CHAPTER ONE

Volumetric Properties of Pure Fluids

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Learning Objectives

- Describe the general nature of PVT behavior of pure fluids.
- Apply different equations of state to estimate the thermodynamic properties of pure substances
- Present some of the best-known equations of state
- Introduce viral equation of state
- Generalized correlations are presented that allow prediction of the PVT behavior of fluids for which experimental data are lacking
- Applications of Viral equations

1. PVT BEHAVIOR OF PURE SUBSTANCES

- Thermodynamic properties, such as **internal energy** and **enthalpy**, from which one calculates the **heat** and **work requirements of industrial processes**, are often evaluated from **volumetric data**.
- Moreover, **Pressure/Volume/Temperature (PVT)** relations are themselves important for such purposes as the **metering of fluids and the sizing of vessels and pipelines.**
- Measurements of the **vapor pressure** of a pure substance, both as a solid and as a liquid, lead to **pressure-vs.-temperature curves** such as shown by lines 1-2 and 2-C in Fig. 1.
- The third line (2-3) gives the solid/liquid equilibrium relationship.

1. PVT BEHAVIOR OF PURE SUBSTANCES

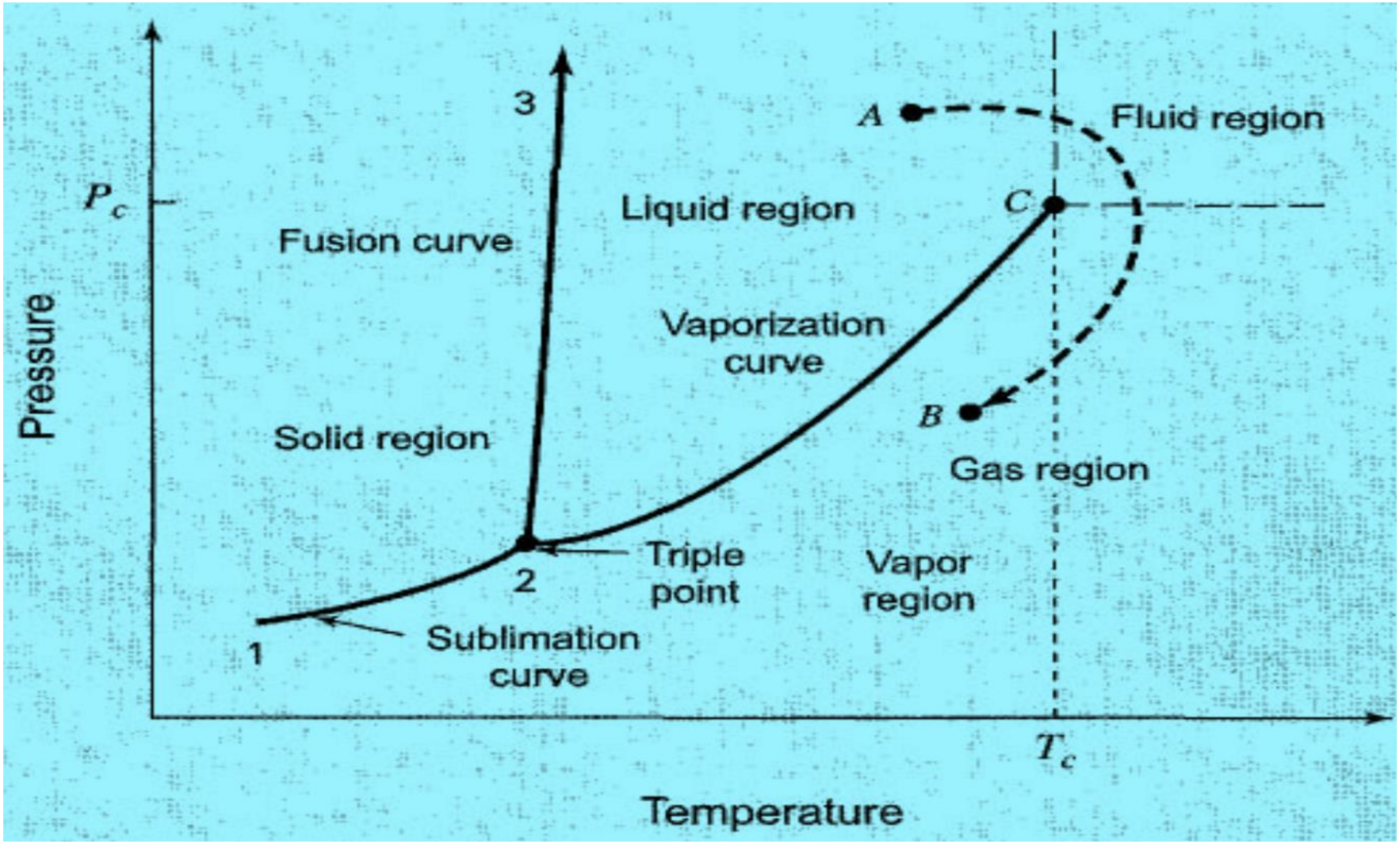


Fig. 1. PT diagram for a pure substance

1. PVT BEHAVIOR OF PURE SUBSTANCES

- The three lines display conditions of **P and T** at which **two phases may coexist**, and are **boundaries** for the **single-phase regions.**

- Line 1-2, the **sublimation curve,** separates the solid and gas

- Line 2-3, the **fusion curve,** separates the solid and liquid
- Line 2-C, the **vaporization curve**, separates the liquid and gas regions and terminates at point C; **Critical point**

the critical pressure Pc and the critical temperature Tc, the highest pressure and highest temperature at which a pure chemical species can exist in vapor/liquid equilibrium.

