
Wednesday	100	3
Thursday	125	7
Friday	175	8
Saturday	125	6
Sunday	150	2

a. Calculate the limits of the *p* chart for the variable sample size to maintain the present level of operation.

Solution: The probability of having defective drum sticks is

$$p = \left(\sum_{i=1}^{k} p_i n_i\right) \Big/ \left(\sum_{i=1}^{k} n_i\right) = 0.038.$$

The *p* chart control parameters are $\text{CL} = p = 0.038, \text{LCL} = p - 3\sqrt{p(1-p)/n}$ and $\text{UCL} = p + 3\sqrt{p(1-p)/n}$. After substituting $n = 100$, 125, 150, and 175, we will calculate the following values of the control limits:

n	100	125	150	175
LCL	0	0	0	0
UCL	0.095	0.089	0.085	0.081

MATLAB® code E.5.33 constructs the control chart.

MATLAB® CODE E.5.33

Command Window:

```
clear all
close all

n=[175 150 100 125 175 125 150 ]; % sample size
d=[5 7 3 7 8 6 2]; % days
np=[5 7 3 7 8 6 2];
pAverage=sum(np)/sum(n) % average probability of the defects

n=100 % you may substitute  n (sample size) here to produce the chart
for the related case
c=1;
while c<8;
```

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```
    CL(c)=pAverage; % centralline vector
    LCL(c)=pAverage-3*((pAverage*(1-pAverage)/n)^(0.5)); % upper control
limit vector
    UCL(c)=pAverage+3*((pAverage*(1-pAverage)/n)^(0.5)); % lower control
limit vector

         if LCL(c)<0; % lower control limit can not be negative
              LCL(c)=0;
         end
    c=c+1;
end

t=1:7; % construct the time vector
plot(t,UCL,':', t,CL,'k--', t,LCL,'*-' ); hold on
legend('UCL','CL','LCL')
xlabel('days')
ylabel('c')
```

When we run the code we will obtain Figure E.5.33.

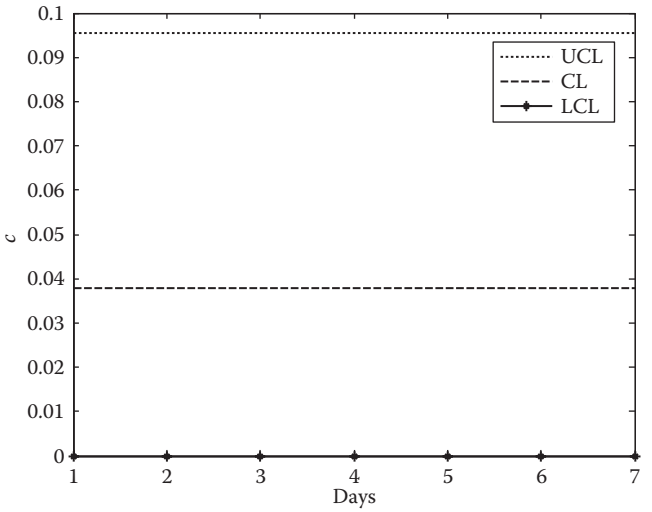


FIGURE E.5.33
The *c* chart for maintaining the present level of the operation when $n = 100$.

b. In a sample with $n = 175$, the number of the defectives was $np = 16$. Is this sample within the previously established acceptable limits?

Solution: The data shows that $p = 0.091$. The control limits when $n = 175$ are LCL = 0 and UCL = 0.081, since p is not within the given range, the sample violates the previously established limits.

The *c charts* are based on a Poisson distribution model and used in processes with *rare defects* to control the number of the defects. It should be noticed that an individual defective unit may have more than one defects. An apple with bruises at three different locations has three defects, but it is a single defective unit. The mean and the standard deviation of a Poisson distribution are (Table 5.1)

$$\mu = \lambda \tag{5.8}$$

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and

$$\sigma = \sqrt{\lambda}. \tag{5.9}$$

For large values of λ, the Poisson distribution curve approaches the normal distribution curve then the properties of the normal distribution may be applied to the Poisson distribution. Confidence limits under these conditions ($p = 0.9973$) with constant sample size n are (Table 5.3)

$$np - 3\sqrt{\lambda} \le (np)_{\exp} \le np + 3\sqrt{\lambda}. \tag{5.29}$$

Parameter c is substituted for λ while constructing the c charts:

$$c = \frac{1}{k}\sum_{i=1}^{k} c_i, \tag{5.75}$$

where k and c_i are the number of the sample sets and counts of the defects in the ith sample set, respectively. The c chart is actually the graphical representation of the confidence limits with

$$\mathrm{CL} = c, \tag{5.76}$$

$$\mathrm{LCL} = c - 3\sqrt{c}, \tag{5.77}$$

and

$$\mathrm{UCL} = c + 3\sqrt{c}. \tag{5.78}$$

Example 5.34: *c* Chart for More than One Type of Defect

The visual quality control of canned dry beans is done by observing five different groups of defects. One can is opened in every batch and each can contains about 1000 beans. The following data were taken with 15 consecutive batches with an acceptable quality level:

Number of Defects/Can

Batch Number	Split Beans	Cracked Beans	Discolored Beans	Wrinkled Beans	Pealed Beans	Total Defects
1	0	2	0	3	0	5
2		0	1	5	0	8
3	3	3	0	2	0	8
4	3	1	2	1	1	8
5	0	3	2	1	0	6
6	1	0	4	0	1	5
7	1	4	2	1	1	9
8	4	2	1	1	1	9
9	1	3	5	1	1	11
10	1	2	1	2	2	8
11	1	6	0	0	2	9
12	1	4	4	1	1	11
13	0	0	5	1	3	9
14	2	2	2	2	2	10
15	2	1	3	1	3	10

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With new batches of beans the following data was obtained

Number of Defects/Can

Batch Number	Split Beans	Cracked Beans	Discolored Beans	Wrinkled Beans	Pealed Beans	Total Defects
1	3	2	1	3	0	9
2	2	7	1	5	0	15
3	0	3	4	2	0	9
4	4	1	4	1	1	11
5	0	0	2	0	3	5

Is the quality of the new beans under control with the standard of the previous ones?

Solution: The total number of defects are used to construct the c charts. Control limits will be determined with the previous data:
$\mathrm{CL} = (1/k)\sum_{i=1}^{k} c_i = 8.4$, $\mathrm{LCL} = c - 3\sqrt{c} = -0.29$, since it is not possible to have a negative number of defective beans, the lower control limits will be reestablished as LCL = 0 and $\mathrm{UCL} = c + 3\sqrt{c} = 17$. Since there are no data points that fall outside the control limits in Figure E.5.34, we may conclude that the process is under statistical control.

MATLAB® code E.5.34 constructs the control chart.

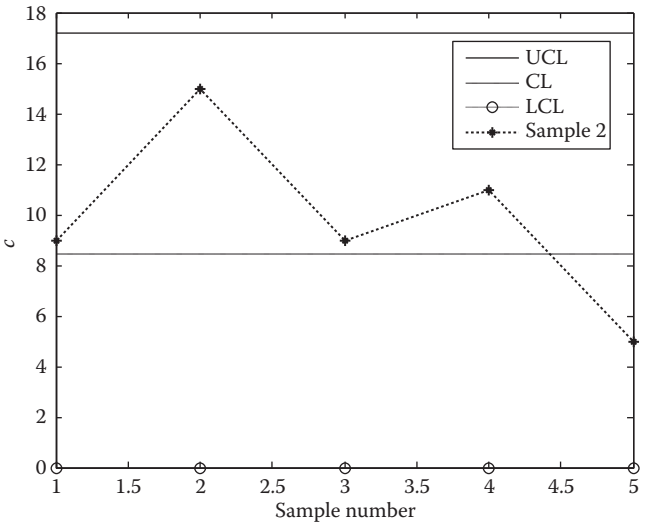


FIGURE E.5.34
Comparison of the data with the control limits.

MATLAB® CODE E.5.34

Command Window:

```
clear all
close all
format compact

% enter the batch1 data
```

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```
batch1=[1:15];
split1=[0 2 3 3 0 1 1 4 1 1 1 1 0 2 2]; % number of the split peas
cracked1=[2 0 3 1 3 0 4 2 3 2 6 4 0 2 1]; % number of the cracked
peas
discolored1=[0 1 0 2 2 4 2 1 5 1 0 4 5 2 3]; % number of the
discolored peas
wrinkled1=[3 5 2 1 1 0 1 1 1 2 0 1 1 2 1]; % number of the wrinkled
peas
pealed1=[0 0 0 1 0 1 1 1 1 2 2 1 3 2 3]; % number of the pealed peas
total1=[split1'+cracked1'+discolored1'+wrinkled1'+pealed1']; % total
number of the defective peas
defects1=[batch1' split1' cracked1' discolored1' wrinkled1' pealed1'
total1]

% enter the batch2 data
batch2=[1:5];
split2=[3 2 0 4 0]; % number of the split peas
cracked2=[2 7 3 1 0]; % number of the cracked peas
discolored2=[1 1 4 4 2]; % number of the discolored peas
wrinkled2=[3 5 2 1 0]; % number of the wrinkled peas
pealed2=[0 0 0 1 3]; % number of the pealed peas
total2=[split2'+cracked2'+discolored2'+wrinkled2'+pealed2']; % total
number of the defective peas
defects2=[batch2' split2' cracked2' discolored2' wrinkled2' pealed2'
total2]

% compute CL, LCL and UCL
n=length(total1);
C=sum(total1(1:length(total1)))/n;
CL=C;
LCL=C-3*C^0.5; % compute the LCL vector
if LCL<0 % LCL can not be negative
    disp('LCL is smaller than 0 so LCL=0')
end
LCL=C-3*C^0.5;
if LCL<0
    disp('LCL is smaller than 0 so LCL=0')
end
UCL=C+3*C^0.5 % compute the UCL vector
total2=[9 15 9 11 5]; % total number of defects in batch 2

if LCL<total2(1,:)< UCL % is batch 2 under control to the given
limits?
    disp('process is under statistical control')
end

if total2(1,:)> UCL % send a message if process is not under control
    disp('process is not under statistical control')
end

% plot the control chart
sampleno=[1:1:5];
for i=1:5;
    CL(i)=C; % CLvector
    LCL(i)=C-3*C^0.5; % compute the LCL vector
        if LCL(i)<0 % LCL can not be negative
           LCL(i)=0;
```

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```
        end
    UCL(i)=C+3*C^0.5; % compute the UCLvector
end
plot(sampleno,UCL,'-', sampleno,CL,'--', sampleno,LCL,'o:' ,
sampleno,total2, '*:'); hold on
xlabel('sample number')
ylabel('c')
legend('UCL','CL','LCL', 'sample2', 'Location', 'Best')
```

When we run the code the following lines and Figure E.5.34 will appear on the screen

```
defects1 =
     1     0     2     0     3     0     5
     2     2     0     1     5     0     8
     3     3     3     0     2     0     8
     4     3     1     2     1     1     8
     5     0     3     2     1     0     6
     6     1     0     4     0     1     6
     7     1     4     2     1     1     9
     8     4     2     1     1     1     9
     9     1     3     5     1     1    11
    10     1     2     1     2     2     8
    11     1     6     0     0     2     9
    12     1     4     4     1     1    11
    13     0     0     5     1     3     9
    14     2     2     2     2     2    10
    15     2     1     3     1     3    10
defects2 =
     1     3     2     1     3     0     9
     2     2     7     1     5     0    15
     3     0     3     4     2     0     9
     4     4     1     4     1     1    11
     5     0     0     2     0     3     5
LCL is smaller than 0 so LCL=0
LCL is smaller than 0 so LCL=0
UCL =
   17.1959
process is under statistical control
```

5.5 Acceptance Sampling by Attributes

Although inspecting each member of a population may be desirable to assure a predetermined level of quality, this is not usually feasible. *Acceptance sampling* is preferred over total analysis of the population for many reasons. Chemical and microbiological tests may require homogenization or destruction of the sample and make total inspection of the population impossible. Accuracy of the inspection may diminish due to fatigue or boredom of the inspector when the same tests are repeated too many times. The cost of inspection increases with the number of the tests due to the need for more staff, laboratory space, chemicals, and so on. It is usually practical to do quality control with samples and extend the results to the whole population.

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A sample is supposed to represent the whole population. Different protocols may be used for sampling. A sample may be taken from a production line with prespecified time intervals (i.e., sampling may be done with two hour intervals and a certain number or weight of a sample may be taken). The same procedure may be applied also with prespecified unit intervals (i.e., five consecutive items may be sampled after every 100 items). The sampling interval may be decided by using random number tables. Most statistics books include random number tables, and some hand calculators have built in programs to generate these numbers. Throwing dice may also be used with the same purpose. From trucks or store houses, samples are taken to represent all locations including the sides, center, and layers. When the commodities are in boxes or cases, samples should be taken from different containers. When the sampling plan does not indicate a number of the containers to be opened, the total sample is collected by opening the boxes or the cases according to the square root or cubic root principles (i.e., nine out of 81 cases or 100 out of 1,000,000 cases may be opened and an equal number of items may be collected from each). One method to randomly select these cases is to place individually numbered slips for each case in a box, shake, and withdraw one slip of paper, record the number, return the slip into the box, shake and repeat until the required sample size have been selected (FAO 1988). A lot may be accepted if the number of defectives in a sample set do not exceed a given *acceptance number* (*c*). The *sample size* to be taken from a lot and the acceptance number are determined with a *sampling plan*. This plan determines the fraction of the defectives acceptable. The acceptable number of defects in the sample is called the *acceptable quality level*. In a sampling plan, probability of accepting a lot (*Pa*) is related to the actual percentage of the defectives in the lot (*p*). The relation between P_a and p is visualized with an OC *(operating characteristics) curve*.

Example 5.35: Construction of an OC Curve by Using the Binomial Distribution Model

Construct OC curves for sampling plans with (i) $n = 10$, $c = 1$ and (ii) $n = 8$, $c = 1$ and compare.

Solution: When we use attributes to classify each unit as confirming or nonconfirming with the constant n and p we use the binomial distribution:

$$f(x,n,p) = \frac{n!}{x!(n-x)!} p^x (1-p)^{(n-x)}, \tag{5.3}$$

where $x \le c$ ($x = 0$ and $x = 1$). The actual fraction of defectives in the lot is p. We may use Equation 5.3 to determine the probability of accepting a lot (P_a) with varying values of p. When $n = 10$ and $p = 0\%$ with $x = 0$, probability of accepting the lot is $f(0,10,0) = 1$; with $x = 1$ the probability of accepting the lot is $f(1,10,0) = 0$. Probability P_a of accepting a sample with no defectives ($p = 0$) is $P_a = f(0,10,0) + f(1,10,0) = 1$. We repeat the same calculation with different levels of p:

p	0	0.1	0.2	0.3	0.4	0.5
P_a	1.0	0.74	0.38	0.15	0.04	0.01

The same procedure is followed to construct the OC curve with $n = 8$, $c = 1$:

p	0	0.1	0.2	0.3	0.4	0.5	0.6
P_a	1.0	0.81	0.50	0.26	0.11	0.03	0.01

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The OC curves for the both sampling plans are given in Figure E.5.35. When $n = 10$, $c = 1$ probability of accepting a lot (P_a) with 10% defectives ($p = 10\%$) is 74% ($P_a = 0.74$); there is $1 - 0.74 = 26\%$ probability for rejecting the lot. With the same plan, probability of accepting a lot with 40% defectives is drastically smaller; that is, 4% ($p = 0.40$, $P_a = 0.04$). It is also shown that when n is constant, P_a at constant p increases with an acceptance number.

MATLAB® code E.5.35 constructs the OC curves.

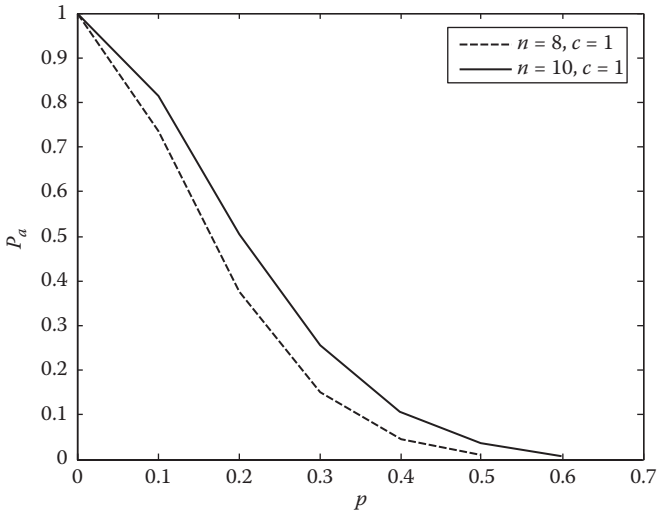


FIGURE E.5.35
OC curves for sampling plans of $n = 10$, $c = 1$, and $n = 8$, $c = 1$.

MATLAB® CODE E.5.35

Command Window:

```
clear all
close all

% construct an OC curves for sampling plan with n=10, c=1
p1=0:0.1:0.5;
table1=[p1; OCcurve1(0,0)+OCcurve1(1,0)
OCcurve1(0,0.1)+OCcurve1(1,0.1) OCcurve1(0,0.2)+OCcurve1(1,0.2)
OCcurve1(0,0.3)+OCcurve1(1,0.3) OCcurve1(0,0.4)+OCcurve1(1,0.4) OCcu
rve1(0,0.5)+OCcurve1(1,0.5)]

% construct an OC curves for sampling plan with n=10, c=1
p2=0:0.1:0.6;
table2=[p2; OCcurve2(0,0)+ OCcurve2(1,0)
OCcurve2(0,0.1)+OCcurve2(1,0.1) OCcurve2(0,0.2)+OCcurve2(1,0.2)
OCcurve2(0,0.3)+OCcurve2(1,0.3) OCcurve2(0,0.4)+OCcurve2(1,0.4)
OCcurve2(0,0.5)+OCcurve2(1,0.5) OCcurve2(0,0.6)+OCcurve2(1,0.6)]

% plot the OC curves
plot(table1(1,:),table1(2,:), '--'); hold on
plot(table2(1,:),table2(2,:), '-')
xlabel('p')
```

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```
ylabel('Pa')
legend('n=8,c=1','n=10,c=1')
```

M-file1:

```
function Pa1=OCcurve1(x,p)
n=10;
Pa1=(factorial(n)/(factorial(x)*factorial(n-x)))*(p^x)*(1-p)^(n-x);
```

M-file2:

```
function Pa2=OCcurve2(x,p)
n=8;
Pa2=(factorial(n)/(factorial(x)*factorial(n-x)))*(p^x)*(1-p)^(n-x);
```

When we run the code the following lines and Figure E.5.35. will appear on the screen:

```
table1 =
         0    0.1000    0.2000    0.3000    0.4000    0.5000
    1.0000    0.7361    0.3758    0.1493    0.0464    0.0107
table2 =
         0    0.1000    0.2000    0.3000    0.4000    0.5000
0.6000
    1.0000    0.8131    0.5033    0.2553    0.1064    0.0352
0.0085
```

MATLAB code 5.12 constructs an OC curve by using the Poisson distribution model for rare defects.

Example 5.36: OC Curve by Using the Poisson Distribution Model

We will employ MATLAB® code E.5.36.a to construct the cumulative Poisson distribution curves for probability of occurrences of $c = 2$ and $c = 3$.

Choose values of p, calculate np, and read P_a from Figure E.5.36.1 and construct the OC curves for (i) $n = 100$, $c = 3$, and (ii) $n = 100$, $c = 2$.

i. $n = 100$, $c = 3$:

p	0.001	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08	0.09	0.10
np	0.1	1	2	3	4	5	6	7	8	9	10
P_a	1.00	0.98	0.86	0.65	0.44	0.26	0.15	0.08	0.04	0.02	0.01

ii. $n = 100$, $c = 2$:

p	0.001	0.01	0.02	0.03	0.04	0.05	0.06	0.07	0.08
np	0.1	1	2	3	4	5	6	7	8
P_a	1.00	0.93	0.67	0.45	0.28	0.12	0.06	0.02	0.005

The OC curves with (-*x*-) $n = 100$, $c = 3$ and (--*o*--) $n = 100$, $c = 2$ are constructed by MATLAB code E.5.36.b and plotted in Figure E.5.36.2, where it should be noticed that when n = constant P_a decreases with c at the same p.

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MATLAB® CODE 5.12

Command Window:

```
close all
clear all

% enter the data
c=[0 1 2 4 6 8 10 15 20 30];
np=0:0.1:50;

% compute the probability of acceptance
for i=1:length(c)
     for j=1:length(np)
        Pa(i,j) = poisscdf(c(i),np(j)); % computes the Poisson cdf
at each of the values in Pa using the corresponding mean parameters
in c
      end
end

% plot the curve
semilogy(np,Pa, 'k-'); hold on
grid on
xlabel('np')
ylabel('Pa')
ylim([0.0001 1]);
text(41.5, 0.024, 'c=30')
text(30, 0.024, 'c=20')
text(24, 0.024, 'c=15')
text(17, 0.024, 'c=10')
text(15, 0.015, 'c=8')
text(12, 0.024, 'c=6')
text(10, 0.015, 'c=4')
text(6, 0.024, 'c=2')
text(5, 0.015, 'c=1')
text(2, 0.024, 'c=0')
```

When we run the code Figure 5.11 will appear on the screen.