- All three lines meet at the **triple point,** where the three phases coexist in equilibrium.

- from A to B, liquid and gas phase become indistinguishable at C.

1. PVT BEHAVIOR OF PURE SUBSTANCES

Phase Rule: For any system at equilibrium, the number of independent variables that must be arbitrarily fixed to establish its intensive state is given by the phase rule of **J. Willard Gibbs;** who deduced it by theoretical reasoning in 1875.

- It is presented here without proof in the form applicable to non-reacting systems:

$F=2-\pi+N$……………………………………………1.1

- Where: **π is the number of phases**, **N is the number of chemical species**, and **F is the degrees of freedom(the number of intensive(T and P) independent variable)** of the system.
- The triple point is **invariant (F = 0).**
- The system exists along any of the two-phase lines is **univariant (F = 1),** and the single-phase regions it is **divariant (F = 2).**

1. PVT BEHAVIOR OF PURE SUBSTANCES

Phase Rule:

Example: How many degrees of freedom have each one of the following systems?

1. Liquid water in equilibrium with its vapor.

The system contains a single chemical species and two phases: F=2-2+1=1

2. Liquid water in equilibrium with a mixture of water vapor and nitrogen.

Two chemical species and two phases are present: F=2-2+2=2

3. A liquid solution of alcohol in water in equilibrium with its vapor.

Two chemical species and two phases are present: F=2-2+2=2

1. PVT BEHAVIOR OF PURE SUBSTANCES

PV Diagram

- Fig.1. does not provide any information about **volume**; it merely displays the **phase boundaries** on a **PT diagram**.
- On a PV diagram **(Fig. 2 (a))** the boundaries become **areas**, i.e., regions where two phases; solid/liquid, solid/vapor, and liquid/vapor, coexist in equilibrium.
- The two-phase **liquid/vapor** region lies under **dome BCD,** whereas the **sub-cooled-liquid** and **superheated-vapor** regions lie to the left and right, respectively.
- Sub-cooled liquid exists at temperatures **below the boiling point**, and superheated vapor, at temperatures **above the boiling point** for the **given pressure.**
- Isotherms in the sub-cooled-liquid region are very steep, **because liquid volumes change little with large changes in pressure**.

1. PVT BEHAVIOR OF PURE SUBSTANCES

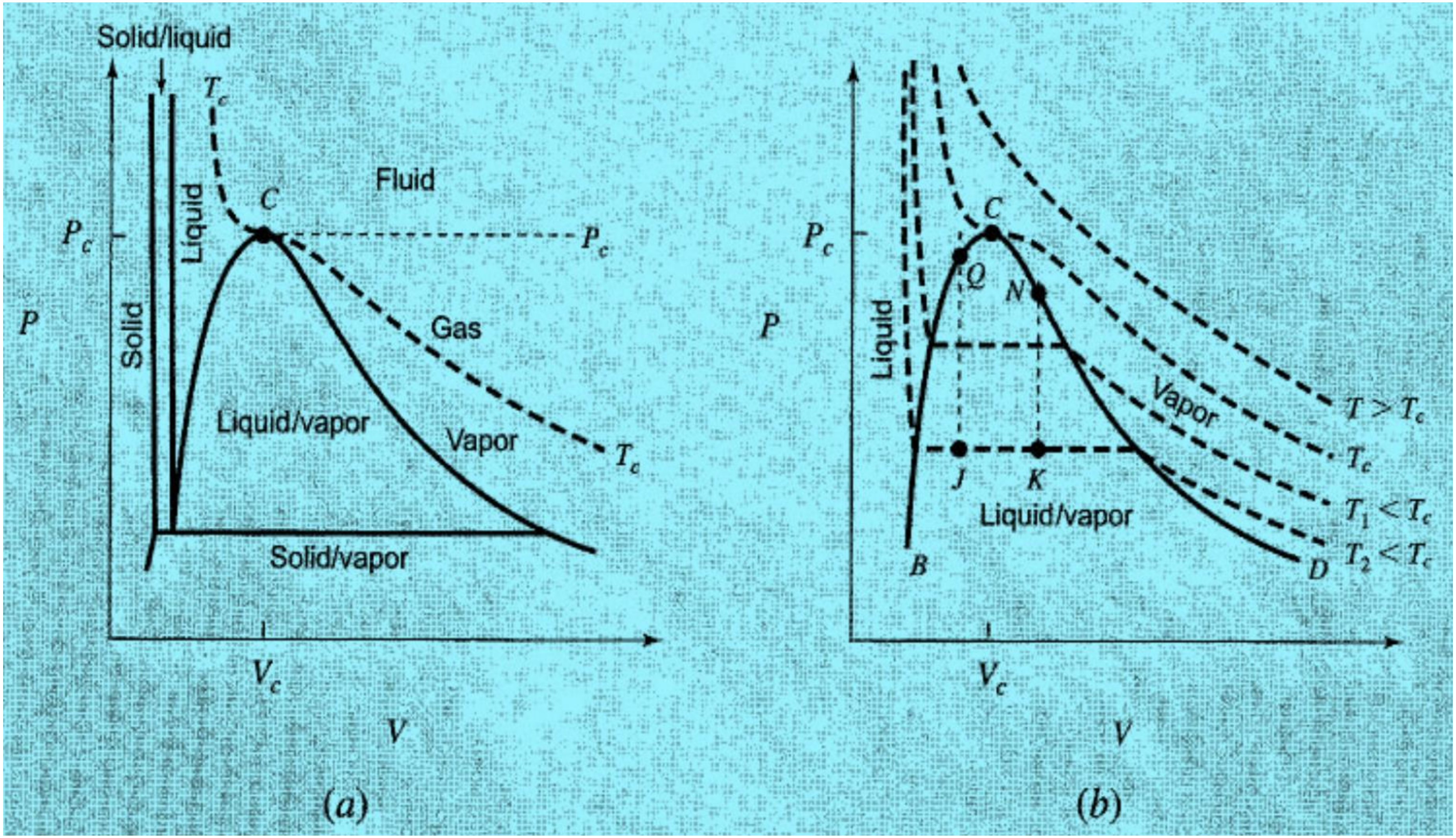


Figure 2: PV diagrams for a pure substance.

(a) Solid, liquid, and gas regions.

(b) Liquid, liquid/vapor, and vapor regions with isotherms

1. PVT BEHAVIOR OF PURE SUBSTANCES

PV Diagram

- The lines labeled Tl and T2 are for subcritical temperatures, and consist of three segments. The horizontal segment of each isotherm represents all possible mixtures of liquid and vapor in equilibrium, ranging from 100% liquid at the left end to 100% vapor at the right end.
- from B to C represents single -phase (saturated) liquids at their vaporization (boiling) temperatures, and the
- From C to D, single-phase (saturated) vapors at their condensation temperatures.

1. PVT BEHAVIOR OF PURE SUBSTANCES

Single-Phase Region

- An ***equation of state*** exists relating **Pressure P, molar or specific Volume v, and Temperature T;** for any pure homogeneous fluid in equilibrium states.
- For the regions of the diagram where a single phase exists, **Fig. 2(b)** implies a relation connecting **P, V,** and **T** which may be expressed by the functional equation:

$$f(P, V, T) = 0 \quad T=T(P<V), P=P(V,T), V=V(P,V)$$

- The simplest equation of state is for an ideal gas, **PV = RT**, a relation which has approximate validity for the **low pressure gas region** of Fig. 2(b).

1. PVT BEHAVIOR OF PURE SUBSTANCES

- An equation of state may be solved for any one of the three quantities **P, V, or T** as a function of the other two.
- For example, if V is considered a function of T and P, then **V = V(T, P),** and

$$dV = \left(\frac{\partial V}{\partial T}\right)_P dT + \left(\frac{\partial V}{\partial P}\right)_T dP \quad \text{..............................1.2}$$

- The partial **derivatives in this equation have definite physical meanings**, and are related to two properties, commonly **tabulated for liquids**, and defined as follows:

1. **Volume expansivity:**

$$\beta \equiv \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \quad \text{................1.3}$$

2. **Isothermal compressibility:**

$$\kappa \equiv -\frac{1}{V}\left(\frac{\partial V}{\partial P}\right)_T \quad \text{...........1.4}$$

Combination of Eqs. (1.2) to (1.4) provides:-

$$\frac{dV}{V} = \beta\, dT - \kappa\, dP \quad \text{..........1.5}$$

1. PVT BEHAVIOR OF PURE SUBSTANCES

- The isotherms for the liquid phase on the left side of Fig. 2(b) are **very steep and closely spaced**.
- Thus both $\left(\frac{\partial V}{\partial T}\right)_P$ and $\left(\frac{\partial V}{\partial P}\right)_T$ and hence both β and k are **small.**
- This characteristic behavior of liquids (outside the critical region) suggests an idealization, commonly employed in fluid mechanics and known as the **incompressible fluid**, for which both , **β and k are zero**
- Integration of Eq. (1.5) then yields:

$$\frac{dV}{V} = \beta\, dT - \kappa\, dP$$

$$\ln \frac{V_2}{V_1} = \beta(T_2 - T_1) - \kappa(P_2 - P_1) \qquad \text{……………………1.6}$$

- For **liquids β is almost positive** (liquid water between 0°C and 4°C is an exception), and **κ is necessarily positive.**
- At conditions not close to the critical point, β and κ are weak functions of temperature and pressure. Thus for small changes in T and P little error is introduced if they are assumed constant.