Consumer and producer interests conflict in a sampling plan. The consumers desire reducing the probability of accepting lots including too many defectives, while the producers desire minimizing the probability of rejection of the lots with an acceptable number of defectives. In any sampling plan there is a risk of accepting a lot with an unacceptable level of defectives. This is called a *type II error* in statistics (Section 5.2) or *consumer's risk* in quality control literature. There is also a risk of rejecting a lot with less than unacceptable level of defectives, this is called a *type I error* in statistics (Section 5.2) or *producer's risk* in quality control literature. The desired quality level at which the probability of acceptance should be high is called the *acceptable quality level* (AQL) and the quality level below which lots are considered unacceptable is called the *lot tolerance percent defective* (LTPD). An OC curve may be constructed to compromise the interests of the consumer and the producer and required to pass through the points defined by (AQL,α) and (LTPD,β). This may be

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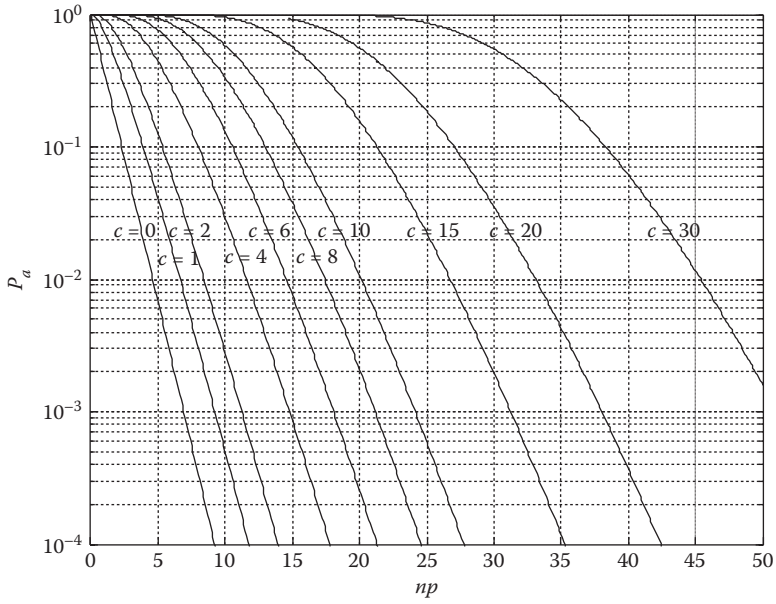


FIGURE 5.11
The cumulative Poisson distribution curves for probability of acceptance of c or less defects in a sample size of n selected from a population where the defective fraction is p.

MATLAB® CODE E.5.36.a

Command Window:

```
close all
clear all

% enter the data
c=[2 3];
np=0:0.1:10;

% compute the probability of acceptance
for i=1:length(c)
     for j=1:length(np)
        Pa(i,j) = poisscdf(c(i),np(j)); % computes the Poisson cdf at
each of the values in Pa using the corresponding mean parameters in c
      end
end

semilogy(np,Pa, 'k-'); hold on
grid on
xlabel('np')
ylabel('Pa')
ylim([0.001 1]);
text(9, 0.02, 'c=3')
text(9, 0.004, 'c=2')
```

When we run the code Figure E.5.36.1 will appear on the screen.

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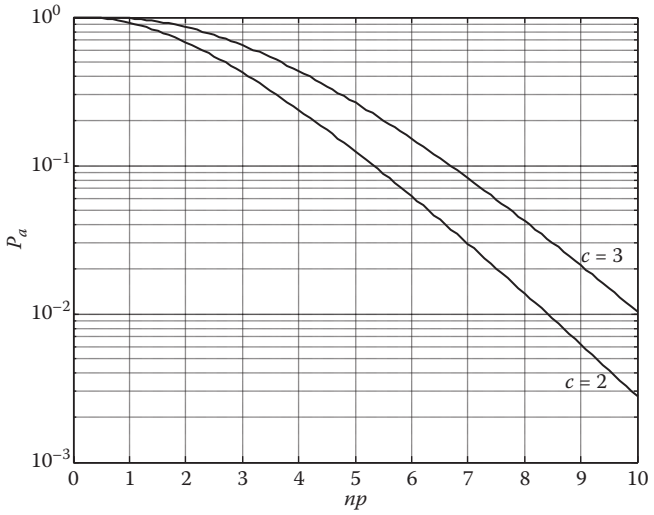


FIGURE E.5.36.1
The cumulative Poisson distribution curves for probability of occurrences of $c = 2$ and $c = 3$.

MATLAB® CODE E.5.36.b

Command Window:

```
clear all
close all

% construct the OC curve with n=100,c=3
p1=[0.001 0.01:0.01:0.10];
np1=[0.1 1:1:10];
Pa1=[1 0.98 0.86 0.65 0.44 0.26 0.15 0.08 0.04 0.02 0.01];
list1=[p1;np1;Pa1]

% construct the OC curve with n=100,c=2
p2=[0.001 0.01:0.01:0.08];
np2=[0.1 1:1:8];
Pa2=[1 0.93 0.67 0.45 0.28 0.12 0.06 0.02 0.005];
list2=[p2;np2;Pa2]

% plot the OC curve
plot(p1,Pa1,'k-')
hold on
plot(p2,Pa2,'--k')
xlabel('p')
ylabel('Pa')
legend('n=100,c=3','n=100,c=2')
```

When we run the code Figure E.5.36.2 will appear on the screen.

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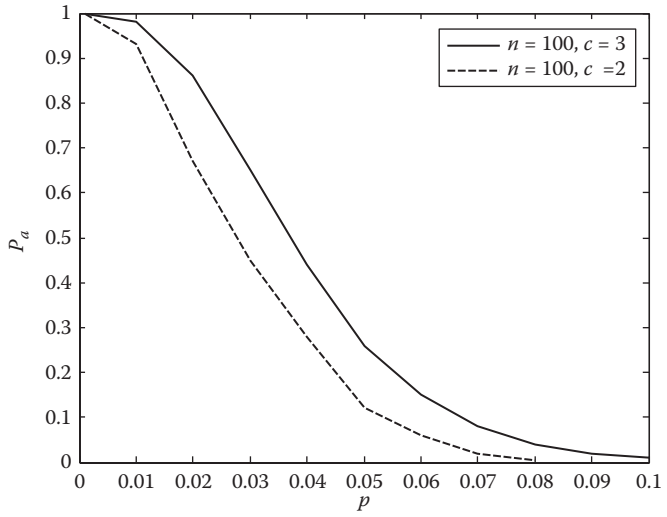


FIGURE E.5.36.2
The OC curves with $n = 100$, $c = 3$ (upper curve) and $n = 100$, $c = 2$ (lower curve).

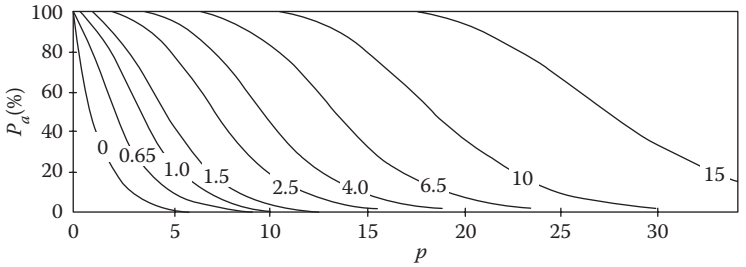


FIGURE 5.12
Operating characteristics curves for Military Plan 105. AQL (%) values are shown near the curves.

achieved by using a trial and error procedure with binomial distribution or with cumulative probability curves (Figure 5.12) when the requirements of the Poisson model are met.

Example 5.37: An OC Curve to Satisfy the Required LTPD and AQL Values

Use the cumulative probability curves (Figure 5.11) to construct an OC curve that (as nearly as possible) satisfies the following requirements: LTPD = 5%, β = 10% (consumer's risk), and AQL = 2%, α = 5% (producer's risk).

Solution: The OC is required to pass through the points (LTPD = 5%, β = 10%); that is, ($p = 0.05$, $P_a = 0.1$) and (AQL = 2%, α = 5%); that is, ($p = 0.02$, $P_a = 1 - \alpha = 0.95$). We will read c and np along $P_a = 0.1$ line from the cumulative probability curves (Figure 5.11):

c	1	2	3	4	5	6	7	8	9	10	11
np	3.9	5.3	6.5	8.0	9.3	10.5	11.8	13.0	14.2	15.5	16.7

(np = LTPDxn)

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When we read c and np along $P_a = 0.95$ line from the cumulative probability curves (Figure 5.11):

c	1	2	3	4	5	6	7	8	9	10	11
np	0.4	0.8	1.4	2.0	2.6	3.3	4.0	4.6	5.4	6.2	7.0

(np = AQLxn)

The required ratio of LTPD/AQL is 2.5. The LTPD/AQL may be calculated for the individual values of c (LTPD/AQL = LTPDxn/AQLxn):

c	1	2	3	4	5	6	7	8	9	10	11
LTPD/AQL	9.75	6.7	4.7	4.1	3.6	3.2	3.0	2.8	2.6	2.5	2.4

The LTPD/AQL = 2.5 when $c = 10$. The above data show that LTPD × n = 15.5 or AQL × n = 6.2 when $c = 10$; therefore, we may easily calculate $n = 310$, implying that we may compromise the producer and the consumer interests when $n = 310$ and $c = 10$. The OC curve is constructed by MATLAB® code E.5.37 and plotted in Figure E.5.37.

MATLAB® CODE E.5.37

Command Window:

```
clear all
close all

c=[1 2 3 4 5 6 7 8 9 10 11];
np1=[3.9 5.3 6.5 8.0 9.3 10.5 11.8 13.0 14.2 15.5 16.7];
np2=[0.4 0.8 1.4 2.0 2.6 3.3 4.0 4.6 5.4 6.2 7.0];
LTPD=0.05;
AQL=0.02;
Pa=[0 0.1 0.2 0.3 0.4 0.5 0.6 0.7 0.8 0.9 1];

% To find the ratio of LTPD/AQL=2.5, np1/np2 relation is used from
% equations of np=LTPD*n and np=AQL*n
for i=1:11;
    np1(i)./np2(i);
    if np1(i)./np2(i)==2.5;
        break
    end
end
cnew=c(i)
n=np1(i)/LTPD

% construct the OC curves for the sampling plan
p=0:0.003:0.032
lambda=n*p
x=0:1:cnew
y1=exp(-lambda);
y2=factorial(x);
y3=lambda.^x;
Pa=(y1.*y3)./y2;
```

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```
% plot the OC curve
plot(p,Pa,'ko-')
xlabel('p')
ylabel('Pa')
```

When we run the code Figure E.5.37 and the following lines will appear on the screen:

```
cnew =
    10

n =
   310

p =
         0    0.0030    0.0060    0.0090    0.0120    0.0150
0.0180    0.0210    0.0240    0.0270    0.0300

lambda =
         0    0.9300    1.8600    2.7900    3.7200    4.6500
5.5800    6.5100    7.4400    8.3700    9.3000

x =
     0     1     2     3     4     5     6     7     8     9    10
```

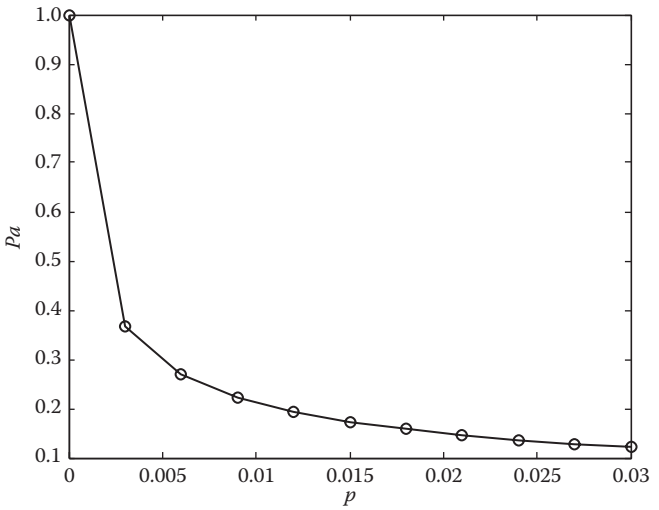


FIGURE E.5.37
OC curve with LTPD = 5%, β = 10%, AQL = 2%, and α = 5%.

The probability for defectives to pass a sampling plan is $P_a \times p$. *Average out going quality percentage* (AOQ%) of a lot is defined as

$$\text{AOQ} = \frac{(P_a)(p)(N-n)}{N}100. \tag{5.79}$$

When we destroy a sample set of n items from a lot of initial size N, we will have a remaining batch of size $N - n$.

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Example 5.38: Construction of the AOQ% Curves

Construct an AOQ% curve for the OC of $n = 10$, $c = 1$ with $N = 200$. The sample is destroyed in the analysis.

Solution: Read values of p and P_a from the previous OC curve example with the same sampling plan. AOQ% may be calculated as

$$\text{AOQ} = \frac{(P_a)(p)(N-n)}{N}100.$$

p	0.05	0.10	0.15	0.20	0.25	0.30	0.35	0.40
P_a	0.90	0.77	0.55	0.37	0.22	0.13	0.08	0.06
AOQ%	4.3	7.3	7.8	7.0	5.2	3.7	2.7	2.4

MATLAB® code E.5.38 computes a variation of the AOQ% with the actual level of the defectives in the product as shown in Figure E.5.38. The average outgoing quality limit (AOQL) is a built-in limit for the maximum probability of the defectives implemented by the sampling plan.

MATLAB® CODE E.5.38

Command Window:

```
clear all
close all

% enter the data
n=10;
p=[0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40];
Pa=[0.90 0.77 0.55 0.37 0.22 0.13 0.08 0.06];
N=200;

% compute the AOQ
i=1;
for i=1:8;
    AOQ(i)=(((Pa(i)*p(i)*(N-n)/N)*100));
    i=i+1;
end

% plot the figure
disp(AOQ)
plot(p,AOQ,'b-*')
xlabel('p')
ylabel('AOQ%')
grid on
```

When we run the code Figure E.5.38 will appear on the screen.

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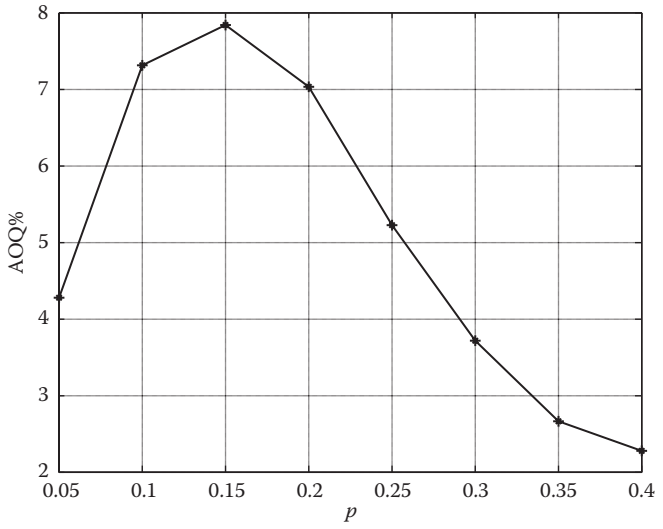


FIGURE E.5.38
Variation of the AOQ% with the actual level of the defectives in the product.

Example 5.39: Average Out Going Quality Limits from the OC Curves

Determine the AOQL from the OC curves of the sampling plans $n = 10$, $c = 1$ and $n = 8$, $c = 1$ for a sample lot size of $N = 200$. Which one of these plans would permit acceptance of a lower number of defectives?

Solution: We may read P_a versus p data from the OC curves of the previous example with the same sampling plans. AOQ% may be calculated as

$$\text{AOQ} = \frac{(P_a)(p)(N-n)}{N}100.$$

i. $n = 10$, $c = 1$

p	0	0.1	0.2	0.3	0.4	0.5
P_a	1.0	0.74	0.38	0.15	0.04	0.01
AOQ%	0	7.0	7.2	4.3	1.5	0.5

ii. $n = 8$, $c = 1$

p	0	0.1	0.2	0.3	0.4	0.5	0.6
P_a	1.0	0.81	0.50	0.26	0.11	0.03	0.01
AOQ%	0	7.8	9.6	7.5	4.2	1.4	0.6

A variation of the AOQ% with the actual level of the defectives p is computed by MATLAB® code E.5.39 and plotted in Figure E.5.39. The AOQL is a built-in limit of a sampling plan for the maximum level of the defectives that may be accepted. A sampling plan with $n = 10$, $c = 1$ permits acceptance of a lower number of defectives than the other one.

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MATLAB® CODE E.5.39

Command Window:

```
clear all
close all

% enter the data
N=200;
c=1;
n1=10;
p1=[0 0.1 0.2 0.3 0.4 0.5];
Pa1=[1.0 0.74 0.38 0.15 0.04 0.01];

% calculate the AOQs
i=1;
for i=1:6;
    AOQ1(i)=(((Pa1(i)*p1(i)*(N-n1)/N)*100));
    i=i+1;
end

n2=8;
p2=[0 0.1 0.2 0.3 0.4 0.5 0.6];
Pa2=[1.0 0.81 0.50 0.26 0.11 0.03 0.01];