2. Virial Equations of State

- It is difficult to represent P-V-T behaviors of pure substances in all regions by a single equation, but for **vapor phase only** there are simple equations.
- At **constant temperature**, the product **PV** is **nearly constant** as compared to the individual parameters P and V.
- For example, PV along an **isotherm** may be expressed by a power series expansion in P:

$$PV = a + bP + cP^2 + dP^3 + \cdots \qquad \text{........................1.7}$$

- Where: the coefficients ***a, b, c, etc.*** are functions only of **temperature** (and not of pressure).
- It can also write as:

$$PV = a(1 + B'P + C'P^2 + D'P^3 + \cdots) \qquad \text{........................1.8}$$

2. Virial Equations of State

- It In fact, P V T data shows that **at low pressures truncation after two terms usually provides satisfactory** results.
- If we plot PV vs. P curve **for four gases** at the triple-point temperature of water (Fig. 3), the limiting value of PV as P→0 is the **same for all of the gases. (Boyle's law)**

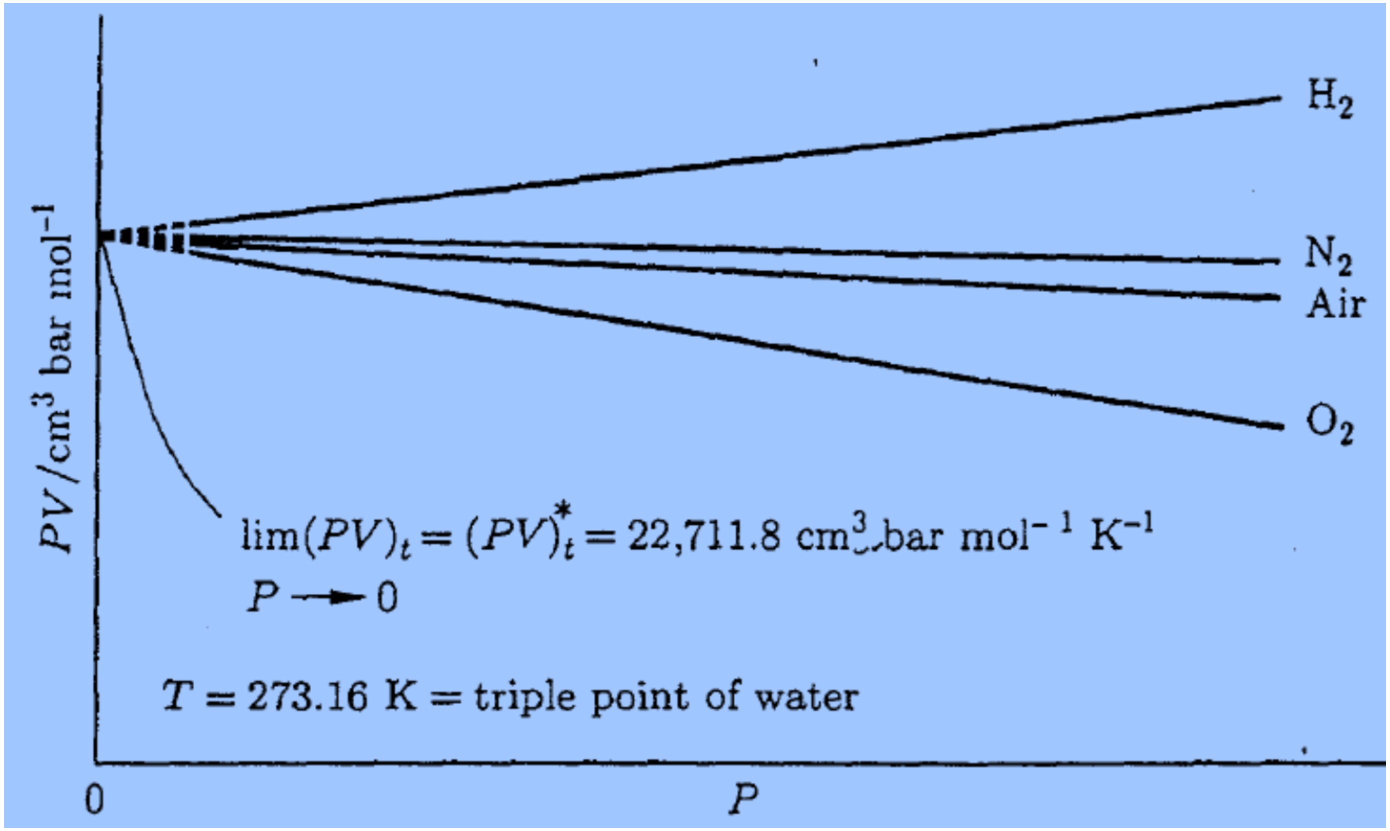


Figure 3: The limit of *PV as* P→0 is independent of the *gas*

2. Virial Equations of State

- **Experimentally**, as the pressure becomes very small (**mathematically**, in the limit (denoted by the asterisk) that *P* goes to zero) the **pressure volume product (*PV*) goes to the same value for all gases.**
- This is used to establish the ***ideal gas temperature scale*** and, in turn, the value of the ***Universal Gas Constant.***
- If we denote the gas independent value of *PV* as the pressure goes to zero as **(*PV*)*,** then we can define the **ideal gas temperature scale** by assigning the quantity **(PV)*** to be proportional to temperature

$$(PV)^* = a = f(T)$$

i. **Make (PV)* directly proportional to T,** with **"R"** as the proportionality constant:

$$(PV)^* = a = RT \quad \text{........................1.9}$$

2. Virial Equations of State

ii. **Assign the value 273.16 K to the temperature of the triple point of water** (denoted by subscript *t*):

$$(PV)^*_t = R * 273.16 \qquad \text{........................1.10}$$

- Division of Eq. (1.9) by Eq. (1.10) gives:

$$\frac{(PV)^*}{(PV)^*_t} = \frac{RT}{R * 273.16K} = \frac{T}{273.16K}$$

$$\frac{T}{K} = 273.16\,\frac{(PV)^*}{(PV)^*_t} \qquad \text{...........................1.11}$$

- The universal gas constant R, numerical value is determined by means of Eq. (1.10) from experimental P V T data: The accepted value of   is **$22.7118\ \mathrm{m^3\ bar\ kmol^{-1}}$**,

$$R = \frac{(PV)^*_t}{273.16} = \frac{22.7118\ \mathrm{m^3\ bar\ kmol^{-1}}}{273.16} = 0.0831447\ \mathrm{m^3\ bar\ kmol^{-1}} = 8.31447\ \mathrm{J\ \ kmol^{-1}}K^{-1}$$

2. Virial Equations of State

Two forms of virial equation

- From the definition of *compressibility factor* (The behavior of *real gases* deviates from that of an *ideal gas)*

$$Z \equiv \frac{PV}{RT} \quad \text{............................}1.12$$

- With this definition and with *a* = *RT* [Eq. (1.9)], and Eq. (1.8) becomes **(Pressure Expansion): Taylor series**

$$\mathbf{Z = 1 + B'P + C'P^2 + D'P^3 + \cdots} \qquad 1.13$$

- An alternative expression for Z is also in common use **(Volume Expansion)**:

$$\mathbf{Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots} \qquad 1.14$$

- Both of these equations are known as ***virial expansions,*** and the parameters ***B', C', D',*** etc., and ***B, C, D,*** etc., are called ***virial coefficients.***
- Parameters ***B'*** **and** ***B*** are ***second*** virial coefficients; ***C' and C*** are ***third*** virial coefficients; etc.

2. Virial Equations of State

- For a given gas the virial coefficients are functions of temperature only.
- The two sets of coefficients in Eqs. (1.13) and (1.14) are related as follows:

$$B' = \frac{B}{RT} \qquad C' = \frac{C - B^2}{(RT)^2} \qquad D' = \frac{D - 3BC + 2B^3}{(RT)^3} \qquad etc.$$

- They are given in Appendix C1,C2 and C3 on Smith J.M., Van Ness H.C. and Abbott M.M. (2001). Introduction to Chemical Engineering Thermodynamics (6th Edition), McGraw-Hill.

3. Application of Virial Equations of State

- For engineering purposes the use of the **two forms of the virial expansion** is practical only where **convergence** is **very rapid**, that is, where two or three terms suffice for reasonably close approximations to the values of the series.
- This is realized for gases and vapors at **low to moderate pressures.**
- For example: Values of the compressibility factor *Z* (as calculated from *P*VT data for **methane** by the defining equation **Z=PV/RT) are plotted vs. pressure** for various **constant temperatures.**
- All isotherms originate at the value **$Z = 1$ for $P = 0$.** In addition the isotherms are nearly straight lines at low pressures.
- Thus the tangent to an isotherm at **$P=0$** is a good approximation of the isotherm from **$P \to 0$** to some finite pressure.