m=1;
for m=1:7;
    AOQ2(m)=(((Pa2(m)*p2(m)*(N-n2)/N)*100));
    m=m+1;
end

% plot the figure
disp(AOQ1)
disp(AOQ2)
plot(p1,AOQ1, 'k-o', p2,AOQ2, 'k-*' ); hold on
xlabel('p')
ylabel('AOQ (%)')
legend('AOQL %=7.3%', 'AOQL %=9.6%')
```

When we run the code Figure E.5.39 will appear on the screen.

5.6 Standard Sampling Plans for Attributes

It is usually easier to use a readily available standard sampling plan, rather than making it. Military Plan 105, Codex Alimentarius sampling plans for aflatoxin contamination and Dodge and Romig tables are some of these plans. The forthcoming discussion describes the standard sampling plans for attributes in concise educational context; a reference to the original plans are strongly advised in commercial practices.

Military Plan 105 (Tables 5.12 through 5.15) was originally developed in the United States, but used internationally and also with nonmilitary purposes. It was made to insure that the average consumer uses the products at a prespecified acceptable quality level or

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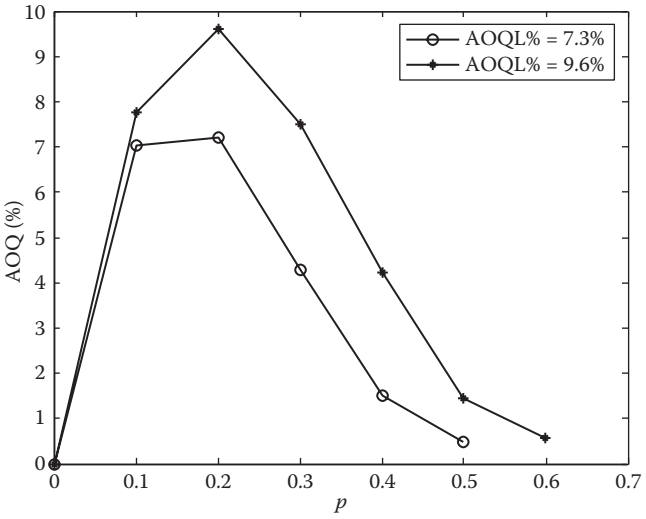


FIGURE E.5.39
Variation of the AOQ% with the actual level of the defectives.

TABLE 5.12

Military Plan 105 Sample Size Code Letters

Lot or Batch Size	I (Reduced)	II (Normal)	III (Tightened)
General Inspection Levels			
2–8	A	A	B
9–15	A	B	C
16–25	B	C	D
26–50	C	D	E
51–90	C	E	F
91–150	D	F	G
151–280	E	G	H
281–500	F	H	J
501–1200	G	J	K
1201–3200	H	K	L
3201–10,000	J	L	M
10,001–35,000	K	M	N
35,001–150,000	L	N	P
150,001–500,000	M	P	Q
500,001 and over	N	Q	R

better. The OC curves of each plan are supplied in Figure 5.11. The Military Sampling Plan 105 is based on the sampling inspection theories of Walter A. Shewhart, Harry Romig, and Harold Dodge. Its original version was issued in 1950. MIL STD 105D was issued in 1963, adopted by the American National Standards Institute (ANSI Z1.4) in 1971 and by the International Organization for Standardization (ISO 2859) in 1974. The latest revision

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TABLE 5.13

Military Plan 105 Master Table at Reduced Inspection Level

	AQL (%) →	0.010		0.015		0.025		0.040		0.065		0.10		0.15		0.25		0.40		0.65		1.0		1.5		2.5		4.0		6.5		10.0	
SC	**SS↓**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	A	R	A	R
A	**2**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	2
B	**2**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	2
C	2	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	0	2
D	**3**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3
E	**5**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4
F	**8**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	2	5
G	**13**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	**2**	**5**	3	6
H	**20**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8
J	**32**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8	7	10
K	**50**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8	7	10	10	13
L	**80**	0	1	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8	7	10	**10**	**13**	10	13
M	**125**	0	1	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8	7	10	**10**	**13**	**10**	**13**	10	13
N	200	0	1	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8	7	10	**10**	**13**	**10**	**13**	**10**	**13**	10	13
P	**315**	0	1	0	1	0	1	**0**	**2**	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8	7	10	**10**	**13**	**10**	**13**	**10**	**13**	**10**	**13**	10	13
Q	**500**	0	1	0	1	0	1	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8	7	10	**10**	**13**	**10**	**13**	**10**	**13**	**10**	**13**	**10**	**13**	10	13
R	**800**	0	1	0	1	**0**	**2**	1	3	1	4	**2**	**5**	3	6	5	8	7	10	**10**	**13**	**10**	**13**	**10**	**13**	**10**	**13**	**10**	**13**	**10**	**13**	10	13

Notes: SC: Sample size code letter
SS: Sample size
A: Acceptance number
R: Rejection number.

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TABLE 5.14

Military Plan 105 Master Table at Normal Inspection Level

		AQL (%) →	0.010		0.015		0.025		0.040		0.065		0.10		0.15		0.25		0.40		0.65		1.0		1.5		2.5		4.0		6.5		10.0	
S	C	SS↓	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R
	A	2	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	1	2
	B	3	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	1	2
	C	5	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	1	2
	D	8	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3
	E	13	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4
	F	20	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	5	6
	G	32	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	**5**	**6**	7	8
	H	50	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11
	J	80	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11	14	15
	K	125	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11	14	15	21	22		
	L	200	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11	14	15	**21**	**22**	21	22		
	M	315	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11	14	15	**21**	**22**	21	22	21	22		
	N	500	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11	14	15	**21**	**22**	**21**	**22**	**21**	**22**	21	22
	P	800	0	1	0	1	0	1	**1**	**2**	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11	14	15	**21**	**22**	**21**	**22**	**21**	**22**	**21**	**22**	21	22
	Q	1250	0	1	0	1	0	1	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11	14	15	**21**	**22**	**21**	**22**	**21**	**22**	**21**	**22**	**21**	**22**	21	22
	R	2000	0	1	0	1	**1**	**2**	2	3	3	4	**5**	**6**	7	8	10	11	14	15	**21**	**22**	**21**	**22**	**21**	**22**	**21**	**22**	**21**	**22**	**21**	**22**	21	22

Notes: SC: Sample size code letter
SS: Sample size
A: Acceptance number
R: Rejection number.

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TABLE 5.15

Military Plan 105 Master Table at Tightened Inspection Level

	AQL (%) →	0.010		0.015		0.025		0.040		0.065		0.10		0.15		0.25		0.40		0.65		1.0		1.5		2.5		4.0		6.5		10.0	
S C	**S S↓**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	**A**	**R**	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R	A	R
A	**2**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1
B	**3**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	1	2
C	**5**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	1	2
D	**8**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	1	2	1	2
E	**13**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3
F	**20**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4
G	**32**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6
H	**50**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6	8	9
J	**80**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6	8	9	12	13
K	**125**	0	1	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6	8	9	**12**	**13**	18	19
L	**200**	0	1	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6	8	9	**12**	**13**	18	19	18	19
M	**315**	0	1	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6	8	9	**12**	**13**	18	19	18	19	18	19
N	**500**	0	1	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6	8	9	**12**	**13**	18	19	18	19	18	19	18	19
P	**800**	0	1	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6	8	9	**12**	**13**	18	19	18	19	18	19	18	19	18	19
Q	**1250**	0	1	0	1	**1**	**2**	**1**	**2**	**1**	**2**	2	3	3	4	5	6	8	9	**12**	**13**	18	19	18	19	18	19	18	19	18	19	18	19
R	**2000**	0	1	0	1	**1**	**2**	1	2	2	3	3	4	5	6	8	9	**12**	**13**	18	19	18	19	18	19	18	19	18	19	18	19	18	19

Notes: SC: Sample size code letter
SS: Sample size
A: Acceptance number
R: Rejection number.

of MIL STD 105 was issued in 1989 but canceled in 1991. The standards that are based on MIL STD 105 are continuously being updated and revised, while the basic tables remain almost the same. MIL STD 105D had the largest number of citations on the Internet by far while this book was in preparation; therefore, the following examples are based on MIL STD 105D. It is strongly advised using the most relevant of the alternative standards in commercial activities. The plan has three inspection levels. *Inspection level I* is *reduced inspection* and applied when the consumer accepts taking greater than the normal risk (i.e., the preceding 10 or more lots has been accepted with no rejections). *Inspection level II* is the *normal inspection* level. *Inspection level III* is *tightened inspection* and used when the buyer wants to minimize his risk. It might be used when frequent rejections (i.e., two lots out of five) have been experienced.

Example 5.40: Use of the Military Plan 105 for Sampling of Apples

a. A truck load (approximately 50,000) of apples are accepted by a processor if they contain less than 1% defectives (AQL = 1%). Make a sampling plan by using the Military Plan 105 with a normal inspection level.

Solution: Lot size is 50,000 (between 35,001 and 150,000) for normal inspection, the code letter is N (Table 5.12) and the sample size is $n = 500$ (Table 5.14). With the given sample size and AQL = 1%, we determine acceptance number = 10 (Table 5.14). The rejection number is 11. MATLAB® code E.5.40.a produces the same result.

MATLAB® CODE E.5.40.a

Command Window:

```
clear all
close all
format compact

% enter the data
LEVEL=2
AQL=1
LotSize=50000

% obtain the result
[SS  AN]=MILSTD105(LEVEL,LotSize,AQL);
SampleSize=SS;
AcceptanceNumber=AN;
fprintf('\nSample size is %2.1f, Acceptance number is %2.1f\n',
SampleSize, AcceptanceNumber);
```

M-file:

```
function [SampleSize AcceptanceNumber] =
MILSTD105(LEVEL,LotSize,AQL)

%  the data employed in this code were taken from MIL STD 105D

% input the data
AcceptanceNumber=123456789;
```

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```
LSL=[2 9 16 26 51 91 151 281 501 1201 3201 10001 35001 150001
500001; 8 15 25 50 90 150 280 500 1200 3200 10000 35000 150000
500000 1500000]; % Lot Size limits

AQLR=[0 0.013 0.020 0.032 0.053 0.083 0.126 0.171 0.33 0.53 0.82
2.0 5.25 7.75;0.012 0.019 0.031 0.052 0.082 0.125 0.170 0.32 0.52
0.81 1.99 5.24 7.74 10.25]; % AQL range

SampleSizeM1=[2 2 2 2 2 3 5 8 13 20 32 50 80 125 200]; % sample
size matrix at REDUCED INSPECTION LEVEL

SampleSizeM2=[2 3 5 8 13 20 32 50 80 125 200 315 500 800 1250]; %
sample size matrix at NORMAL INSPECTION LEVEL

SampleSizeM3=[3 5 8 13 20 32 50 80 125 200 315 500 800 1250 2000];
% sample size matrix at TIGHTENED INSPECTION LEVEL

cMatrix1=[0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;0 0 0 0 0 0 0 0 0 0 0 0 0
0 0 0;0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
0;0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;0
0 0 0 0 0 0 0 0 0 0 0 0 0 0 1;0 0 0 0 0 0 0 0 0 0 0 0 0 0 1 1;0 0 0
0 0 0 0 0 0 0 0 0 1 1 2;
0 0 0 0 0 0 0 0 0 0 0 0 1 1 2 3;0 0 0 0 0 0 0 0 0 0 0 1 1 2 3 5;0 0
0 0 0 0 0 0 0 0 1 1 2 3 5 7;
0 0 0 0 0 0 0 0 0 1 1 2 3 5 7 10;0 0 0 0 0 0 0 0 1 1 2 3 5 7 10
10;0 0 0 0 0 0 0 1 1 2 3 5 7 10 10 10;
0 0 0 0 0 0 1 1 2 3 5 7 10 10 10 10]; % acceptance number at
REDUCED INSPECTION LEVEL

cMatrix2=[0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;0 0 0 0 0 0 0 0 0 0 0 0 0 0
0;0 0 0 0 0 0 0 0 0 0 0 0 0 0 1;0 0 0 0 0 0 0 0 0 0 0 0 1 1;0 0 0
0 0 0 0 0 0 0 1 1 2;0 0 0 0 0 0 0 0 0 0 1 1 2 3;0 0 0 0 0 0 0
0 0 1 1 1 2 3 5;0 0 0 0 0 0 0 0 0 1 1 2 3 5 7;0 0 0 0 0 0 0 1 1 2
3 5 7 10;0 0 0 0 0 0 1 1 1 2 3 5 7 10 14;
0 0 0 0 0 0 1 1 2 3 5 7 10 14 21;0 0 0 0 0 1 1 2 3 5 7 10 14 21
21;0 0 0 1 1 1 2 3 5 7 10 14 21 21 21;
0 0 1 1 2 3 5 7 10 14 21 21 21 21 21;1 1 1 2 3 5 7 10 14 21 21 21
21 21 21]; % acceptance number at NORMAL INSPECTION LEVEL

cMatrix3=[0 0 0 0 0 0 0 0 0 0 0 0 0 0 0;0 0 0 0 0 0 0 0 0 0 0 0 0
0 1;
0 0 0 0 0 0 0 0 0 0 0 0 0 1 1;0 0 0 0 0 0 0 0 0 0 0 1 1 1 2;0 0
0 0 0 0 0 0 0 0 1 1 1 2 3;
0 0 0 0 0 0 0 0 0 0 1 1 1 2 3 5;0 0 0 0 0 0 0 0 1 1 1 2 3 5 8;0 0
0 0 0 0 0 1 1 1 2 3 5 8 12;
0 0 0 0 0 0 0 1 1 1 2 3 5 8 12 18;0 0 0 0 0 0 1 1 1 2 3 5 8 12 18
18;0 0 0 0 0 1 1 1 2 3 5 8 12 18 18 18;0 0 0 0 1 1 1 2 3 5 8 12 18
18 18 18;0 0 0 1 1 1 2 3 5 8 12 18 18 18 18 18;0 0 1 1 1 2 3 5 8 12
18 18 18 18 18 18;0 1 1 1 2 3 5 8 12 18 18 18 18 18 18 18]; %
acceptance number at TIGHTENED INSPECTION LEVEL

if LEVEL==1
   cMatrix=cMatrix1;
   SampleSizeM= SampleSizeM1;
end
```

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```
if LEVEL==2
   cMatrix=cMatrix2;
   SampleSizeM= SampleSizeM2;
end

if LEVEL==3
   cMatrix=cMatrix3;
   SampleSizeM=SampleSizeM3;
end

for i=1:length(LSL)
if LotSize >= LSL(1, i)
   if LotSize<=LSL(2 ,i)
          for j=1:length(AQLR)
            if AQL>=AQLR(1,j)
              if AQL<=AQLR(2,j)
                 SampleSize=SampleSizeM(i);
                 AcceptanceNumber=cMatrix(i,j);
              end
            end
          end
    end
  end
end

if AcceptanceNumber==123456789
   fprintf('CODE CAN NOT OFFER A SAMPLING PLAN, at leat one of the
input parameters LEVEL, AQL or LotSize is exceeding the range of
the database\n');
end
```

When we run the code the following lines will appear on the screen:

```
LEVEL =
     2
AQL =
     1
LotSize =
       50000

Sample size is 500.0, Acceptance number is 10.0
```

b. What is P_a (probability of acceptance) of this plan when $p = 1\%$ and $p = 8\%$?

   Solution: OC curves of the Military Plan 105 is given in Figure 5.11. The curve for AQL = 1% shows that when $p = 1\%$ P_a is 94%; when $p = 8\%$ P_a is 4%.

c. Make a tightened sampling plan.

   Solution: Lot size is 50,000 (between 35,001 and 150,000) for tightened inspection, the code letter is P (Table 5.12) and the sample size is $n = 800$. With the given sample size and AQL = 1%, we determine the acceptance number = 12 (Table 5.15). MATLAB code E.5.40.b produces the same result.

d. Make a sampling plan if the apples are shipped in crates (100 crates, 500 apples in each crate).

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MATLAB® CODE E.5.40.b

Command Window:

```
clear all
close all
format compact

% enter the data
LEVEL=3
AQL=1
LotSize=50000

% obtain the result
[SS  AN]=MILSTD105(LEVEL,LotSize,AQL);
SampleSize=SS;
AcceptanceNumber=AN;
fprintf('\nSample size is %2.1f, Acceptance number is %2.1f\n',
SampleSize, AcceptanceNumber);
```

When we run the code the following lines will appear on the screen:

```
LEVEL =
     3
AQL =
     1
LotSize =
       50000

Sample size is 800.0, Acceptance number is 12.0
```

Solution: Since no levels are specified we may use the previous sampling plan at a normal level: $n_{apples} = 500$, an acceptance number = 10. We should also determine how many crates should be opened for sampling. There are 100 crates, the sample size is between 91 and 150 corresponding to the code letter F at a normal inspection level (Table 5.12) with $n_{crates} = 20$ (Table 5.15). The $n_{apples}/n_{crates} = 25$, implying that we should open 20 crates and take 25 apples from each. If we should find 10 or less defectives we may accept the lot, we will reject it otherwise. Details of the computations are presented in MATLAB code E.5.40.c.

Example 5.41: Use of the Military Plan 105 for Sampling of Individually Wrapped Sliced Cheese

A cheese producer markets its products in boxes of 100 packages. Each package contains 18 individually wrapped slices. Make an acceptance sampling plan for a purchase of 100 boxes of cheese. Find out how many slices should be analyzed. How many boxes and packages should be opened? The supplier has been doing business with this company for 6 months and it is known that none of their shipments has ever been rejected. The AQL of the sampling plan is required to be 0.065%.

Solution: We may use Military Plan 105 with *reduced inspection level* since the supplier has been doing business with this company for 6 months and none of their shipments has ever been rejected. Lot size of boxes is 100 (between 91 and 150), for the reduced inspection, the code letter is D (Table 5.12) and $n_{box} = 3$ (Table 5.13).

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MATLAB® CODE E.5.40.c

Command Window:

```
clear all
close all
format compact

% enter the data
LEVELapples=2;
AQLapples=1;
LotSizeApples=50000;

% determine the number of the apples to be sampled
[SS1  AN1]=MILSTD105(LEVELapples,LotSizeApples,AQLapples);
SampleSizeApples=SS1;
fprintf('\n\nSample size for the apples is %2.1f \n', SS1)
fprintf('Acceptance number for the apples is %2.1f\n', AN1)

% Determine the number of the crates to be opened
LEVELcrates=2;
AQLcrates=1;
LotSizecrates=100;
[SS2  AN2]=MILSTD105(LEVELcrates,LotSizecrates,AQLcrates);
SampleSizeCrates=SS2;
fprintf('Sample size for the crates is %2.1f \n', SS2)
fprintf('Acceptance number for the crates is %2.1f \n', AN2)


[N1 N2 N3 N4]=NPI(SampleSizeCrates,SampleSizeApples);
fprintf('take %2.1f apples from %2.1f crates and %2.1f apples from
%2.1f crates \n', N3, N2, N1, N4)
```

M-file:

```
function [N1 N2 N3 N4]=NPI(SSSU,SSLU)
% NPI=Number of the Smaller Items Per Larger Item
% SSSU=Sample Size of the Smaller Unit
% SSLU=Sample Size of the Larger Unit

% Determine the number of the smaller units to be taken from each
of the larger units opened
N1=fix(SSLU/SSSU);
%  function fix(n) rounds the elements of n to the nearest integers
towards zero
N2=SSLU-(SSSU*N1);
N3=N1+1;
N4=SSSU-N2;
```

When we run the code the following lines will appear on the screen:

```
Sample size for the apples is 500.0
Acceptance number for the apples is 10.0
```

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```
Sample size for the crates is 20.0
Acceptance number for the crates is 0.0
take 26.0 apples from 0.0 crates and 25.0 apples from 20.0 crates
```

It should be noted here that 500 apples should be sampled from 20 crates. If 10 or less of the apples have some kind of damage we can accept the lot. Acceptance number 0 of crates means that none of the crates should have any kind of damage. We will take 25 apples from each of the 20 crates.

Lot size of the packages is (100)(100) = 10,000, for reduced inspection the code letter is J (Table 5.12) and $n_{packages} = 32$ (Table 5.13).

Lot size of the slices (100)(100)(18) = 180,000. For the reduced inspection the code letter is M (Table 5.12), $n_{slices} = 125$, with AQL = 0.065% acceptance number = 0 and rejection number = 1 (Table 5.13).

The sampling plan implies that three boxes should be opened, 11 packages should be taken from two of them and 10 packages should be taken from the third box. Since 125/32 = 3.9 (not an integer) we may make the partitioning of the slices as $125 = 29 \times 4 + 3 \times 3$, therefore 4 slices should be taken from each of the first 29 packages and 3 slices should be taken from the remaining 3 packages. If any of the slices are defective, the lot should be rejected. The same results are also produced with MATLAB® code E.5.41.

Example 5.42: Use of the Military Plan 105 for Sampling of Products with Seasonally Changing Risk of Spoilage

One thousand cases of eggs are inspected by the purchasing department of a market at each delivery. Each case contains 20 boxes. There are 12 eggs in each box. It is known that the eggs may spoil fast in the summer and there is a very small possibility for spoilage in winter. Make separate sampling plans for each season (i.e., fall/spring, winter and summer). Determine how many eggs should be taken from how many boxes and cases; also determine the acceptance number. The AQL is required to be maintained as small as possible.

Solution: We may use the normal inspection level in spring and fall, reduced inspection level in winter, and tightened inspection level in the summer. The lot size is 1000 with cases (1000)(20) = 20,000 with boxes (1000)(20)(12) = 240,000 with eggs. The following sampling plans may be suggested at different levels:

	Cases	Boxes	Eggs (AQL = 0.01%)
Level I	code letter = G $n_{cases} = 13$	code letter = K $n_{boxes} = 50$	code letter = M $n_{eggs} = 125$, c = 0
Level II	code letter = J $n_{cases} = 80$	code letter = M $n_{boxes} = 315$	code letter = P $n_{eggs} = 800$, c = 0
Level III	code letter = K $n_{cases} = 125$	code letter = N $n_{boxes} = 500$	code letter = Q $n_{eggs} = 1250$, c = 0

Code letters were determined from Table 5.12. Sample size and acceptance numbers were determined from Tables 5.13, 5.14, and 5.15 for levels I, II, and III, respectively.

	n_{boxes}/n_{cases}	n_{eggs}/n_{boxes}
Level I	3.84	2.5
Level II	3.93	2.53
Level III	4	2.5

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MATLAB® CODE E.5.41

Command Window:

```
clear all
close all
format compact

% data
LEVEL=1
LotSizeSlices=180000;
LotSizePackages=10000;
LotSizeBoxes=100;
AQL=0.065;

% sampling plan for boxes
[SS1 AN1]=MILSTD105(LEVEL,LotSizeBoxes,AQL);
SampleSizeBoxes=SS1;
AcceptanceNumberBoxes=AN1;
fprintf('Sample size for the boxes is %2.1f \n', SS1)
fprintf('Acceptance number for the boxes is %2.1f \n', AN1)

% sampling plan for packages
[SS2  AN2]=MILSTD105(LEVEL,LotSizePackages,AQL);
SampleSizePackages=SS2;
AcceptanceNumberPackages=AN2;
fprintf('Sample size for the packages is %2.1f \n', SS2)
fprintf('Acceptance number for the packages is %2.1f \n', AN2)

% sampling plan for slices
[SS3  AN3]=MILSTD105(LEVEL,LotSizeSlices,AQL);
SampleSizeSlices=SS3;
AcceptanceNumberSlices=AN3;
fprintf('Sample size for the slices is %2.1f \n', SS3)
fprintf('Acceptance number for the slices is %2.1f \n', AN3)

% determine the number of the packages taken from each box opened
[N1 N2 N3 N4]=NPI(SampleSizeBoxes,SampleSizePackages);
fprintf('take %2.1f packages from %2.1f boxes and %2.1f packages
from %2.1f boxes \n', N3, N2, N1, N4)

% determine the number of the slices taken from each package opened
[N5 N6 N7 N8]=NPI(SampleSizePackages,SampleSizeSlices);
fprintf('take %2.1f slices from %2.1f packages and %2.1f slices
from %2.1f packages \n', N7, N6, N5, N8)
```

When we run the code the following lines will appear on the screen:

```
LEVEL =
     1
Sample size for the boxes is 3.0
Acceptance number for the boxes is 0.0
```