3. Application of Virial Equations of State

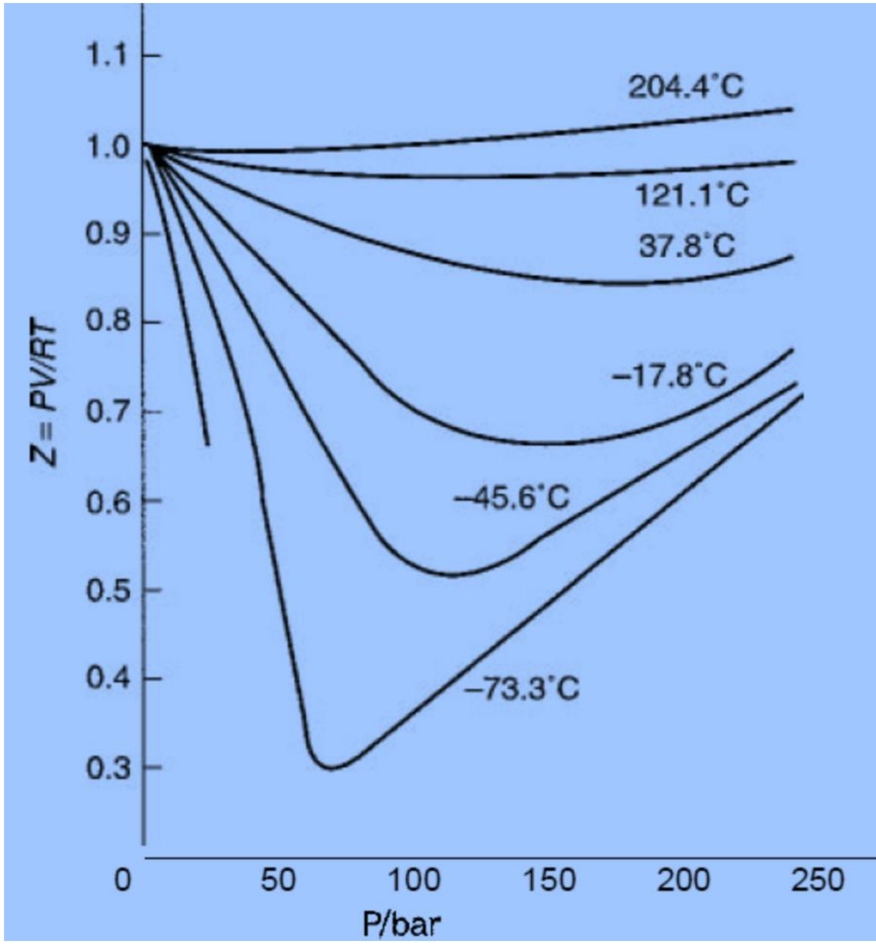
- Differentiation of Eq. (1.13) for a given temperature gives:

$$Z = 1 + B'P + C'P^2 + D'P^3 + \cdots$$

$$\left(\frac{\partial Z}{\partial P}\right)_T = B' + 2C'P + 3D'P^2 + \cdots$$

And, at P = 0 i.e., $$\left(\frac{\partial Z}{\partial P}\right)_{T;P=0} = B'$$

- And the equation of the tangent line is:



$$\frac{Z-1}{P-0} = B' \qquad \text{Thus: } Z = 1 + B'P$$

3. Application of Virial Equations of State

- The result is the same as **truncating** Eq. (1.14) to **two terms**. Substituting; **B' = B/RT:**

$$\mathbf{Z = 1 + \frac{B}{V} + \frac{C}{V^2} + \frac{D}{V^3} + \cdots} \qquad \mathbf{1.14}$$

$$\mathbf{Z = \frac{PV}{RT} = 1 + \frac{B}{V}} \qquad \mathbf{1.27}$$

- Eq. (1.27) is more convenient in application and it represents the PVT behavior of many vapors at subcritical temperatures up to a **pressure of about 5 bar.**

4. THE IDEAL GAS

- Since the terms **B/V**, **C/V2,** etc., of the virial expansion [Eq. (1.14)] arise on account of **molecular interactions**, the virial coefficients B, C, etc., would be **zero if no such interactions existed**.

- The virial expansion would then reduce to:

$$\boldsymbol{Z = 1 \quad \text{or} \quad \mathrm{PV} = RT} \qquad \mathbf{1.15}$$

- The internal energy of gas depends on temperature only:

$$\mathbf{U = U(T)} \qquad \mathbf{1.16}$$

- The heat capacity at constant volume for an ideal gas C_v (is a measure of the variation of internal energy of a substance with temperature) is a function of temperature only:, and

$$\boldsymbol{C_v = \left(\frac{\partial U}{\partial T}\right)_V = \frac{dU}{dT} = C_v(T)} \qquad \mathbf{1.17}$$

4. THE IDEAL GAS

- The enthalpy, H also is a function of temperature only:

$$\mathbf{H = U + PV = U(T) + RT = H(T)} \qquad \mathbf{1.18}$$

- The heat capacity at constant pressure for an ideal gas Cp (is a measure of the variation of enthalpy of a substance with temperature) is a function of temperature only:

$$C_P = \left(\frac{\partial H}{\partial T}\right)_P = \frac{dH}{dT} = C_P(T) \qquad \mathbf{1.19}$$

- A useful relation between Cp and Cv for an ideal gas comes from differentiation of Eq. (1.18)

$$C_P = \frac{dH}{dT} = \frac{dU}{dT} + R = C_V + R \qquad \mathbf{1.20}$$

- This equation **does not imply** that C_P and C_V are themselves **constant for** an ideal gas, but only that they vary with temperature in such a way that their difference is **equal to R.**

4. THE IDEAL GAS

Equations for Process Calculations: Ideal Gases

- For an ideal gas in any mechanically reversible closed-system process:
- Using first law of thermodynamics and ideal gas equation:-

$$\mathrm{dQ} = \frac{C_V}{R} V dP + \frac{C_P}{R} P dV$$

- For isothermal process?
- For isobaric process?
- For isochoric process?
- For Adiabatic process?