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```
Sample size for the packages is 32.0
Acceptance number for the packages is 0.0
Sample size for the slices is 125.0
Acceptance number for the slices is 0.0
take 11.0 packages from 2.0 boxes and 10.0 packages from 1.0 boxes
take 4.0 slices from 29.0 packages and 3.0 slices from 3.0 packages
```

	Sampling Plan
Level I	Open 13 cases, take 3 boxes from the first 2 and 4 boxes from the remaining 11 cases. Take 2 eggs from the first 25 boxes, take 3 eggs from the remaining 25 boxes.
Level II	Open 80 cases, take 3 boxes from the first 5 and 4 boxes from the remaining 75 cases. Take 2 eggs from the first 145 boxes, take 3 eggs from the remaining 170 boxes.
Level III	Open 125 cases, take 4 boxes from each. Take 2 eggs from the first 250 boxes, take 3 eggs from the remaining 250 boxes.

The same results are also produced with MATLAB® code E.5.42.

The International Commission on Microbiological Specifications on Foods (ICMSF) provides two-class and three-class sampling plans for microbiological assessment of the foods. Two-class plans are essentially for pathogens, where a presence/absence test is performed, where a unit with the microbial presence is named defective regardless of the number of the colony forming units. Three-class plans are frequently used as hygiene indicators, where microbial counts are also important. In three-class plans, parameter m distinguishes good quality from marginally acceptable quality. Parameter M is the maximum allowable microbial presence to regard a food marginally acceptable. If a two-class plan is used in a hygiene related study, parameter m may be employed as a criterion to distinguish a defective unit from an acceptable unit, where a unit may be regarded acceptable as long as its microbial presence does not exceed m. Parameters m and M may be expressed either as number or log number of the colony forming units per gram of the food (cfu/g). Parameter m is referred to as *"Food Safety Objective"* (European Commission Report 1999; Legan, et al. 2001). Parameters n, c, m, and M are given explicitly for different food groups regarding the microorganism involved, for example, for cheese other than hard or fresh made from raw or thermized milk $n = 5$, $c = 2$, $m = 1000$ cfu/g, and $M = 10{,}000$ cfu/g for *Staphylococcus aureous*; while $n = 5$, $c = 0$ for *Listeria monocytogenes* (European Commission Report 1999).

Example 5.43: ICMSF Sampling Plans for Microbiological Analysis

The following table gives values of parameters n and c employed in EU applications of the ICMSF sampling plans (European Commission Report 1999). The similarity of the levels of concern to those of the Military Plan 105 is obvious.

Health Hazard	Reduced Degree of Concern	Normal Degree of Concern	Increased Degree of Concern
Low and indirect	Case 4 $n = 5$, $c = 3$	Case 5 $n = 5$, $c = 2$	Case 6 $n = 5$, $c = 1$
Moderate, direct with limited spread	Case 7 $n = 5$, $c = 2$	Case 8 $n = 5$, $c = 1$	Case 9 $n = 10$, $c = 1$
Moderate, direct with potentially extensive spread	Case 10 $n = 5$, $c = 0$	Case 11 $n = 10$, $c = 0$	Case 12 $n = 20$, $c = 0$
Severe and direct	Case 13 $n = 15$, $c = 0$	Case 14 $n = 30$, $c = 0$	Case 15 $n = 60$, $c = 0$

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MATLAB® CODE E.5.42

Command Window:

```
clear all
close all
format compact

fprintf('\n SAMPLING PLAN FOR WINTER\n')
LEVEL=1
SeasonalPlan(LEVEL)

fprintf('\n SAMPLING PLAN FOR SPRING & FALL\n')
LEVEL=2
SeasonalPlan(LEVEL)

fprintf('\n SAMPLING PLAN FOR SUMMER\n')
LEVEL=3
SeasonalPlan(LEVEL)
```

M-file1:

```
function SeasonalPlan(LEVEL)

% data
LotSizeEggs=240000;
LotSizeBoxes=20000;
LotSizeCases=1000;
AQL=0.01;

% sampling plan for eggs
[SS1 AN1]=MILSTD105(LEVEL,LotSizeEggs,AQL);
SampleSizeEggs=SS1;
AcceptanceNumberEggs=AN1;
fprintf('Sample size for the eggs is %2.1f \n', SS1)
fprintf('Acceptance number for the eggs is %2.1f \n', AN1)

% sampling plan for boxes
[SS2  AN2]=MILSTD105(LEVEL,LotSizeBoxes,AQL);
SampleSizeBoxes=SS2;
AcceptanceNumberBoxes=AN2;
fprintf('Sample size for the boxes is %2.1f \n', SS2)
fprintf('Acceptance number for the boxes is %2.1f \n', AN2)

% sampling plan for cases
[SS3  AN3]=MILSTD105(LEVEL,LotSizeCases,AQL);
SampleSizeCases=SS3;
AcceptanceNumberCases=AN3;
fprintf('Sample size for the cases is %2.1f \n', SS3)
fprintf('Acceptance number for the cases is %2.1f \n', AN3)

% determine the number of the boxes taken from each case opened
[N1 N2 N3 N4]=NPI(SampleSizeCases,SampleSizeBoxes);
fprintf('take %2.1f boxes from %2.1f cases and %2.1f boxes from
%2.1f cases \n', N3, N2, N1, N4)
```

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```
% determine the number of the eggs taken from each box opened
[N5 N6 N7 N8]=NPI(SampleSizeBoxes,SampleSizeEggs);
fprintf('take %2.1f eggs from %2.1f boxes and %2.1f eggs from %2.1f
boxes \n', N7, N6, N5, N8)
```

When we run the code the following lines will appear on the screen:

```
 SAMPLING PLAN FOR WINTER
LEVEL =
     1
Sample size for the eggs is 125.0
Acceptance number for the eggs is 0.0
Sample size for the boxes is 50.0
Acceptance number for the boxes is 0.0
Sample size for the cases is 13.0
Acceptance number for the cases is 0.0
take 4.0 boxes from 11.0 cases and 3.0 boxes from 2.0 cases
take 3.0 eggs from 25.0 boxes and 2.0 eggs from 25.0 boxes

 SAMPLING PLAN FOR SPRING & FALL
LEVEL =
     2
Sample size for the eggs is 800.0
Acceptance number for the eggs is 0.0
Sample size for the boxes is 315.0
Acceptance number for the boxes is 0.0
Sample size for the cases is 80.0
Acceptance number for the cases is 0.0
take 4.0 boxes from 75.0 cases and 3.0 boxes from 5.0 cases
take 3.0 eggs from 170.0 boxes and 2.0 eggs from 145.0 boxes

 SAMPLING PLAN FOR SUMMER
LEVEL =
     3
Sample size for the eggs is 1250.0
Acceptance number for the eggs is 0.0
Sample size for the boxes is 500.0
Acceptance number for the boxes is 0.0
Sample size for the cases is 125.0
Acceptance number for the cases is 0.0
take 5.0 boxes from 0.0 cases and 4.0 boxes from 125.0 cases
take 3.0 eggs from 250.0 boxes and 2.0 eggs from 250.0 boxes
```

MATLAB® code E.5.43 data files are introduced in the form of [n c m M]. The code performs the ICMSF sampling test for the given number of the units tested, number of the positive microbial counts, and the number of the colonies found in each count.

The Dodge and Romig tables (Dodge and Romig 1959) were constructed for rectifying inspection where rejected lots are subjected to 100% inspection. There are Dodge–Romig tables for the desired LTPD (Tables 5.16 and 5.17) or AOQL levels (Tables 5.18 and 5.19). The AOQL tables gained more popularity than the others. They show the sample size, *n*, and acceptance number, *c*, for the specified AOQL. They also show the resulting LTPD when the probability of acceptance, P_a, on the OC curve is equal to 0.10. During the recent years more efficient ways of using the Dodge and Romig method after minimizing the average total inspection ATI = $n + (N - n) \times (1 - P_a)$ by using a computer program have gained popularity.

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MATLAB® CODE E.5.43

Command Window:

```
clear all
close all
format compact

% data files
FILE1=[5 2 5e5 5e6]; % aerobic mesophilic bacteria in minced meat
(cfu/g, guideline)
FILE2=[5 2 50 500]; % Escherichia coli in minced meat (cfu/g,
guideline)
FILE3=[5 0 0 0]; % Salmonella in minced meat (cfu/25 g minced meat)
FILE4=[5 2 5e2 5e3]; % Escherichia coli in meat preparations (cfu/g,
guideline)
FILE5=[5 1 5e2 5e3]; % Staphylococcus aureous  in meat preparations
(cfu/g, guideline)
FILE6=[5 0 0 0]; % Salmonella in meat portions (cfu/5 g meat)
FILE7=[5 0 0 0]; % Salmonella in egg products (cfu/25 g or mL egg
product)
FILE8=[5 2 0 0]; % aerobic mesophilic bacteria in egg products
(cfu/25 g or mL egg product)
FILE9=[5 0 0 0]; % Salmonella in raw cow's drinking milk (cfu/25 g
milk)
FILE10=[5 2 1e3 1e5]; % Staphylococcus aureous in hard cheese made
from raw or thermized milk (cfu/g chese)

%  ENTER THE EXPERIMENTAL DATA
units=5; % number of the units tested
positives=2; % number of the unts with microbial growth
COUNTS=[4.7e6 3e3  4.5e6 4.9e6 4.9e6];
%  choose a data file
FILE=FILE1;
maxCOUNTS=max(COUNTS);
fprintf('\n units tested=%2i, positives=%2i, maxCount=%3.2g',units,p
ositives,maxCOUNTS);

if units<FILE(1)
     fprintf(', number of units tested is smaller than expected,
SAMPLE IS REJECTED');
end

if positives>FILE(2)
     fprintf(',  there are more defectives than expected, SAMPLE IS
REJECTED');
end
     if maxCOUNTS>FILE(4)
        fprintf(', microbial presence is too high, SAMPLE IS
REJECTED');
end

if units>=FILE(1)
        if positives<=FILE(2)
            if maxCOUNTS<FILE(3)
```

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```
                fprintf(', SAMPLE IS ACCEPTED');
            end
        end
end

if units>=FILE(1)
    if positives<=FILE(2)
         if maxCOUNTS>FILE(3)
               if maxCOUNTS<FILE(4)
                fprintf(', SAMPLE IS MARGINALLY ACCEPTABLE');
            end
        end
     end
end
```

With the given number of units, acceptance sampling tests were performed for aerobic mesophilic bacteria in minced meat after setting data file as:

```
FILE=FILE1; % aerobic mesophilic bacteria in minced meat
```

when
`COUNTS=[1e5 3e5  6e5 5e5 4.5e5];` the following lines will appear on the screen:

```
units tested= 5, positives= 2, maxCount=3e+007, microbial presence
is too high, SAMPLE IS REJECTED
```

when
`COUNTS=[1e3 3e3  6e3 5e3 4.5e3];` the following lines will appear on the screen:

```
units tested= 5, positives= 2, maxCount=6e+003, SAMPLE IS ACCEPTED

units tested= 3, positives= 2, maxCount=6e+003, number of units
tested is smaller than expected, SAMPLE IS REJECTED
```

when
`COUNTS=[5.7e6 3e3  5.5e6 5e6 5.9e6];`
the following lines will appear on the screen:

```
units tested= 3, positives= 2, maxCount=5.9e+006, number of units
tested is smaller than expected, SAMPLE IS REJECTED, microbial
presence is too high, SAMPLE IS REJECTED
```

when
`COUNTS=[4.7e6 3e3  4.5e6 4.9e6 4.9e6];`
the following lines will appear on the screen:

```
units tested= 5, positives= 2, maxCount=4.9e+006, SAMPLE IS
MARGINALLY ACCEPTABLE
```

Example 5.44: Sampling Plan with Dodge and Romig (1959) Tables for Apples

a. A truck load (approximately 50,000) of apples is required not to pass inspection if they contain more than (i) 3% defectives (LTPD = 3%) and (ii) 2% defectives (LTPD = 2%). An average load is expected to have 0.61–0.80% defectives. Make a sampling plan. (iii) Make the above sampling plans when an average load is expected to have 0–0.02% defectives.

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TABLE 5.16

Single Sampling Table for LTPD = 2.0%

	Process Average 0 to 0.02%			Process Average 0.03 to 0.20%			Process Average 0.21 to 0.40%			Process Average 0.41 to 0.60%			Process Average 0.61 to 0.80%			Process Average 0.81 to 1.00%		
Lot Size	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**
1–75	All	0	0	All	0	0	All	0	0	All	0	0	All	0	0	All	0	0
76–100	70	0	0.16	70	0	0.16	70	0	0.16	70	0	0.16	70	0	0.16	70	0	0.16
101–200	85	0	0.25	85	0	0.25	85	0	0.25	85	0	0.25	85	0	0.25	85	0	0.25
201–300	95	0	0.26	95	0	0.26	95	0	0.26	95	0	0.26	95	0	0.26	95	0	0.26
301–400	100	0	0.28	100	0	0.28	100	0	0.28	160	1	0.32	160	1	0.32	160	1	0.32
401–500	105	0	0.28	105	0	0.28	105	0	0.28	165	1	0.34	165	1	0.34	165	1	0.34
501–600	105	0	0.29	105	0	0.29	175	1	0.34	175	1	0.34	175	1	0.34	235	2	0.36
601–800	110	0	0.29	110	0	0.29	180	1	0.36	240	2	0.40	240	2	0.40	300	3	0.41
801–1000	115	0	0.28	115	0	0.28	185	1	0.37	245	2	0.42	305	3	0.44	305	3	0.44
1001–2000	115	0	0.30	190	1	0.40	255	2	0.47	325	3	0.50	380	4	0.54	440	5	0.56
2001–3000	115	0	0.31	190	1	0.41	260	2	0.48	385	4	0.58	450	5	0.60	565	7	0.64
3001–4000	115	0	0.31	195	1	0.41	330	3	0.54	450	5	0.63	510	6	0.65	690	9	0.70
4001–5000	195	1	0.41	260	2	0.50	335	3	0.54	455	5	0.63	575	7	0.69	750	10	0.74
5001–7000	195	1	0.42	265	2	0.50	335	3	0.55	515	6	0.69	640	8	0.73	870	12	0.80
7001–10,000	195	1	0.42	265	2	0.50	395	4	0.62	520	6	0.69	760	10	0.79	1050	15	0.86
10,001–20,000	200	1	0.42	265	2	0.51	460	5	0.67	650	8	0.77	885	12	0.86	1230	18	0.94
20,001–50,000	200	1	0.42	335	2	0.58	520	6	0.73	710	9	0.81	1060	15	0.93	1520	23	1.0
50,001–100,000	200	1	0.42	335	2	0.58	585	7	0.76	770	10	0.84	1180	17	0.97	1690	26	1.1

Source: Dodge, H. F. and Romig, H. G., *Sapling Inspection Tables,* John Wiley and Sons, New York, 1959. Reproduced with permission from John Wiley & Sons, Inc.

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TABLE 5.17

Single Sampling Table for LTPD3.0%

	Process Average 0 to 0.03%			Process Average 0.04 to 0.30%			Process Average 0.31 to 0.60%			Process Average 0.61 to 0.90%			Process Average 0.91 to 1.20%			Process Average 1.21 to 1.50%		
Lot Size	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**	***n***	***c***	**AOQL %**
1–40	All	0	0	All	0	0	All	0	0	All	0	0	All	0	0	All	0	0
41–55	40	0	0.18	40	0	0.18	40	0	0.18	40	0	0.18	40	0	0.18	40	0	0.18
56–100	55	0	0.30	55	0	0.30	55	0	0.30	55	0	0.30	55	0	0.30	55	0	0.30
101–200	65	0	0.38	65	0	0.38	65	0	0.38	65	0	0.38	65	0	0.38	65	0	0.38
201–300	95	0	0.40	95	0	0.40	70	0	0.40	110	1	0.48	110	1	0.48	110	1	0.48
301–400	70	0	0.43	70	0	0.43	115	1	0.52	115	1	0.52	115	1	0.52	155	2	0.54
401–500	70	0	0.45	70	0	0.45	120	1	0.53	120	1	0.53	160	2	0.58	160	2	0.58
501–600	70	0	0.43	75	0	0.43	120	1	0.56	160	2	0.63	160	2	0.63	200	3	0.65
601–800	70	0	0.44	125	1	0.57	125	1	0.57	165	2	0.66	205	3	0.71	240	4	0.74
801–1000	75	0	0.45	125	1	0.59	170	2	0.67	210	3	0.73	250	4	0.76	290	5	0.78
1001–2000	75	0	0.47	130	1	0.60	175	2	0.72	260	4	0.85	300	5	0.90	380	7	0.95
2001–3000	75	0	0.48	130	1	0.62	220	3	0.82	300	5	0.95	385	7	1.0	460	9	1.1
3001–4000	75	0	0.63	175	2	0.75	220	3	0.84	305	5	0.96	425	8	1.1	540	11	1.2
4001–5000	75	0	0.63	175	2	0.76	260	4	0.91	345	6	1.0	465	9	1.1	620	13	1.2
5001–7000	130	1	0.63	175	2	0.76	265	4	0.92	390	7	1.1	505	10	1.2	700	15	1.3
7001–10,000	130	1	0.64	175	2	0.77	265	4	0.93	390	7	1.1	550	11	1.2	775	17	1.4
10,001–20,000	130	1	0.64	175	2	0.78	305	5	1.0	430	8	1.2	630	13	1.3	900	20	1.5
20,001–50,000	130	1	0.65	225	3	0.86	350	6	1.1	520	10	1.2	750	16	1.4	1090	25	1.6
50,001–100,000	130	1	0.65	265	4	0.96	390	7	1.1	590	12	1.3	830	18	1.5	1215	28	1.6

Source: Dodge, H. F. and Romig, H. G., *Sapling Inspection Tables,* John Wiley and Sons, New York, 1959. Reproduced with permission from John Wiley & Sons, Inc.

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TABLE 5.18

Single Sampling Table for AOQL = 1.0%

	Process Average 0 to 0.02%			Process Average 0.03 to 0.20%			Process Average 0.21 to 0.40%			Process Average 0.41 to 0.60%			Process Average 0.61 to 0.80%			Process Average 0.81 to 1.00%		
Lot Size	***n***	***c***	***p*%**	***n***	***c***	***p*%**	***n***	***c***	***p*%**	***n***	***c***	***p*%**	***n***	***c***	***p*%**	***n***	***c***	***p*%**
1–25	All	0	—	All	0	—	All	0	—	All	0	—	All	0	—	All	0	—
26–50	22	0	7.7	22	0	7.7	22	0	7.7	22	0	7.7	22	0	7.7	22	0	7.7
51–100	27	0	7.1	27	0	7.1	27	0	7.1	27	0	7.1	27	0	7.1	27	0	7.1
101–200	32	0	6.4	32	0	6.4	32	0	6.4	32	0	6.4	32	0	6.4	32	0	6.4
201–300	33	0	6.3	33	0	6.3	33	0	6.3	33	0	6.3	33	0	6.3	65	1	5.0
301–400	34	0	6.1	34	0	6.1	34	0	6.1	70	1	4.6	70	1	4.6	70	1	4.6
401–500	35	0	6.1	35	0	6.1	35	0	6.1	70	1	4.7	70	1	4.7	70	1	4.7
501–600	35	0	6.1	35	0	6.1	75	1	4.4	75	1	4.4	75	1	4.4	75	1	4.4
601–800	35	0	6.2	35	0	6.2	75	1	4.4	75	1	4.4	75	1	4.4	120	2	4.2
801–1000	35	0	6.3	35	0	6.3	80	1	4.4	80	1	4.4	120	2	4.3	120	2	4.3
1001–2000	36	0	6.2	80	1	4.5	80	1	4.5	130	2	4.0	130	2	4.0	180	3	3.7
2001–3000	36	0	6.2	80	1	4.6	80	1	4.6	130	2	4.0	185	3	3.6	235	4	3.3
3001–4000	36	0	6.2	80	1	4.7	135	2	3.9	135	2	3.9	185	3	3.6	295	5	3.1
4001–5000	36	0	6.2	85	1	4.6	135	2	3.9	190	3	3.5	245	4	3.2	300	5	3.1
5001–7000	37	0	6.1	85	1	4.6	135	2	3.9	190	3	3.5	305	5	3.0	420	7	2.8
7001–10,000	37	0	6.2	85	1	4.6	135	2	3.9	245	4	3.2	310	5	3.0	430	7	2.7
10,001–20,000	85	1	4.6	135	2	3.9	195	3	3.4	250	4	3.2	435	7	2.7	635	10	2.4
20,001–50,000	85	1	4.6	135	2	3.9	255	4	3.1	380	6	2.8	575	9	2.5	990	15	2.1
50,001–100,000	85	1	4.6	135	2	3.9	255	4	3.1	445	7	2.6	790	12	2.3	1520	22	1.9

Source: Dodge, H. F. and Romig, H. G., *Sapling Inspection Tables,* John Wiley and Sons, New York, 1959. Reproduced with permission from John Wiley & Sons, Inc.

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TABLE 5.19

Single Sampling Table for AOQL = 2.0%

	Process Average 0 to 0.04%			Process Average 0.05 to 0.40%			Process Average 0.41 to 0.80%			Process Average 0.81 to 1.20%			Process Average 1.21 to 1.60%			Process Average 1.61 to 2.00%		
Lot Size	***n***	***c***	***p*%**	***n***	***c***	***p*%**	***n***	***c***	***p*%**	***n***	***c***	***p*%**	***n***	***c***	***p*%**	***n***	***c***	***p*%**
1–15	All	0	—	All	0	—	All	0	—	All	0	—	All	0	—	All	0	—
16–50	14	0	13.6	14	0	13.6	14	0	13.6	14	0	13.6	14	0	13.6	14	0	13.6
51–100	16	0	12.4	16	0	12.4	16	0	12.4	16	0	12.4	16	0	12.4	16	0	12.4
101–200	17	0	12.2	17	0	12.2	17	0	12.2	17	0	12.2	35	1	10.5	35	1	10.5
201–300	17	0	12.3	17	0	12.3	17	0	12.3	37	1	10.2	37	1	10.2	37	1	10.2
301–400	18	0	11.8	18	0	11.8	38	1	10.0	38	1	10.0	38	1	10.0	60	2	8.5
401–500	18	0	11.9	18	0	11.9	39	1	9.8	39	1	9.8	60	2	8.6	60	2	8.6
501–600	18	0	11.9	18	0	11.9	39	1	9.8	39	1	9.8	60	2	8.6	60	2	8.6
601–800	18	0	12.0	40	1	9.6	40	1	9.6	65	2	8.0	65	2	8.0	85	3	7.5
801–1000	18	0	12.0	40	1	9.6	40	1	9.6	65	2	8.1	65	2	8.1	90	3	7.4
1001–2000	18	0	12.0	41	1	9.4	65	2	8.2	65	2	8.2	95	3	7.0	120	4	6.5
2001–3000	18	0	12.0	41	1	9.4	65	2	8.2	95	3	7.0	120	4	6.5	180	6	5.8
3001–4000	18	0	12.0	42	1	9.3	65	2	8.2	95	3	7.0	155	5	6.0	210	7	5.5
4001–5000	18	0	12.0	42	1	9.3	70	2	7.5	125	4	6.4	155	5	6.0	245	8	5.3
5001–7000	18	0	9.3	42	1	9.3	95	3	7.0	125	4	6.4	185	6	5.6	280	9	5.1
7001–10,000	42	1	9.3	70	2	7.5	95	3	7.0	155	5	6.0	220	7	5.4	350	11	4.8
10,001–20,000	42	1	9.3	70	2	7.6	95	3	7.0	190	6	5.6	290	9	4.9	460	14	4.4
20,001–50,000	42	1	9.3	70	2	7.6	125	4	6.4	220	7	5.4	395	12	4.5	720	21	3.9
50,001–100,000	42	1	9.3	95	3	7.0	160	5	5.9	290	9	4.9	505	15	4.2	955	27	3.7

Source: Dodge, H. F. and Romig, H. G., *Sapling Inspection Tables,* John Wiley and Sons, New York, 1959. Reproduced with permission from John Wiley & Sons, Inc.

Solution: We will use the Dodge and Romig tables (Tables 5.16 and 5.17).

Lot Size	*p*	LTPD	*n*	*c*	AOQL
50,000	0.61–0.90%	3%	520	10	1.2%
50,000	0.61–0.90%	2%	1060	15	0.93%
50,000	0–0.02%	3%	130	1	0.65%
50,000	0–0.02%	2%	200	1	0.42%

Observations: (1) with a constant lot size and *p,* the acceptance number/sample size ratio increases, AOQL decreases with decreasing LTPD. (2) With a constant lot size and LTPD, the acceptance number/sample size ratio and AOQL decreases with decreasing *p*.

b. Make a sampling plan for inspecting the same lot to assure (i) AOQL = 1.0%, when the average defects is 0.61–0.80%. (ii) AOQL = 2.0%, when the average defects are expected to be in the range of 0.61–0.80%. (iii) Make the above sampling plans when an average load is expected to have 0 to 0.02% defectives.

Solution: We will use the Dodge and Romig (1959) tables (Tables 5.18 and 5.19).

Lot Size	*p*	AOQL	*n*	*c*	LTPD
50,000	0.61–0.80%	1%	575	9	2.5
50,000	0.61–0.80%	2%	125	4	6.4
50,000	0–0.02%	1%	85	1	4.6
50,000	0–0.02%	2%	42	1	9.3

Observations: (1) with constant lot size and *p*, the acceptance number/sample size ratio and LTPD increases with AOQL. (2) With constant lot size and AOQL, the acceptance number/sample size ratio decreases, LTPD increases with decreasing *p*.

c. The Dodge and Romig tables recommended $n = 575$ and $c = 9$ for inspection of the lot size of 50,000 when $0.0061 \le p \le 0.0080$ and AOQL = 0.01. We may obtain a more accurate sampling plan for the same lot when $p = 0.0061$ and $p = 0.0080$ by employing MATLAB® code E.5.44.1, also determine the ATI.

MATLAB® CODE E.5.44.1

Command Window:

```
clear all
close all
format compact

[ATI n c] = DodgeRomig(50000,0.01,0.0061)
```

M-file:

```
function [ATI n c] = DodgeRomig(N,AOQL,p)

% this code is based on the Poisson distribution model

c=0;
index = false;
```

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```
ATI1 = 0;
while index==false
    x=0:c;
    y =@(lambda) -exp(-lambda)*sum(lambda.^(x+1)./factorial(x));

% function Lmin=fminsearch(y,x0) starts at x0 and attempts to find a
local minimizer Lmin of the function y

    Lmin = fminsearch(y,5);
    n = -y(Lmin)*N/(N*AOQL-y(Lmin));
    n = ceil(n);

%  function ceil(n) rounds the elements of n to the nearest integers
towards infinity

    ATI2 = n+(N-n)*(1-binocdf(c,n,p));
    if ATI2 < ATI1
        x=0:c+1;
        y1 =@(lambda) -exp(-lambda)*sum(lambda.^(x+1)./
factorial(x));
        Lmin1 = fminsearch(y1,5);
        n1 = -y1(Lmin1)*N/(N*AOQL-y1(Lmin1));
        n1 = ceil(n1);
        ATI3 = n1+(N-n1)*(1-binocdf(c+1,n1,p));
        if ATI3 > ATI2
            ATI = ATI2;
            index = true;
        else
            c=c+1;
            ATI1 = ATI2;
        end
    else
        c=c+1;
        ATI1 = ATI2;
    end
end
```

When we run the code the following lines will appear on the screen:

```
ATI =
  739.8926
n =
   510
c =
     8
```

When we run the code with

```
[ATI n c] = DodgeRomig(50000,0.01,0.008)
```

The followings will appear in the screen:

```
ATI =
  1.3522e+003
n =
   923
c =
    14
```

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It should be noticed that although the Dodge and Romig tables give the same result for $0.0061 \le p \le 0.0080$, the code predicts totally different ATI, n, and c.

Example 5.45: Codex Alimentarius Sampling Plan for Aflatoxin Contamination

The Codex Alimentarius sampling plan (Codex Alimentarius Comission 2008) sets the aflatoxin contamination limits as 8 ng/g in ready-to-eat and 15 ng/g in destined for further processing for almonds, hazelnuts, pistachios, and Brazil nuts. Codex also requires each lot or sublot not to exceed 20 tonnes. If a lot is larger than 20 tonnes it is recommended that it be divided into sublots. The minimum aggregate sample size is required to be 20 kg. The number of the incremental samples are determined according to the weight of the lot as

W (lot or sublot weight in tones)	$W < 1$	$1 \le W < 5$	$5 \le W < 10$	$10 \le W < 15$	$15 \le W$
Minimum number of incremental samples	10	25	50	75	100

The Codex Alimentarius sampling plan may be applied to both static and dynamic lots. A static lot may be defined as a large mass of tree nuts contained in a large single container such as a wagon, or a truck. The containment may be placed into the container in sacks, boxes, or packages. Sampling may also be done from a process stream or while the tree nuts are being transported on a conveyor, for example. This is referred to as dynamic sampling.

Sampling from a static lot is usually more difficult, since the incremental samples are required to be taken from everywhere. This may require using special sampling probes or unloading the container. Dynamic sampling is easier in the sense that the incremental samples may be taken as a stream with a predetermined frequency.

MATLAB® code E.5.45 offers a sampling plan.

A sample will be collected in accordance with the appropriate sampling plan. It will be ground and the amount of the aflatoxin will be determined. If it should not exceed the allowable limit the lot will be accepted.

In the United States, official U.S. grade standards designate the levels of quality. These standards serve as a basis for the online or lot inspection and grading of commodities.

Example 5.46: USDA Sampling Plan for Verification of the Grade Standards of the Canned Peas

According to the United States Standards for Canned Peas (Federal Register, October 18, 1994; 59 FR 52630), the size of the peas are designated in terms of the diameter of the circular openings that they can pass or not pass through. MATLAB® code E.5.46.a and E.5.46.b simulates the sieving operation.

In a real process the peas retained between the sieves of two consecutive openings are collected in different bins and labeled with the corresponding size designation.

Classified quality factors of the peas are maturity; extraneous vegetable material; blemished, spotted, or discolored peas; seriously blemished or seriously discolored peas; and the broken peas. MATLAB code E.5.46.c tests the acceptance of a lot by using the maturity as a quality factor, which is determined in terms of the number of the sinkers in a standard salt solution. It is also possible to write similar codes in terms of the other quality factors. Acceptance of a lot is finalized if it should pass all of the acceptance tests performed in accordance with all of the quality factors.

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MATLAB® CODE E.5.45

Command Window:

```
clear all
close all
format compact

Nincrements=1e6;

%  enter the data
Wlot=80; % tonnes
%  enter the number of the sublots
Nsublot=3;
Wsublot=Wlot/Nsublot;
Waggregate=20; % weight of the aggregate sample (kg)

if Wsublot<1; % tonnes
     Nincrements=10; % minimum number of the increments
end

if Wsublot>=1; % tonnes
   if Wsublot<5; % tonnes
      Nincrements=25; % minimum number of the increments
   end
end

if Wsublot>=5; % tonnes
   if Wsublot<10; % tonnes
      Nincrements=50; % minimum number of the increments
   end
end

if Wsublot>=10; % tonnes
   if Wsublot<15; % tonnes
      Nincrements=75; % minimum number of the increments
   end
end

if Wsublot>=15; % tonnes
   if Wsublot<=20; % tonnes
      Nincrements=100; % minimum number of the increments
   end
end

if Wsublot>20; % tonnes
   if Wsublot<=25; % tonnes
       fprintf('%3.2f tonnes is permitted, but it is not a
recommended sublot weight',Wsublot);
        Nincrements=100; % minimum number of the increments
    end
end

Wincrements=Waggregate/ Nincrements;
```

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```
if Nincrements<999999
fprintf('\nNumber of the Increments=%2i, Weight of each
increment=%3.2f kg\n', Nincrements, Wincrements);
end

if Wsublot>25; % tonnes
       fprintf('%3.2f tonnes is not a permitted sublot
weight\n',Wsublot);
end
```

When we run the code with

```
Wlot=45; % tonnes
Nsublot=3;
```

the following lines will appear on the screen:

Number of the Increments=100, Weight of each increment=0.20 kg

When we run the code with

```
Wlot=74; % tonnes
Nsublot=3;
```

the following lines will appear on the screen:

```
24.67 tonnes is permitted, but it is not a recommended sublot weight
Number of the Increments=100, Weight of each increment=0.20 kg
```

When we run the code with

```
Wlot=80; % tonnes
Nsublot=3;
```

the following line will appear on the screen:

```
26.67 tonnes is not a permitted sublot weight
```

5.7 HACCP and FMEA Principles

In food processing, quality control is applied to achieve the required quality level. The Hazard Analysis Critical Control Point (HACCP) is an additional preventive system designed to assure safety. It is designed to prevent potential microbiological, chemical, and physical hazards, rather than catch them. The HACCP plan is a written document prepared that consider the hazards associated with growing or harvesting the raw materials and the ingredients; and processing, distribution, marketing, preparation, and consumption of the food. The HACCP plans were used in the chemical processing industry and nuclear power plants in the 1950s, then in the space missions by NASA in the 1960s. NASA recommended the use of HACCP concepts to prevent foodborne illness of space crews. The U.S. Army Natick Laboratories used these concepts to prepare the space food for NASA. Pillsbury Company, a contractor of space food, adapted and expanded the concept for commercial applications (Snyder 1992). In Pillsbury's hazard and quality control plan, the HACCP system was combined with statistical quality control. In the overall system there were critical control points (CCPs), control points (CPs), and manufacturing control points (MCPs). The CCPs were required for HACCP, hazards including *Salmonella*, aflotoxin, antibiotics, inadequate pasteurization, and cross-contamination were monitored. The CPs were required for regulatory and economic reasons; coliforms, insects, food color, fumigant, net weight, and labeling controls are made. The MCPs were required for statistical quality control

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MATLAB® CODE E.5.46.a

Command Window:

```
clear all
close all
format compact
%  the data employed in this code were taken from United States
standards for grades of peas

% data
Size=[9 11.4 3.2 9.1 12 6.5 8.3 8.7 5.3 9.1 9.9 10.7 7.8 7.2 8.6
10.5 9.6 8.3 4.3 7.9 9.4 10.5 8.0 8.6 5.7 8.9 8.3 10.0 9.3 7.9]; %
size of the peas in the lot (mm)
SizeL=[7.1 7.9 8.7 9.5 10.3 11.1]; % size limits (mm)
SizeD=[1 2 3 4 5 6 7]; % size designation
counter=0;

for i=1:length(Size)
     if Size(i)<=SizeL(1)
         counter=counter+1;
    end
end
SIZE=SizeD(1);
fprintf('There are %2i peas in the group designated size
%2i\n',counter, SIZE);

counter=0;
for i=2:length(SizeL)
   k=i-1;
  for j=1:length(Size)
     if Size(j)>=SizeL(k)
        if Size(j)<SizeL(i)
         counter=counter+1;
        end
     end
  end
SIZE=SizeD(i);
fprintf('There are %2i peas in the group designated size
%2i\n',counter, SIZE);
counter=0;
end

for i=1:length(Size)
     if Size(i)>=SizeL(6)
         counter=counter+1;
    end
end
SIZE=SizeD(7);
fprintf('There are %2i peas in the group designated size
%2i\n',counter, SIZE);
```

When we run the code the following lines will appear on the screen:

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```
There are  5 peas in the group designated size  1
There are  2 peas in the group designated size  2
There are  8 peas in the group designated size  3
There are  7 peas in the group designated size  4
There are  3 peas in the group designated size  5
There are  3 peas in the group designated size  6
There are  2 peas in the group designated size  7
```

MATLAB® CODE E.5.46.b

Command Window:

```
clear all
close all
format compact

% GRADE MATRICES
GradeA=[1 1 1 1 1];
GradeB=[1 1 2 1 1];
GradeC=[1 2 3 1 1];

Grade=4;

% enter Property(1)=1 if varietal properties are similar;
% enter Property(1)=2 if varietal properties are different
Property(1)= input('Property(1):');

% enter Property(2)=1 if appearance is good
% enter  Property(2)=2 if appearance is reasonably good
% enter Property(2)=3 if apparance is not good or reasonably good
Property(2)= input('Property(2):');

% enter Property(3)=1 if the lot has not more than 1% blond peas by
count
% enter Property(3)=2 if the lot has not more than 1.5 % blond peas
by count
% enter Property(3)=3 if the lot has not more than 2 % blond peas
by count
% enter Property(3)=4 if the lot has more than 2 % blond peas by
count
Property(3)= input('Property(3):');

% enter Property(4)=1 if the can has good liquor
% enter Property(4)=2 if the can has reasonably good liquor
% enter Property(4)=3 if the can does not have good or reasonably
good liquor
Property(4)= input('Property(4):');

% enter Property(5)=1 if the peas have good flavor and odor
% enter Property(5)=2 if the peas have reasonably good flavor and
odor
% enter Property(5)=3 if the peas does not have good or have
reasonably good flavor and odor
Property(5)= input('Property(5):');
```

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```
if Property(1)==GradeA(1)
if Property(2)==GradeA(2)
if Property(3)==GradeA(3)
if Property(4)==GradeA(4)
if Property(5)==GradeA(5)
fprintf('PRODUCT IS US GRADE A\n');
Grade=1;
end
end
end
end
end

if Grade==4
if Property(1)==GradeB(1)
if Property(2)==GradeB(2)
if Property(3)==GradeB(3)
if Property(4)==GradeB(4)
if Property(5)==GradeB(5)
fprintf('PRODUCT IS US GRADE B\n');
Grade=2;
end
end
end
end
end
end

if Grade==4
if Property(1)==GradeC(1)
if Property(2)<=GradeC(2)
if Property(3)<=GradeC(3)
if Property(4)==GradeC(4)
if Property(5)==GradeC(5)
fprintf('PRODUCT IS US GRADE C\n');
Grade=3;
end
end
end
end
end
end

if Grade==4
fprintf('PRODUCT IS SUBSTANDARD\n');
end
```

Three sample runs of the code are given here:

```
Property(1):1
Property(2):2
Property(3):2
Property(4):1
Property(5):1
PRODUCT IS US GRADE C
```

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```
Property(1):1
Property(2):1
Property(3):2
Property(4):1
Property(5):1
PRODUCT IS US GRADE B

Property(1):1
Property(2):1
Property(3):4
Property(4):2
Property(5):2
PRODUCT IS SUBSTANDARD
```

MATLAB® CODE E.5.46.c

Command Window:

```
clear all
close all
format compact

% GRADE CODES
% GradeCode=1 means Grade A
% GradeCode=2 means Grade B
% GradeCode=3 means Grade C

% enter the Grade Code
GradeCode= input('GradeCode:');

% TYPE CODES
% TypeCode=1 means Sweet Peas
% TypeCode=2 means Early Peas

% enter the Type Code
TypeCode= input('TypeCode:');

% enter the Rejection Code
RejectionCode=6;
% (Sample Size) = (Number of the Sample Units)*(Sample Unit Size)
%  Sample Unit Size = 50 (fixed)
% enter the Number of the Sample Units
SampleUnits= input('SampleUnits:');
SampleSize=50*SampleUnits
% enter the Number of the Sinkers
NumberOfSinkers= input('NumberOfSinkers:');

if SampleUnits==1
i=1;
end

if SampleUnits==3
i=2;
end
```

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```
if SampleUnits==6
i=3;
end

if SampleUnits==13
i=4;
end

if SampleUnits==21
i=5;
end

if SampleUnits==29
i=6;
end

if TypeCode==1
if GradeCode==1
AcceptanceNumber=[8 21 39 78 122 165];
AN=AcceptanceNumber(i)
if NumberOfSinkers<=AN
RejectionCode=1;
fprintf('LOT IS ACCEPTED, Number Of Sinkers is Less than the
Acceptance Number \n');
fprintf('Sample Size is %2i, Number Of Sinkers is %2i, Acceptance
Number is %2i\n',SampleSize, NumberOfSinkers,AN);
end
end
end

if TypeCode==2
if GradeCode==1
AcceptanceNumber=[13 34 63 130 205 279];
AN=AcceptanceNumber(i)
if NumberOfSinkers<=AN
RejectionCode=2;
fprintf('LOT IS ACCEPTED, Number Of Sinkers is Less than the
Acceptance Number \n');
fprintf('Sample Size is %2i, Number Of Sinkers is %2i, Acceptance
Number is %2i\n',SampleSize, NumberOfSinkers,AN);
end
end
end

if TypeCode==1
if GradeCode==2
AcceptanceNumber=[10 26 48 98 154 209];
AN=AcceptanceNumber(i)
if NumberOfSinkers<=AN
RejectionCode=3;
fprintf('LOT IS ACCEPTED, Number Of Sinkers is Less than the
Acceptance Number \n');
fprintf('Sample Size is %2i, Number Of Sinkers is %2i, Acceptance
Number is %2i\n',SampleSize, NumberOfSinkers,AN);
```

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```
end
end
end

if TypeCode==2
if GradeCode==2
AcceptanceNumber=[18 50 94 195 309 422];
AN=AcceptanceNumber(i)
if NumberOfSinkers<=AN
RejectionCode=4;
fprintf('LOT IS ACCEPTED, Number Of Sinkers is Less than the
Acceptance Number \n');
fprintf('Sample Size is %2i, Number Of Sinkers is %2i, Acceptance
Number is %2i\n',SampleSize, NumberOfSinkers,AN);
end
end
end

if GradeCode==3
AcceptanceNumber=[7 18 33 65 101 137];
AN=AcceptanceNumber(i)
if NumberOfSinkers<=AN
RejectionCode=5;
fprintf('LOT IS ACCEPTED, Number Of Sinkers is Less than the
Acceptance Number \n');
fprintf('Sample Size is %2i, Number Of Sinkers is %2i, Acceptance
Number is %2i\n',SampleSize, NumberOfSinkers,AN);
end
end

if RejectionCode==6;
fprintf('LOT IS REJECTED\n');
end
```

Three sample runs of the code are given here:

```
GradeCode:3
TypeCode:2
SampleUnits:6
SampleSize =
   300
NumberOfSinkers:45
AN =
    33
LOT IS REJECTED

GradeCode:1
TypeCode:2
SampleUnits:29
SampleSize =
        1450
NumberOfSinkers:77
AN =
   279
```

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```
LOT IS ACCEPTED, Number Of Sinkers is Less than the Acceptance
Number
Sample Size is 1450, Number Of Sinkers is 77, Acceptance Number is
279