Equations for Process Calculations

1st Law: $\delta Q + \delta W = dU$ where; $dU = C_V dT$, and $\delta W = -PdV$

Ideal Gas: $Z = \frac{PV}{RT}$ and for ideal gas, $Z = 1$

- $\delta Q = C_V\,dT + PdV$ $\quad$ **1.21**
  - Using the ideal gas equation: **PV=RT**; let **P=RT/V**
- $\delta Q = C_V\,dT + RT\frac{dV}{V}$ $\quad$ **1.22**
- $\delta W = -RT\frac{dV}{V}$ $\quad$ **1.23**
  - Alternatively, let **V=RT/P**
- $\delta Q = C_V\,dT + P\left(\frac{R}{P}dT - \frac{RT}{P^2}dP\right) = C_P\,dT - RT\frac{dP}{P}$ $\quad$ **1.24**
- $\delta W = -RdT + RT\frac{dP}{P}$ $\quad$ **1.25**
  - Finally let, **T=PV/R**
- $\delta Q = C_V\left(\frac{V}{R}dP + \frac{P}{R}dV\right) + PdV = \frac{C_V}{R}VdP + \frac{C_P}{R}PdV$ $\quad$ **1.26**

Equations for Process Calculations

Isothermal (Constant - T) Process:

- $\Delta U = \Delta H = 0$
- $\text{By Eqs. (1.22) and (1.24):} \qquad Q = RT\ln\frac{V_2}{V_1} = -RT\ln\frac{P_2}{P_1}$
- $\text{By Eqs. (1.23) and (1.25):} \qquad W = -RT\ln\frac{V_2}{V_1} = RT\ln\frac{P_2}{P_1}$

Isobaric (Constant - P) Process:

- $\Delta U = \int C_V dT \qquad \text{and} \qquad \Delta H = \int C_P dT$
- $\text{By Eqs. (1.24)and (1.25):}\ Q = \int C_P dT\ \text{and}\ W = -R(T_2 - T_1)$
- $Therfore, \qquad Q = \Delta H = \int C_P dT$

Isochoric (Constant - V) Process:

- $\Delta U = \int C_V dT \qquad \text{and} \qquad \Delta H = \int C_P dT$
- $Q = \int C_V dT = \Delta U \qquad \text{and} \qquad W = 0$

Adiabatic Process: Constant Heat Capacities (δQ=0):

- $\text{By Eq. (1.22):} \qquad \frac{dT}{T} = -\frac{R}{C_v}\frac{dV}{V}$
  - Integration with C_V constant then gives:
- $\frac{T_2}{T_1} = \left(\frac{P_2}{P_1}\right)^{R/C_V} \quad and \quad \frac{P_2}{P_1} = \left(\frac{V_1}{V_2}\right)^{C_p/C_V} \quad where;\ \gamma = {C_p}/{C_V} = 1 + {R}/{C_V}$

Example-1

- ☐ An ideal gas undergoes the following sequence of mechanically reversible processes in a closed system.

  A) From an initial state of 343.15 K and 1bar, it is **compressed adiabatically** to 423.15 K