GradeCode:2
TypeCode:1
SampleUnits:6
SampleSize =
   300
NumberOfSinkers:56
AN =
    48
LOT IS REJECTED
```

purposes; where total microbial counts, formulation controls, viscosity measurements were made (Sperber 1991).

In a specific food system any point (or process) where loss of control may result in unacceptable health risk is called a critical control point (CCP; USDA November 1989, updated on March 2008). Control points (CP) are differentiated from the CCPs on the basis that loosing the control in the CPs will not result in unacceptable health risk. Control points are generally nonsafety points related to product quality or regulatory compliance. In yogurt production, lactic acid bacteria decreases the pH and prevents growth of the pathogenic microorganisms; here, the hazard is the pathogens and CCP is the acid fermentation. Losing control in the acid fermentation (i.e., failing to achieve safe pH) may cause an unacceptable health risk. Microorganisms that contaminate the *low acid foods* may form heat stable spores, therefore processing requires temperatures above 100°C for a certain time (Section 4.1). In the process of canning low acid foods the hazard is *Clostridium botulinum*, and the CCP is the thermal process (temperature and duration). Failing to achieve a safe time–temperature combination may cause an unacceptable health risk. The HACCP principles are applied to assure food safety by monitoring CCPs during food processing and preservation. The critical points are continuously monitored to keep the critical parameters within tolerable limits.

In order to implement the HACCP concept, an analysis is done in a plant to determine the hazards and the CCPs. The critical limits like maximum pesticide level or minimum processing time are determined for each critical point to eliminate or reduce the hazard to an acceptable level. The CCP monitoring activities are established to ensure that the process is under control. Corrective actions are established for deviations from the critical limits. Records to document the monitoring of CCPs, critical limits, verification activities, and the handling of processing deviations are established. Procedures for ensuring the HACCP system is working as intended are established (USDA November 1989, updated on March 2008).

Processing and handling practices of the foods are conducted according to their risk category (Table 5.20). Category VI is assigned to the nonsterile foods designated to consumption by high risk groups. Categories V–0 show the total number of hazard characteristics (Hazard B–Hazard F) associated with the food. The above considerations allow identifying the areas in which hazards in the food system may be reduced. This analysis may result in changing the form of an ingredient (e.g., fresh to canned) or changing

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TABLE 5.20

Hazard Characteristics of the Foods

Hazard A	Food is nonsterile and intended to be consumed by high-risk populations (i.e., infants, elderly, hospitalized people)
Hazard B	Food contains microbiologically sensitive ingredients
Hazard C	There is no control step to effectively destroy the microorganisms
Hazard D	There is a significant risk of postprocessing contamination by microorganisms and toxins before packaging
Hazard E	There is substantial potential for abusive handling in distribution or by consumer
Hazard F	There is no terminal heat process after packaging or cooking at home

Source: USDA. National Agricultural Library. USDA Food Safety Research Information Office. November 1989, updated on March 2008. http://fsrio.nal.usda.gov/document_fsheet.php?product_id=155

a step in the manufacturing process (e.g., chilled to frozen) to reduce the risk. If the supplier of food ingredients develops a HACCP program, lot acceptance tests may be replaced by reduced frequency audit programs to verify that the HACCP plan is working correctly (Microbiology and Food Safety Committee of the National Food Processors Association 1993).

There is a possibility that a risk or hazard may escape with the HACCP plan if there is not an obvious relationship between the risk and the physical, chemical, and microbiological hazards. The Failure Mode and Effect Analysis (FMEA) improves operational performance of the production cycle and points out the potential causes for the failure of the HACCP plan (Scipioni et al. 2002; Varzakas and Arvanitoyannis 2007). The FMEA technique considers each item that comprises the total system. The analysis is made based on the best expert opinion and historic information about similar items or processes. The risk priority number (RPN) for any element of the total system may be computed as:

$$\text{RPN} = \text{S} \times \text{O} \times \text{D}. \tag{5.80}$$

Where S is severity, O is occurrence, and D is the detection probability of the element contributing to the risk. Although there is no generally agreed upon procedure yet, parameters S, O, and D may be scored between 1 and 10. Scores 1 and 10 may describe very low and very high severity or occurrence of the hazard, respectively. Scores 1 and 10 may refer to very high and very low detection probability of the hazard, respectively. Equation 5.81 may be used to compute the RPN_i of *i*th element of the process. The percentage RPN associated with any element may be computed as

$$\%\text{RPN}_i = \frac{100 \times \text{RPN}_i}{\sum_{j=1}^{n} \text{RPN}_j}. \tag{5.81}$$

Example 5.47: FMEA Analysis for Cake Mix

Simplified flow diagram of a cake mix production process is given in Figure E.5.47. FMEA analysis of the process is performed by employing the major hazards pointed out in the study of the Microbiology and Food Safety Committee of the National Food Processors Association (1993).

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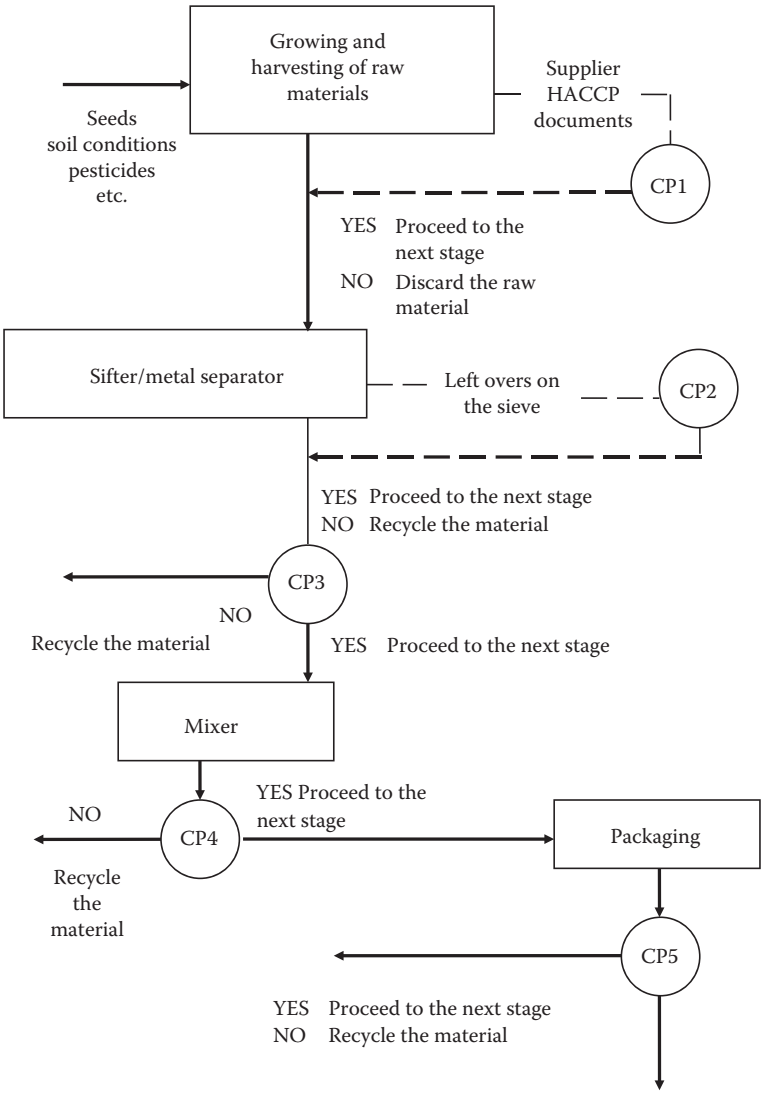


FIGURE E.5.47
The cake mix production process and its critical control points.

The simplified process consists of four main stages. Severity (S), occurrence (O), and detection probability (D) of each element contributing to the risk in each stage is summarized.

CP1. Improper application of the chemicals beyond the limits set by the Environmental Protection Agency (in the United States) or its counterparts in the other countries constitute the hazard associated with the growing and harvesting stage of raw materials. Grower records and random QC records including chemical assays and a certificate of guarantee provided by the audit is needed for control. In case of the failure at CP1 the lot is rejected. Frequency of audit/record review is increased in the forthcoming practices. CP1 controls are conducted by the shipment receiver and the QC audit.

D = 2 (improper application of the chemicals are easy to detect, when the grower and the audit records are examined)

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S = 9 (they may cause intoxication or even death)
O = 8 (there is a widespread risk associated with the raw materials grown in the underdeveloped countries)

CP2. Physical hazards (wood, metal, glass, plastics, etc.) are controlled in the leftovers after sifting. No hazardous material is expected to be found in the leftovers. Sifter and metal remover operator checks and records of findings of after each lot or after every two hours. In case of any hazardous findings, the supervisor and QC are notified. All products since last OK check are placed on hold. The ingredient lot rejected back to supplier**.** Line operator: QC notified and handles disposition of held product and rejection.

D = 2 (physical hazards are easy to detect)
S = 3 (they may be detected by the consumer while eating the product, therefore not expected to cause a severe health hazard, but negatively affect the reliability of the brand)
O = 2 (physical hazards are rare in the environmentally sensitive locations, they may get in accidentally)

CP3. Physical hazards may pass through the sifter if there is a hole in screen allowing physical hazards (wood, metal, glass, plastics, etc.) to pass through. The hazard is controlled by routine monitoring of the sifter screen. The sifter screens are required to be well placed and intact. Operator records are checked with the control purposes. A defective screen will result in all products, since last check, placed on hold. System emptied and cleaned. Screen replaced. Lot rejected back to supplier. Sifter operator is responsible for the controls at this stage.

D = 2 (physical hazards are easy to detect)
S = 3 (they may be detected by the consumer while eating the product, therefore not expected to cause a severe health hazard, but negatively affect the reliability of the brand)
O = 2 (the screens are made to last longer without causing any problems)

CP4. The cake mix is a visual observation by mixer operator during dumping of bagged ingredients for metal, glass, plastics, and so on. No hazardous material is permitted. Any hazardous finding reported to the supervisor and the batch is diverted and placed on hold. Mixer cleaned. Lot rejected back to supplier.

D = 3 (physical hazards are easy to detect)
S = 3 (they may not cause severe health hazard, but negatively affect the reliability of the brand)
O = 2 (this is a rare problem)

CP5. Improper labeling of the packages may cause health hazard and loss of consumer confidence. Labels or packages are checked at every 2 hours or at changeover. Improper packages or labels must be reported to supervisor and QC. All products since last OK are placed on hold. The products are also subjected to a final metal test.

D = 1 (packaging problems are easy to detect)
S = 3 (packaging problems not expected to cause a severe health hazard, but negatively affect the reliability of the brand)
O = 2 (this is a rare problem)

MATLAB® code E.5.47 makes the FMEA analysis.

The printout of the code implies that if the HACCP plan should fail, the most likely point of failure will be associated with improper chemicals application (RPN percentage = 75%). The D, S, and O matrices constructed in this example are subjective in nature. They may change with the coverage and depth of the analysis and the local influences imposed on the process.

Example 5.48: FMEA Analysis for the Pickle Making Process

Simplified flow diagram of a pickle production process is given in Figure E.5.48. Table E.5.48 describes the severity (S), occurrence (O) and detection probability (D) associated with each CP. The flowers may cause some allergic reactions; therefore, the severity of the risk is relatively high,

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MATLAB® CODE E.5.47

Command Window:

```
clear all
close all
format compact

% data files
D= [2 2 2 3 1];
S= [9 3 3 3 3];
O= [8 2 2 2 2];

% compute the RPNs (risk priority numbers)
RPN=D.*S.*O;

% compute the RPN percentages (risk priority numbers)
RPNpercentage=(RPN(1,:)/sum(RPN))*100
```

When we run the code the following lines will appear on the screen:

```
RPNpercentage =
   75.0000    6.2500    6.2500    9.3750    3.1250
```

when compared to those of the others. FMEA analysis for the pickle making process is carried out by MATLAB® code E.5.48.

The printout shows that the highest RPN percentage was 30.09% and associated with risk number 5, pesticide residue on the raw material. The second highest RPN percentage was 11.75% and associated with risk numbers 4 and 6, presence of bugs and foreign material in the incoming raw material. Implying that if the HACCP plan should fail, these points will be the most likely locations of the failure.

5.8 Quality Assurance and Improvement through Mathematical Modeling

Senarios that are presented as mathematical models are employed to improve the quality and safety of the foods as explained in Examples 5.49 through 5.53.

Example 5.49: Predictive Quality Modeling by Using Microbial Lag Time

Predictive microbial models provide rapid, inexpensive and reliable estimates of the shelf life. A food may be regarded safe as long as the microorganisms remain inactive after processing. Although various other definitions are available, time required for the initial microbial load to increase twofold may be referred to as the lag time. Predictive microbial modeling is usually a two-step process: first, kinetic models are developed for a full description of the process; then these models are used, with their predetermined constants, to predict the microbial quality of the food. An extended logistic equation may be used to simulate microbial growth (Alavi et al. 1999):

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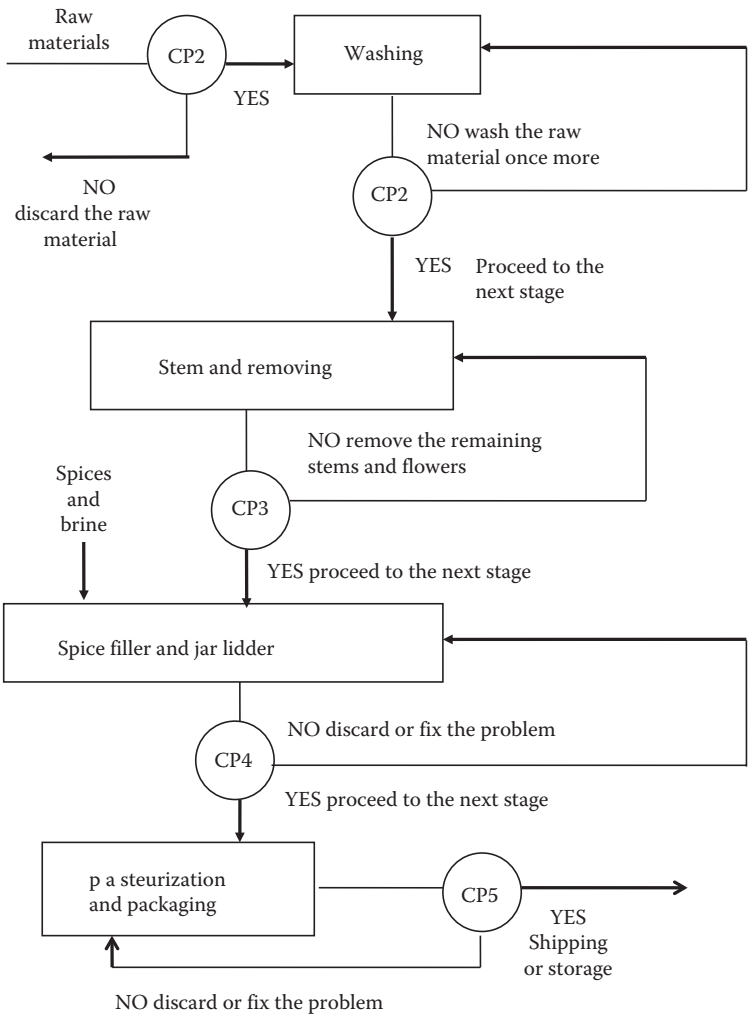


FIGURE E.5.48
The pickle production process and its critical control points.

$$\frac{dx}{dt} = \mu_0 \left[T(t) - T_{\min}\right]^2 \left(\frac{q(t)}{1+q(t)}\right) x \left(1 - \frac{x}{x_{\max}}\right), \tag{E.5.49.1}$$

where μ_0 = constant, $T(t)$ = temperature at time t, $T_{\min}$ = minimum temperature required for microbial growth. Most of the intracellular chemical reactions follow Michaelis-Menten kinetics. The empirical term $q(t)/1 + q(t)$ may describe the rate-determining step involved in the healing of a cellular damage or adaptation to a new growth medium. It is not possible to associate $q(t)$ with a specific metabolite, since the rate determining reactions are usually case specific and may change with time even in the same case. The temperature dependence term $T(t) - T_{\min} = 0$ when $T(t) < T_{\min}$. MATLAB® code E.5.49.a gives a prediction of the shelf life of ice cream contaminated with *Listeria monocytogenes*.

MATLAB code E.5.49.b gives prediction of the shelf life of ice cream subjected to temperature fluctuations after contaminated with *Listeria monocytogenes*.

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TABLE E.5.48

Describes the Details of the Risks Associated With Each CP

CP	Risk	Risk Number	S	O	D
CP1	Improper size	1	2	5	1
	Rotten raw material	2	5	5	1
	Worm	3	5	5	1
	Bug	4	5	5	3
	Pesticide residue	5	8	8	3
	Foreign material	6	5	5	3
CP2	Dust	7	2	6	5
	Mud	8	2	6	5
	Rot	9	5	2	2
CP3	Stem	10	2	3	2
	Flower	11	5	2	3
CP4	Smashed pickles	12	2	2	1
	Pickles with improper shape	13	2	1	1
	Rotten pickles	14	5	1	3
	Improper brix of the filler	15	4	1	1
	Improper acidity of the filler	16	6	1	1
	Problems with the lid	17	3	1	1
	Problems with the spice	18	3	1	1
CP5	Improper package weight	19	2	1	1
	Improper vacuum	20	2	1	3
	Improper pH of the filler	21	4	1	1
	Improper fluidity of the filler	22	2	1	1
	Other packaging problems	23	3	1	1

MATLAB® CODE E.5.48

Command Window:

```
clear all
close all
format compact

% data files
S=[2 5 5 5 8 5 2 2 5 2 5 2 2 5 4 6 3 3 2 2 4 2 3];
O=[5 5 5 5 8 5 6 6 2 3 2 2 1 1 1 1 1 1 1 1 1 1 1];
D=[1 1 1 3 3 3 5 5 2 2 3 1 1 3 1 1 1 1 1 3 1 1 1];

% compute the RPNs (risk priority numbers)
RPN=D.*S.*O;

% compute the RPN percentages (risk priority numbers)
RPNpercentage=(RPN(1,:)/sum(RPN))*100;
```

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When we run the code the following lines will appear on the screen:

```
RPNpercentage =
  Columns 1 through 15
    1.5674    3.9185    3.9185   11.7555   30.0940   11.7555
9.4044    9.4044    3.1348    1.8809    4.7022    0.6270    0.3135
2.3511    0.6270
  Columns 16 through 23
    0.9404    0.4702    0.4702    0.3135    0.9404    0.6270
0.3135    0.4702
```

MATLAB® CODE E.5.49.a

Command Window:

```
clear all
close all

% enter the data
TemperatureD=[4 6 8 10 12 14 16];
TimeD=[310 175 115 85 60 50 45];

% plot the data
plot(TemperatureD,TimeD,'*'); hold on

% enter the parameters of the model
mu0=4e-4; % 1/min
Tmin=-2.1; % oC
x0=1; % cfu/g
xMax=1e9; % cfu/g
deltaTime=60; % min
T=(4:1:16);
for i=1:1:13
    q(i)=16e-3+3e-4*(T(i)-4);
     xk=1;
      counter=1;
        for j=1:1:60000
          x=xk+mu0*((T(i)-Tmin)^2)*(q(i)/(1+q(i)))*xk*(1-(xk/
xMax))*deltaTime;
           if x>=100
            if counter==1;
              time(i)=j;
              counter=2;
           end
         end
        xk=x;
      end
end
plot(T,time,'-'); hold on
ylabel('Time (h)');
xlabel('Temperature (oC)');
```

When we run the code Figure E.5.49.1 will appear on the screen.

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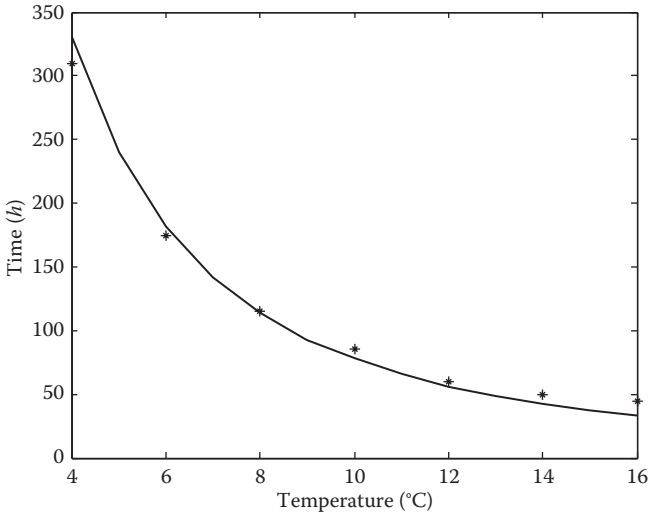


FIGURE E.5.49.1
Predicted shelf life of ice cream when subject to contamination with *Listeria monocytogenes*. It was assumed that x_0 = 1 cfu/g was sufficient to start deterioration and ice cream was inedible when x = 100 cfu/g. (Adapted from Gougouli, M., Angelidis, A. S., and Koutsoumanis, K., *Journal of Dairy Science*, 91, 523–30, 2007.)

MATLAB® CODE E.5.49.b

Command Window:

```
clear all
close all

% enter the data
Temperature=[4 2 1 -1 5 3 2 4 6 -2 -2 -1  0 5 7 1 -2 -3 5 2 7 4  -2
6 5]; % average daily storage temperatures

n=length(Temperature);
Time=[0:1:n-1]; % storage time

% plot the data
plot(Time,Temperature,':'); hold on
ylabel('storage temperature (oC)');
xlabel('storage time (days)');

% enter the parameters of the model
mu0=4e-4; % 1/min
Tmin=-2.1; % oC
x0=1; % cfu/g
xMax=1e9; % cfu/g
deltaTime=60*24; % min

% microbial growth model
counter=1;
xk=1; % it is assumed that the ice cream is contaminated with 1
cfu/g at the beginning of storage
```

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```
for i=1:1:n
time(i)=(i-1)*24; % storage time (hours)
timeDays(i)=time(i)/24; % number of the days in storage
N=timeDays(i);
   TTmin=((Temperature(i)-Tmin))^2;
       if Temperature(i)<=Tmin
          TTmin=0;
       end
             q(i)=16e-3+3e-4*(Temperature(i)-4);
               x(i)=xk+mu0*TTmin*(q(i)/(1+q(i)))*xk*(1-(xk/
xMax))*deltaTime;
                  if x(i)>=100
                    if counter==1;
                        fprintf('\nshelf life of ice cream is %.2f
days in storage',N)
                        counter=2;
                    end
                  end
              xk=x(i);
      end
figure
plot(timeDays,x,'-'); hold on
ylabel('x (cfu/g)');
xlabel('storage time (days)');
```

When we run the code the following line and Figures E.5.49.2 and E.5.49.3 will appear on the screen:

```
shelf life of ice cream is 23.00 days in storage
```

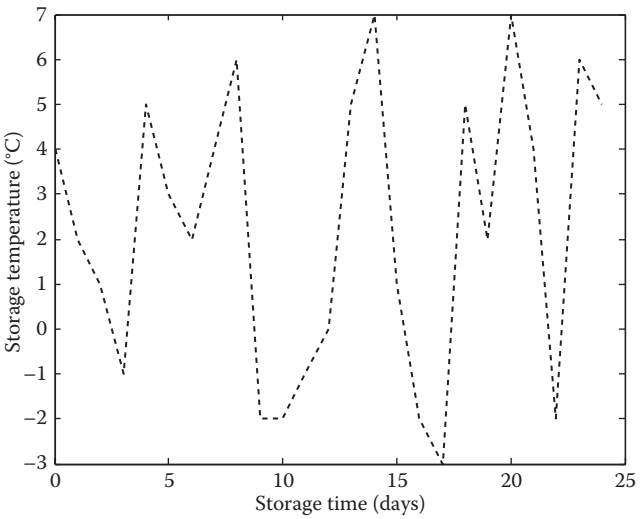


FIGURE E.5.49.2
Storage temperature fluctuations of the ice cream.

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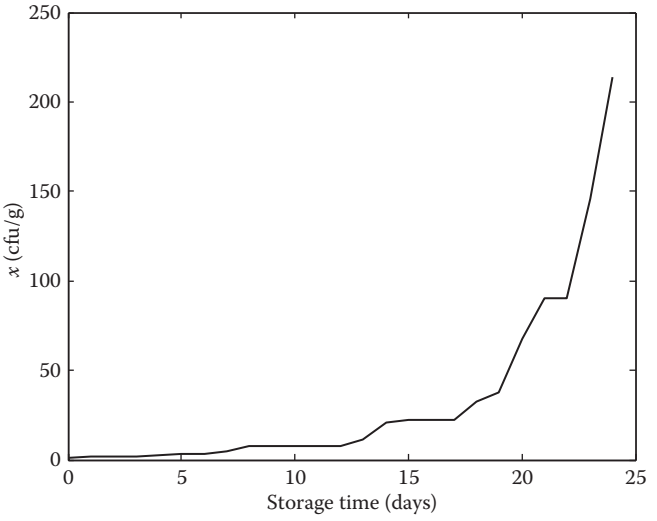


FIGURE E.5.49.3
Predicted microbial population of ice cream that is contaminated with $x_0 = 1$ cfu/g of *Listeria monocytogenes* at $t = 0$ in and subjected to temperature fluctuations in storage. It was assumed that $x_0 = 1$ cfu/g was sufficient to start deterioration and ice cream was inedible when $x = 100$ cfu/g. (Adapted from Gougouli, M., Angelidis, A. S., and Koutsoumanis, K., *Journal of Dairy Science*, 91, 523–30, 2007.)

Example 5.50: Predictive Modeling for Estimation of the Color of a Product after Thermal Processing

Barreiro, Milano, and Sandoval (1997) studied the kinetics of the color change (variation of the Hunter *L*, *a*, *b* tristimulus values) of tomato paste during heating. They obtained a model to predict the color change as summarized in the following table:

Huntel lab parameter	Order of the Degradation Reaction	Constants of the Arrhenius Model
L	first order	$E_a = 4.8e4$ kJ/kg mol, $\ln k_o = 11.3$ min^{-1} (valid when $0 \le t < 15$ min) $E_a = 2.4e4$ kJ/kg mol, $\ln k_o = 1.28$ min^{-1} (valid when $t \ge 15$ min)
a	first order	$E_a = 4.1e4$ kJ/kg mol, $\ln k_o = 9.10$ min^{-1}
b	first order	$E_a = 8.6$ kJ/kg mol, $\ln k_o = 22.2$ min^{-1}

In the Hunter scale, *L* measures lightness and varies from 100 for perfect white to zero for black, approximately, as the eye would evaluate it. The chromaticity dimension *a* measures redness when positive, gray when zero, and greenness when negative. The chromaticity dimension *b* measures yellowness when positive, gray when zero, and blueness when negative.

At time $t = 0$ the color dimensions were: $L_0 = 22.9$, $a_0 = 22.6$, $b_0 = 10.9$. MATLAB® code E.5.50 computes and prints out $L(t)$, $a(t)$, and $b(t)$ at the center of the can by using the temperature profiles predicted by Equation E.4.5.5 of Example 4.5.

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MATLAB® CODE E.5.50

Command Window:

```
clear all
close all
clc;

L = 3.015; % cm
Rcan = 4.36; % cm
alpha = 0.0938;
TR = 87.8;
T0 = 7.2;
R=8.314; % kJ/kg mol K

% kinetic constants of  parameter L
k01L= 8.0822e+004;
k02L= 3.5966;
Ea1L=4.8e4;
Ea2L=2.4e4;
lnL(1)=log(22.9);

% kinetic constants of  parameter a
k0a= 8.0822e+004;
Eaa=4.1e4;
lna(1)= 3.12;

% kinetic constants of  parameter b
k0b= 4.3786e+009;
Eab=8.6e4;
lnb(1)= 2.39;

% Predict the temperature of the thermal center with Equation 4.8.5
times= [1:75];
deltaTime=1; % min
for i=1:length(times)
    R_over_sqrt_etc(i) = (Rcan/(sqrt(pi*alpha*times(i))));
    if isinf(R_over_sqrt_etc(i))==1 ; R_over_sqrt_etc(i)=0; end;
    expon(i) = exp((-Rcan^2)/(8*alpha*times(i)));
    K14_besselfunction(i) = besselk(0.25,(Rcan^2)/
(8*alpha*times(i)));
    if isnan(K14_besselfunction(i))==1; K14_besselfunction(i)=0;
end;
    error_func(i) = erfc(L/(2*sqrt(alpha*times(i))));
    Tcan(i) = (1-2*error_func(i)) * (1-(R_over_sqrt_etc(i)*expon(i)
* K14_besselfunction(i)));
    T(i) = TR - (Tcan(i) * (TR-T0));
end

% Predict variation of Hunter Lab color patameter L
for i=2:length(times)
k=i-1;
```

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```
if times(i)<=15
    lnL(i)=lnL(k)-(k01L*exp(-Ea1L/(R*(T(k)+273))))*deltaTime;
end
if times(i)>15
    lnL(i)=lnL(k)-(k02L*exp(-Ea2L/(R*(T(k)+273))))*deltaTime;
end
end

% Predict variation of Hunter Lab color patameters a and b
for i=2:length(times)
k=i-1;
    lna(i)=lna(k)-(k0a*exp(-Eaa/(R*(T(k)+273))))*deltaTime;
    lnb(i)=lnb(k)-(k0b*exp(-Eab/(R*(T(k)+273))))*deltaTime;
end

% plot the variation of the Hunter Lab color parameter L, a, b and
temperature at the thermal center  with time
plot(times,lnL,'-'); hold on
plot(times,lna,':'); hold on

[AX,H1,H2] = plotyy(times,lnb, times,T,'plot'); hold on
set(H1,'LineStyle','-.')
set(H2,'LineStyle','+')
xlabel('Time (min)')
ylabel('ln(Hunter Lab color parameters L, a and b)')
set(get(AX(2),'ylabel'), 'string', 'Temperature ( \circ C)')
legend('L','a','b','T','Location','SouthEast')

% Surface attains the retort temperature immediately
T(1:length(times))=87.8;
% Predict variation of Hunter Lab color patameter L
for i=2:length(times)
k=i-1;
if times(i)<=15
    lnL(i)=lnL(k)-(k01L*exp(-Ea1L/(R*(T(k)+273))))*deltaTime;
end
if times(i)>15
    lnL(i)=lnL(k)-(k02L*exp(-Ea2L/(R*(T(k)+273))))*deltaTime;
end
end

% Predict variation of Hunter Lab color patameters a and b
for i=2:length(times)
k=i-1;
    lna(i)=lna(k)-(k0a*exp(-Eaa/(R*(T(k)+273))))*deltaTime;
    lnb(i)=lnb(k)-(k0b*exp(-Eab/(R*(T(k)+273))))*deltaTime;
end

% plot the variation of the Hunter Lab color parameter L, a, b and
temperature near the surface with time
figure
plot(times,lnL,'-'); hold on
plot(times,lna,':'); hold on

[AX,H1,H2] = plotyy(times,lnb, times,T,'plot'); hold on
set(H1,'LineStyle','-.')
```

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```
set(H2,'LineStyle','+')
xlabel('Time (min)')
ylabel('ln(Hunter Lab color parameters L, a and b)')
set(get(AX(2),'ylabel'), 'string', 'Temperature ( \circ C)')
legend('L','a','b','T','Location','SouthEast')
```

When we run the code the Figures E.5.50.1 and E.5.50.2 will appear on the screen.

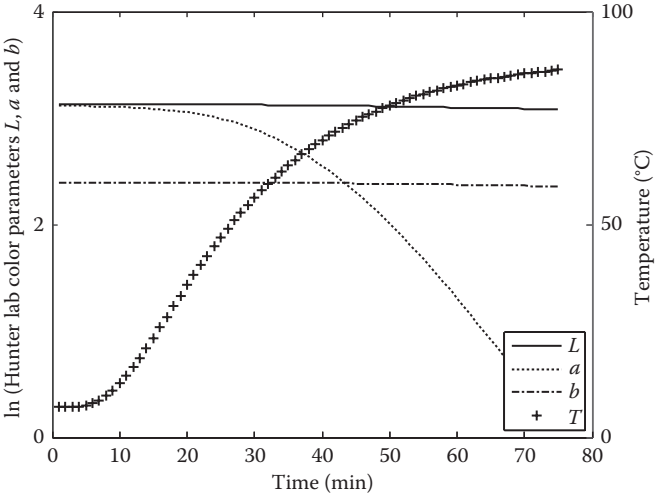


FIGURE E.5.50.1
Variation of the Hunter color parameters *L*, *a*, *b*, and temperature at the can center during thermal treatment of tomato paste.

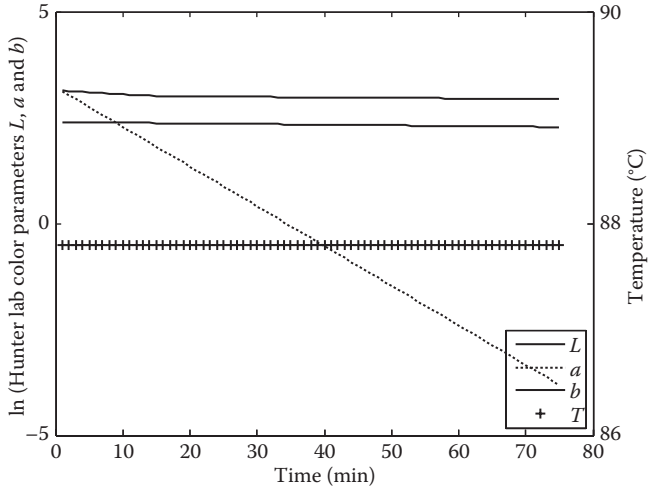


FIGURE E.5.50.2
Variation of the Hunter color parameters *L*, *a*, *b*, and temperature near the surface of the can during thermal treatment of tomato paste.

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Example 5.51: Sensory Shelf-Life Predictions by Survival Analysis

Hough, Garitta, and Gomez (2006) reported that the times required for unacceptable color development in ground beef samples may be expressed with a log-normal distribution model. The standard normal variable of the rejection times is

$$z_{\ln(t)} = \frac{\ln(t) - \ln(\mu)}{\sigma}. \tag{E.5.51.1}$$

Standard deviation σ is assumed to be independent of the temperature variations, but the populations mean rejection time μ is temperature dependent:

$$\mu = \mu_0 \exp\left(\frac{E_a}{RT}\right). \tag{E.5.51.2}$$

MATLAB® code E.5.51 estimates the cumulative fraction of the rejected samples as a function of the storage time at two different temperatures.

MATLAB® CODE E.5.51

Command Window:

```
clear all
close all

%  enter the experimental data
tData2=[24 48 96 144 192 240]; % experimentally determined failure
times (h) at 2 oC
fData2=[0.06 0.16 0.59 0.795 0.86 0.87]; % experimentally determined
fractions of  failure at 2 oC
tData19=[6 12 18 24 36]; % experimentally determined fractions of
failure at 19 oC
fData19=[0.08 0.23 0.433 0.745 0.90]; % experimentally determined
fractions of  failure at 19 oC

%  plot the experimental data
loglog(tData2,fData2, 'x'); hold on
loglog(tData19,fData19, 'o'); hold on
legend(' T= 2 ^0C', ' T=19 ^0C','Location','SouthEast')
xlabel('Storage Time')
ylabel('Fraction Failing')

% enter the model constants
lnMu0=-24; % Beta0=muRef-Ea/(R Tref)
Er=7820; % Er=Ea/R
Temp2=2+273; %  T=2 oC expressed in Kelvin
Temp19=19+273; % T=19 oC expressed in Kelvin
sigma=0.70;

%  plot the model
t=[0:240]; % model times (h)
lnMuTemp2=lnMu0+(Er/Temp2); % T=2 oC
```

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```
fModel2=normcdf(log(t),lnMuTemp2,sigma);  % model fractions of
failures at 2 oC
loglog(t,fModel2,'-'); hold on

% plot the model at 19^0C
lnMuTemp19=lnMu0+(Er/Temp19); % T=19 oC
fModel19=normcdf(log(t),lnMuTemp19,sigma); % model fractions of
failures at 19 oC
loglog(t,fModel19,':'), hold on

xlim([0 500]);
ylim([0.02 1]);
```

When we run the code Figure E.5.51 will appear on the screen.

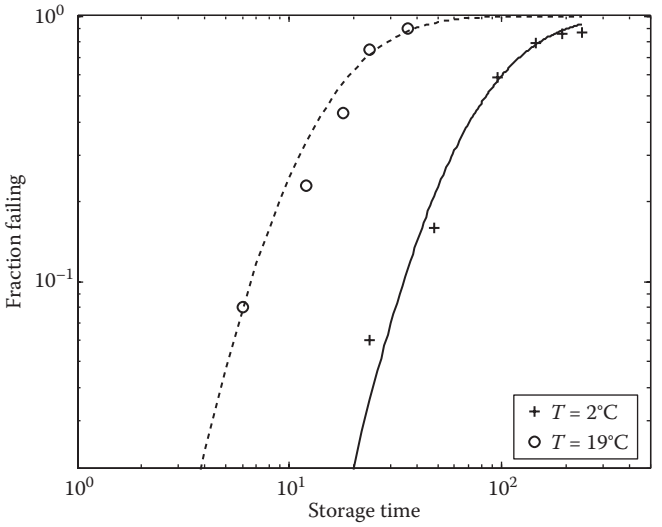


FIGURE E.5.51
Comparison of the model with the data. Experimental data of the fraction failing were determined by visual inspection of the samples by a consumer panel. (Adapted from Hough, G., Garitta, L., and Gomez, G., *Food Quality and Preference*, 17, 468–73, 2006.)

Example 5.52: Optimization of the Freeze Drying Conditions

During the freeze-drying process, on the interface the thermal energy balance may be expressed as (Lou and Zhou 2008):

$$k_{\text{crust}}\left(\frac{\partial T_{\text{crust}}}{\partial z}\right)_{z,\text{crust}} - k_{\text{core}}\left(\frac{\partial T_{\text{core}}}{\partial z}\right)_{z,\text{crust}} + \frac{\partial z_{\text{crust}}(t)}{\partial t}\left(\rho_{\text{crust}} c_{p,\text{crust}} T_{\text{crust}} - \rho_{\text{core}} c_{p,\text{core}} T_{\text{core}}\right) = -V\left(\Delta H_{\text{phase change}} + c_{p,\text{vapor}} T_{\text{phasechange}}\right). \quad \text{(E.5.52.1)}$$

Lou and Zhou (2008) assumed quasi steady state conditions on the interface, for example, $(dT_{\text{crust}}/dz)_{z,\text{crust}} = 0$ and $(dT_{\text{core}}/dz)_{z,\text{core}} = 0$ and integrated Equation E.5.52.1 to obtain an expression

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to compute the time required for complete freeze drying of an infinite slab. Constants of this integrated theoretical expression were related with the physical properties and the experimental conditions, but, unfortunately the number of these constants were discouragingly high for reliable analysis. Lou and Zhou (2008) preferred using the following empirical expression for optimization:

$$t = 1.398L - 0.070P - 0.097T + 0.082L^2 + 0.001P^2 + 0.001T^2 - 0.007LP - 0.016LT + 0.001PT + 2.074, \quad \text{(E.5.52.2)}$$

where t = freezing times (h), L = thickness of the slab (cm), P = pressure under which the freeze drying occurred (Pa), and T = temperature in the freeze-drying chamber (°C). Constants of Equation E.5.52.1 were determined from the experimental data by regression. MATLAB® code E.5.52 computes variation of the model freeze-drying times with pressure, temperature, and thickness.

Figures E.5.52.1 and E.5.52.2 show that a decrease in the slab thickness, operating pressure, and temperature cause a decrease of the freeze-drying times. Therefore, in the present example the shortest freeze-drying time is expected to be obtained when all of these parameters are maintained at their lowest attainable values.

MATLAB® CODE E.5.52

Command Window:

```
clear all
close all
format compact
L=[4:1:12];
P=[26:4:74];

% constant temperature
[L,P]=meshgrid(L,P);
for T=50:25:75
t=1.398.*L-0.070.*P-0.097.*T+0.082.*L.^2+0.001.*P.^2+0.001.*T.^
2-0.007.*L.*P-0.016.*L.*T+0.001.*P.*T+2.074;
surf(L,P,t); hold on
colormap gray
end

xlabel('L (mm)')
ylabel('P (Pa)')
zlabel('t')
text(5,80,9, 'T=75 ^o C'); % insert text to the mesh
text(7,20,7, 'T=50 ^o C'); % insert text to the mesh

% constant pressure
L=[4:2:12];
T=[53:4:77];
figure
[L,T]=meshgrid(L,T);

for P=26:48:74; % constant pressures (Pa)
t=1.398.*L-0.070.*P-0.097.*T+0.082.*L.^2+0.001.*P.^2+0.001.*T.^
2-0.007.*L.*P-0.016.*L.*T+0.001.*P.*T+2.074;
```

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```
surf(L,T,t); hold on
colormap gray
end

xlabel('L (mm)')
ylabel('T (\circC)')
zlabel('t (h)')
text(5,80,9, 'P=74 Pa'); % insert text to the mesh
text(5,50,4, 'P=26 Pa'); % insert text to the mesh
```

When we run the code Figures E.5.52.1 and E.5.52.2 will appear on the screen.

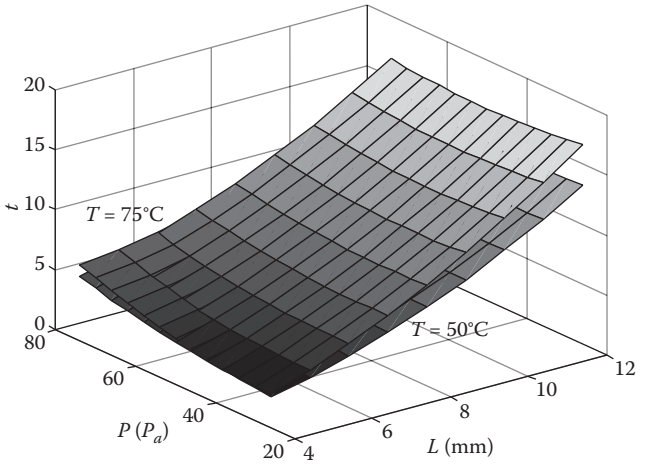


FIGURE E.5.52.1
Variation of the model freeze-drying times with pressure and thickness at 50°C and 75°C.

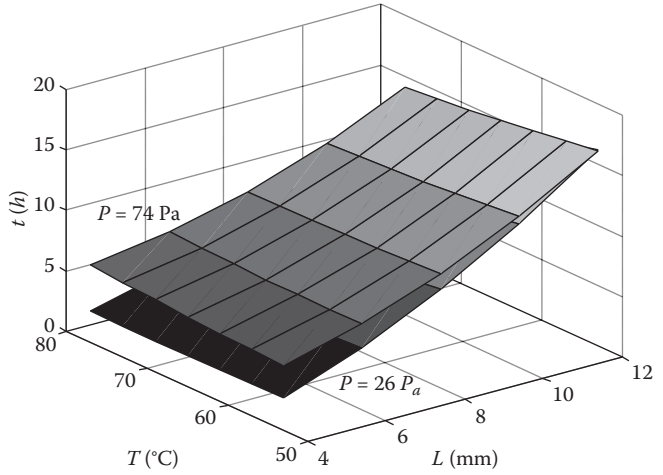


FIGURE E.5.52.2
Variation of the model freeze-drying times with temperature and thickness at 26 Pa and 74 Pa.

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Example 5.53: A Desorption Model for Moisture Loss and Color Change on the Surface of the Potatoes During Frying

Achir, Vitrac, and Tystram (2008) suggested an asymptotic desorption model for water content of a potato crust in a frying process as

$$x(t) = x_{sat} - \gamma(T(t) - T_{sat}), \tag{E.5.53.1}$$

where $x(t)$ = water content of potato surface at time = t (g water/g dry matter), x_{sat} = water content of potato when the capillaries are saturated with (monolayer) water (g water/g dry matter), $T(t)$ = temperature in the crust at time t, T_{sat} = temperature of the crust when the capillaries are saturated with adsorbed water (the frying process occurs when $T > T_{sat}$) and γ is a desorption constant. After long mathematical derivations they have ended up with the following moisture loss expression:

$$\frac{dw(t)}{dt} = -\left(\frac{T_{oil} - T_{sat}}{\alpha}\right)\left(\frac{w(t) - w_\infty}{1 - w_\infty}\right), \tag{E.5.53.2}$$

where α = constant (1/°C s), $w(t) = x(t)/x_0$ = reduced water content (g water at time t/g of water at $t = 0$), $w_\infty = x(t)/x_\infty$ reduced water content when the water content of the crust is in equilibrium with the water content of the frying oil (g water when $t \to \infty$/g of water at $t = 0$), T_{oil} = temperature of the frying oil.

Convective heat balance on the surface (oil-potato interface) leads to the equation:

$$-\Delta H_{\text{phase change}} x_0 \frac{dw}{dt} = h\left(T_{oil} - T_{surface}\right). \tag{E.5.53.3}$$

Where h = convective heat transfer coefficient on the crust-oil interface and $\Delta H_{\text{phase change}}$ is the latent heat of evaporation of water. Equation E.5.53.3 may be combined with Equation E.5.53.2 and rearranged to compute $T_{surface}$ (temperature of the crust at the crust-oil interface) as

$$T_{surface} = T_{oil} - \alpha_0\left(\frac{T_{oil} - T_{sat}}{\alpha}\right)\left(\frac{w(t) - w_\infty}{1 - w_\infty}\right), \tag{E.5.53.4}$$

where $\alpha_0 = h/\Delta H_{\text{phase change}} x_0$.

The color of the crust changes during the frying process due to the Maillard reactions, where the reducing sugars (RS) react with amino acids (A) to produce Shiff's base (AR), which produce brown pigments (B) after the reaction step named the Amadori rearrangement:

$$\mathrm{RS} + \mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} \mathrm{RA} \xrightarrow{k_2} \mathrm{AR} \to \mathrm{B}. \tag{E.5.53.5}$$

The color change of the surface may be assessed by amino acid consumption rate (Achir, Vitrac, and Tystram 2008):

$$\left[\frac{dc_A}{dt}\right]_{\text{Surface}} = k_{\text{surface}} c_A^2, \tag{E.5.53.6}$$

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where $k_{surface}$ is the reaction rate constant evaluated at the temperature of the crust surface and expressed as

$$k_{surface} = k_{ref} \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_{surface}} - \frac{1}{T_{ref}}\right)\right]. \quad \text{(E.5.53.7)}$$

Equation E.5.53.7 is an Arrhenius type expression. Where c_A is the amino acid concentration, k_{ref} is the reaction rate constant at reference temperature T_{ref}. Equation E.5.53.6 will be solved as

$$c_A(t) = \frac{c_{A0}}{1 + k_{surface} t c_{A0}}. \quad \text{(E.5.53.8)}$$

Where MATLAB® code E.5.53 plots the expected reduced water contents, surface temperature, and amino acid consumption rates of a potato slab when all the constants of Equations E.5.53.2, E.5.53.4, and E.5.53.8 are available.

MATLAB® CODE E.5.53

Command Window:

```
clear all
close all
format compact

global Toil Xinfinity Xo alpha alpha0

% enter the constants of the model and the operating parameters
Xinfinity=0.01; % Xinfinity= moisture content attainable at the end
of the frying process (kg water/kg dry matter
Xo=0.5; % Xo= initial water content (kg water/kg dry matter)
alpha=30e3/60; % time constant (1/min C) (adapted from Achir et al.,
2008)
alpha0=200;

for Toil=120:20:180
   [t,w]=ode45('WaterFraction',[0 60],1);

    if Toil==120  plot(t,w, '-');  hold on;  end
    if Toil==140  plot(t,w, ':');  hold on;  end
    if Toil==160  plot(t,w, '.-');  hold on;  end
    if Toil==180  plot(t,w, '--');  hold on;  end

end

xlabel('time (min)')
ylabel('w (fraction of water remaining)')
legend('Toil=120 oC', 'Toil=140 oC' , 'Toil=160 oC' , 'Toil=180 oC'
,  'Location','Best')

% MODELING OF THE SURFACE TEMPERATURES
figure

for Toil=120:20:180
    if Toil==120  Tsat=100; end
    if Toil==140  Tsat=90; end
```

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```
    if Toil==160  Tsat=82; end
    if Toil==180  Tsat=75; end

 [t,w]=ode45('WaterFraction',[0 60],1);
Tsurface=Toil-alpha0*((Toil-Tsat)/alpha)*((w-(Xinfinity/Xo))/
(1-(Xinfinity/Xo)));
    if Toil==120  plot(t,Tsurface, '-');  hold on;  end
    if Toil==140  plot(t,Tsurface, ':');  hold on;  end
    if Toil==160  plot(t,Tsurface, '.-');  hold on;  end
    if Toil==180  plot(t,Tsurface, '--');  hold on;  end

end

ylim([100 200]);
xlabel('time (min)')
ylabel('T (\circC )')
legend('Toil=120 oC', 'Toil=140 oC' , 'Toil=160 oC' , 'Toil=180 oC'
,  'Location','Best')

% MODELING THE VARIATION OF THE AMINO ACID  CONCENTRATIONS ON THE
SURFACE
figure
kref=60*2.38e-7; % (1/(m mol kg))
Ea =3e3; % J/mol
R=8.31; % J/mol K
cA0=0.2; % mol/kg dry matter

for Toil=120:20:180

    if Toil==120  Tsat=100;  end
    if Toil==140  Tsat=90; end
    if Toil==160  Tsat=82; end
    if Toil==180  Tsat=75;  end

[t,w]=ode45('WaterFraction',[0 60],1)
time(1:length(t))=t;
w1(1:length(w))=w;

for i=1:length(time);
Tsurface(i)=Toil-alpha0*((Toil-Tsat)/alpha)*((w1(i)-(Xinfinity/Xo))/
(1-(Xinfinity/Xo)));
k(i)=kref*(exp(-(Ea/R)*((1/Tsurface(i))-(1/(Tsat+273)))));
     cA(i)=cA0/(1+k(i)*time(i)*cA0);
end

    if Toil==120  plot(time,cA, '-');  hold on;  end
    if Toil==140  plot(time,cA, ':');  hold on;  end
    if Toil==160  plot(time,cA, '.-');  hold on;  end
    if Toil==180  plot(time,cA, '--');  hold on;  end

end

xlabel('time (min)')
ylabel('c (mol/kg dry matter)')
legend('Toil=120 oC', 'Toil=140 oC' , 'Toil=160 oC' , 'Toil=180 oC'
,  'Location','Best')
```

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M-File

```
function [dwdt]=WaterFraction(t,w)
global Toil Xinfinity Xo alpha alpha0
    if Toil==120  Tsat=100;  end
    if Toil==140  Tsat=90; end
    if Toil==160  Tsat=82; end
    if Toil==180  Tsat=75;  end

dwdt=-((Toil-Tsat)/alpha)*((w-(Xinfinity/Xo))/(1-(Xinfinity/Xo)));
When we run the code Figures E.5.53.1, E.5.53.2 and E.5.53.1 will
appear on the screen.
```

When we run the code Figures E.5.53.1, E.5.53.2 and E.5.53.3 will appear on the screen.

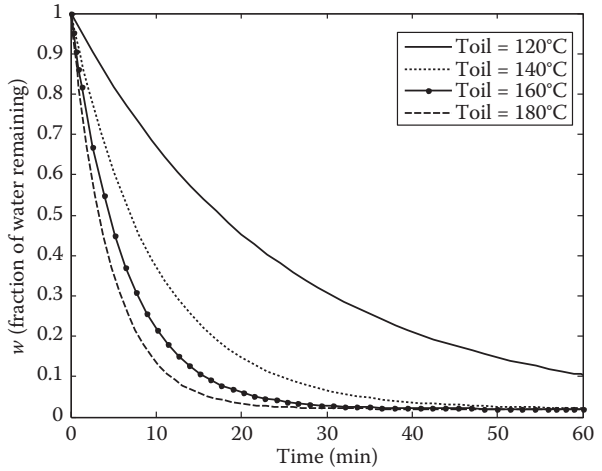


FIGURE E.5.53.1
Predicted average fraction of water in the crust during the frying process.

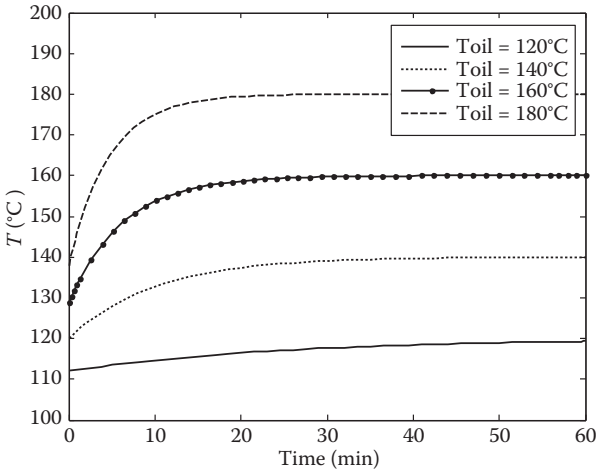


FIGURE E.5.53.2
Predicted surface temperatures during the frying process.

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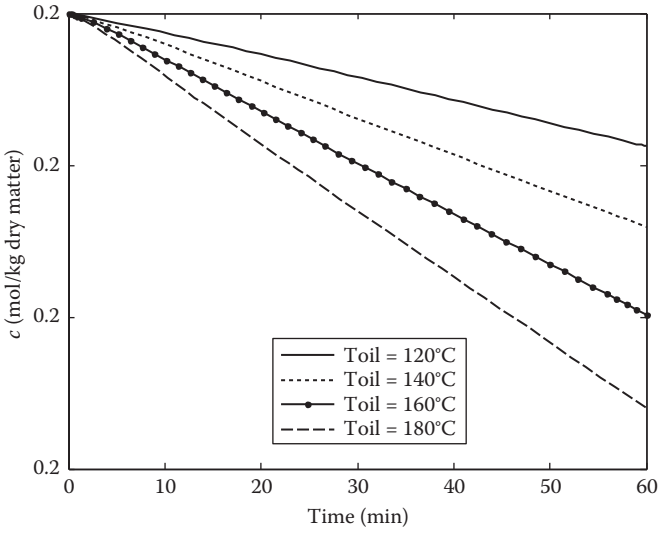


FIGURE E.5.53.3
Predicted amino acid concentrations remaining on the surface during the frying process. (Adapted from Achir, N., Vitrac, O., and Tystram, G., *Chemical Engineering and Processing*, 47, 1953–67, 2008.)

Questions for Discussion and Problems

A. Distribution Model Problems

1. Under what conditions are we permitted to use:
   i. The Gaussian distribution model
   ii. The Poisson distribution model
   iii. The Binomial distribution model
2. If the measurements of a data set are not normally distributed what would you do to be able to use the statistical tools you learned in this book?
3. What is the central limit theorem? What are its consequences in sampling?
4. Although the concept of 6σ range is theoretically related with the Gaussian distribution only, it is also used with binomial and Poisson distributions in practice. What is the basis for that?
5. What are type 1 and type 2 errors?
6. What is the probability of having exactly seven cans with less than 500 g of contents when eight cans are taken randomly from a population where 90% of all cans have more than 500 g of contents?
7. A fruit juice mix is produced by mixing two different juices. The first juice has a sugar content of $\mu_I = 7\%$ and $\sigma_I = 0.5\%$, the other one has the sugar content with $\mu_{II} = 6\%$ and $\sigma_{II} = 1.5\%$. If the juice mix is made with using 30% of the first juice and 70% of the second juice what percentage of the final products contain more than 6.7% sugar?
8. The following set of data with $\mu = 3.16$ g/ml and $\sigma = 0.22$ g/ml are pertinent to CO_2 measurements in bottled beer. Are these data distributed normally?

Number of Measurements	9	15	20	12	9	8	2	2	1
Measurement (g/ml)	3.0	3.1	3.2	3.3	3.4	3.5	3.6	3.8	4

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9. Vegetable oil samples (A, B, C) were tasted in three laboratories. The following iodine numbers (x) were reported.

Laboratory	x_A	X_B	X_C
1	139	135	140
2	135	140	130
3	118	100	120

i. Is there an actual difference in the iodine numbers of the samples?
ii. Is there an actual difference between the scores of the different laboratories?

xv. Four inspectors evaluated four products and their scores are listed as

Inspector → **Lot number ↓**	**I**	**II**	**III**	**IV**
1	73	75	80	69
2	82	82	90	80
3	65	66	73	64
4	70	73	83	69

i. Is there any significant difference between the scores of the products?
ii. Is there any significant difference between the scores of the inspectors?

B. Quality Control Charts

1. Five sets of samples were taken every other hour from a fruit juice production line. The following sugar contents were measured:

X_1: 5.3, 5.5, 4.0, 4.5, 5.0 g/L
X_2: 4.7, 4.7, 6.0, 4.0, 5.3 g/L
X_3: 3.9, 5.1, 5.5, 5.7, 3.0 g/L
X_4: 4.4, 5.7, 5.4, 5.9, 4.0 g/L
X_5: 3.9, 5.8, 5.4, 4.0, 3.2 g/L

i. With the given data, determine the CL, UCL, and the LCL of the quality control chart.
ii. Can we regard the fluctuations in the data as "random process fluctuations"?
iii. Why do we prepare BOTH $\bar{x}$ and R charts when we prepare the statistical control charts for measurements?
iv. The USL for the process is 6.0 g/L, the higher sugar content makes the product unacceptably sweet. There is no LSL. Determine the "process capability index" and discuss your results.

2. Power-law fluids have apparent viscosity of the form $\eta = K\dot{\gamma}^{n-1}$, where η is the apparent viscosity (Pa s), $\dot{\gamma}$ is the shear rate (s^{-1}), K is the consistency coefficient (Pa s^n), and n is the dimensionless flow behavior index. It is required to have $\bar{K}$ within the limits of 6.40 ± 0.08 and $\bar{n}$ within the limits of 0.550 ± 0.04 for a mayonnaise of acceptable quality. Draw appropriate control charts to determine whether this process with the following K and n values is under control to the given limits.

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Sample Set	K (Pa s^n)	n
1	6.40, 6.35, 6.45, 6.38, 6.60	0.550, 0.530, 0.551, 0.560, 0.558
2	6.38, 6.37, 6.35, 6.28, 6.50	0.551, 0.532, 0.543, 0.561, 0.547
3	6.40, 6.35, 6.45, 6.38, 6.60	0.550, 0.530, 0.555, 0.560, 0.558
4	6.38, 6.28, 6.35, 6.28, 6.50	0.551, 0.532, 0.549, 0.561, 0.547
5	6.40, 6.43, 6.45, 6.39, 6.60	0.550, 0.530, 0.550, 0.550, 0.558
6	6.38, 6.37, 6.45, 6.55, 6.50	0.531, 0.533, 0.545, 0.571, 0.549
7	6.43, 6.45, 6.47, 6.27, 6.60	0.550, 0.530, 0.565, 0.560, 0.558
8	6.39, 6.27, 6.39, 6.44, 6.50	0.558, 0.539, 0.561, 0.561, 0.547
9	6.68, 6.39, 6.35, 6.458, 6.50	0.551, 0.532, 0.535, 0.572, 0.547
10	6.50, 6.32, 6.55, 6.27, 6.59	0.540, 0.520, 0.562, 0.548, 0.580

Hint: Construct $\bar{K}$ and $\bar{n}$ charts with $UCL_K = 0.648$, $LCL_K = 0.632$, and $UCL_n = 0.554$, $LCL_n = 0.546$.

C. Standard Sampling Plans for Attributes

1. Determine the AOQL percentage for the sampling plan with $N = 200$, $n = 5$, and $c = 0$ when the method of analysis is (i) nondestructive and (ii) destructive.
2. 100 kg of a food grade chemical will be purchased by a factory. The raw material is highly hygroscopic. The raw material is provided in 500 g sealed containers. There are 20 containers in a box, and 5 boxes in a carton. Make a detailed sampling plan.

D. Process Analysis Problems

Read the following paragraphs about (i) coffee, (ii) lipstick (Johnson 1999), and (iii) tablet-making processes then answer the following questions separately for each case:

i. All green coffee fruit are sorted by immersion in water, where the good ripe ones sink while others float. A fraction of the skin and pulp are removed by pressing the fruit in water through a screen, the remainder is removed by fermentation for several days followed by washing. The water content of the beans are reduced to 12–13% by sun-drying and further down to 10% in driers. The dried beans are screened and roasted at 188 to 282°C, which may last up to about 30 minutes. The roasters are horizontal rotating drums that tumble the green coffee beans in hot combustion gases. The stones, metal fragments, and other wastes are removed from the beans in the "destoners." The beans are then pneumatically conveyed into hoppers, where they are kept for a while to equilibrate their moisture content. After the equilibration stage, the roasted beans are packed either as ground or whole beans.
ii. Lipstick contains a variety of waxes, oils, pigments, and skin smoothers. The bee, carnauba plant, and/or candelilla plant wax give lipstick its shape and ease of application. The oils and fats used in lipstick include olive oil, mineral oil, castor oil, cocoa butter, lanolin, and petrolatum. Castor oil forms a tough, shiny film when it dries after application. However, ingestion of large amounts of castor oil may cause frequent restroom visits. Ingredients such as moisturizers, vitamin E, aloe vera, collagen, amino acids, and sunscreen are also added to the lipstick. Lipstick gets its color from the added pigments, such as bromo acid, D&C Red No. 21, D&C Red No. 27, and insoluble dyes known as lakes, such as D&C Red No. 34, Calcium lake, and D&C Orange No. 17. During the lipstick production process, the mixture of the raw materials is finely ground, the waxes, oils, and lanolin are added and heated up. The hot liquid is poured into cold metal molds where

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it solidifies. The formed lipstick is put through a flame for about half a second to create a smooth and glossy finish and to remove imperfections.

There are frosted, matte, sheer, stain, and long-lasting color lipsticks available in the stores. Frosted lipsticks include a pearlizing agent—often a bismuth compound—that adds luster to the color. Bismuth oxychloride, which is synthetic pearl, imparts a frost or shine. Bismuth subcarbonate is used as a skin protective. Most bismuth compounds used in cosmetics have low toxicity when ingested, but they may cause allergic reactions when applied to the skin.

iii. Food supplement or artificial sweetener tablets are produced by pressing the well-mixed ingredients. The ingredients must be dry, uniform in particle size, and freely flowing. Mixed particle sized powders can segregate and result in nonuniform contents. The tablet formulations include a binder to hold the tablet together and give it strength. Lactose, dibasic calcium phosphate, sucrose, corn starch, microcrystalline, and modified cellulose are among the preferred binders. Ingredients include a disintegrant that hydrates in water to aid tablet dispersion. Starch and cellulose, are also excellent disintegrants. Small amounts of lubricants are added to the formulations to help the tablets to be easily ejected from the die after pressing. Magnesium stearate, stearic acid, hydrogenated oil, and sodium stearyl fumarate are among the common lubricants.

Tablets can be coated after being pressed with a combination of polymers, polysaccharides, plasticizers, and pigments. Coatings must be strong enough to survive handling and prevent the tablets from being sticky. Coatings may facilitate printing on tablets, make them easier to swallow and extend the shelf life via protecting the moisture or oxidation sensitive ingredients. Coatings with pearlescent effects may enhance brand recognition. Tablet machines range from benchtop models that make one tablet at a time to the ones that make millions of tablets in an hour.

1. Draw the process flow charts.
2. Locate the MCPs and the CCPs on the flow charts. What is the difference between the MCPs and CCPs?
3. What kind of a sampling procedure may you apply at these points?

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