  B) It is then cooled from 423.15 K to 343.15 K at **constant pressure**

  C) Finally, it is expanded **isothermally** to its original state

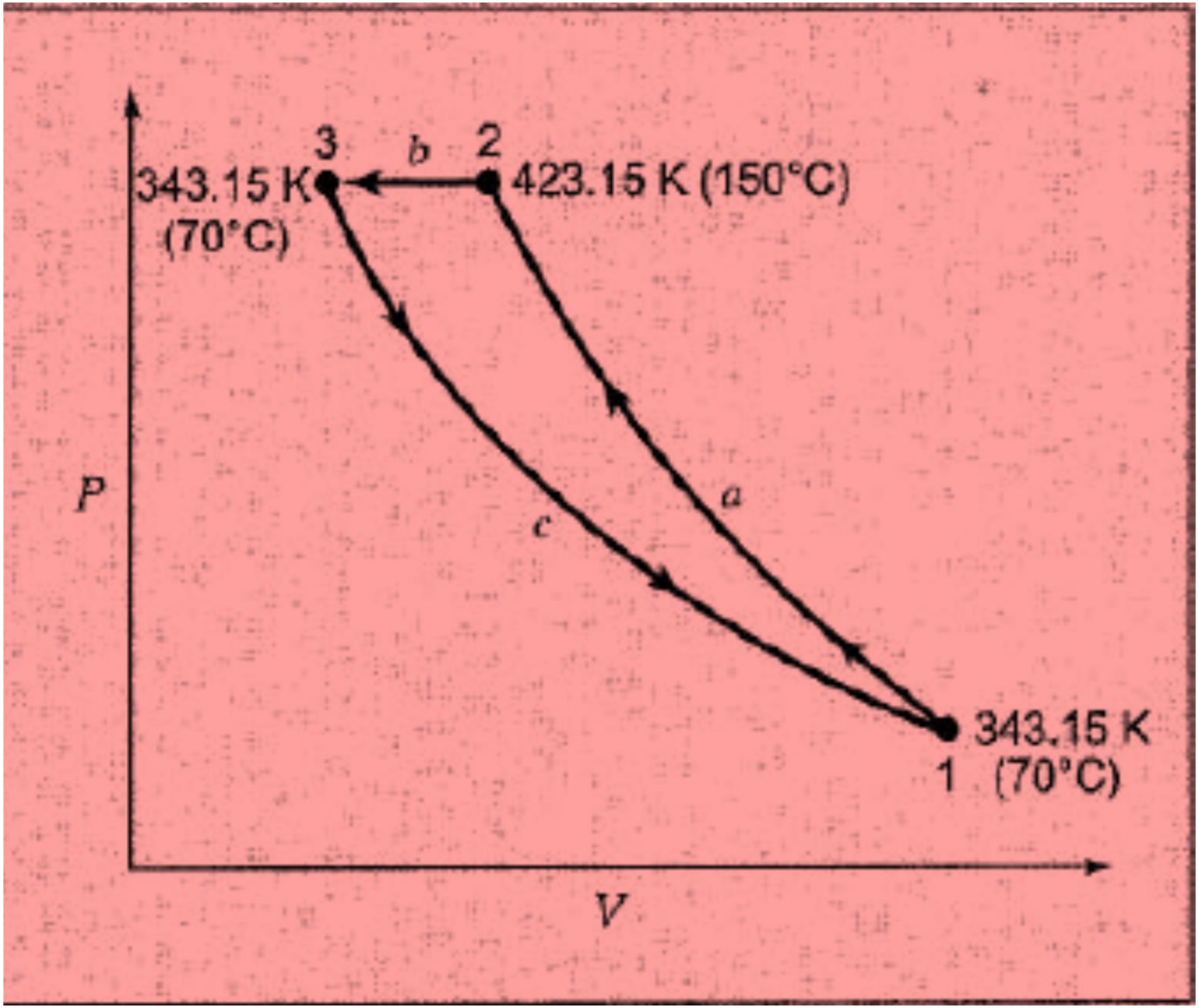
- ✓ Calculate **W, Q, U** and **H** for each of the three processes and for the entire cycle.

  Take **$C_v = (3/2)R$** and **$C_P = (5/2)R$,R=8.314J/mol.K**

  - ➢ In these processes are carried out irreversibly but so as to accomplish exactly the same changes of state (i.e, the same changes in P, T, U and H), then different values of Q and W result.

- ✓ Calculate **Q** and **W** if each step carried out with an **efficiency of 80%**

Example-1

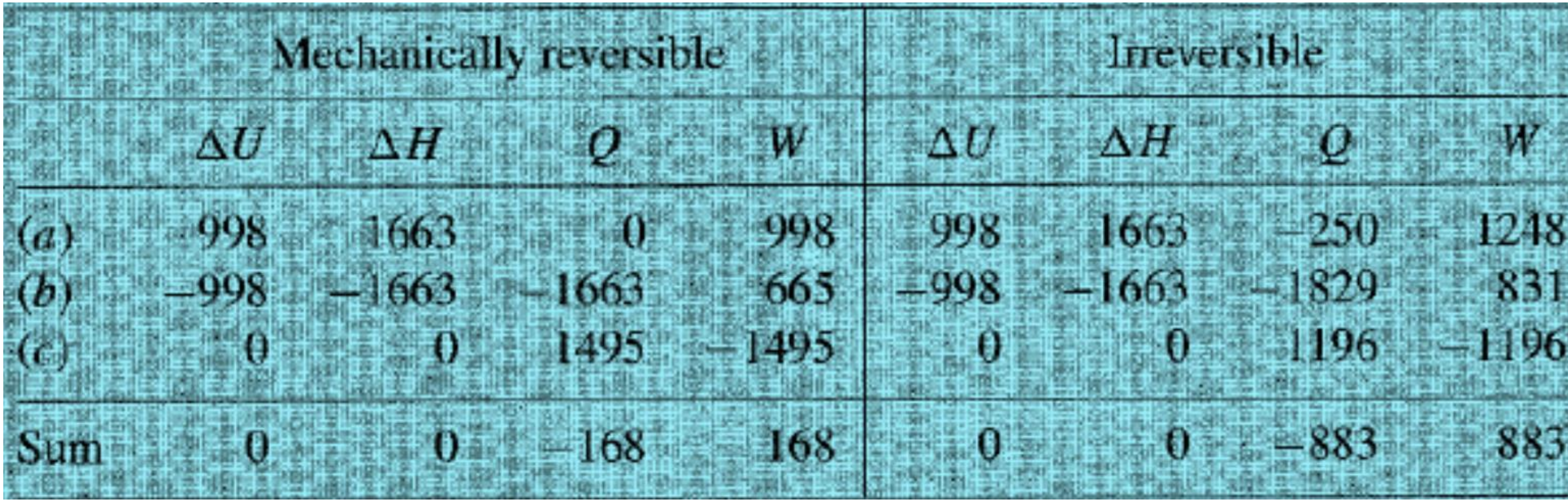


Example-1

Irreversible Process

- The equations developed have been derived for mechanically reversible, closed system processes for ideal gases.
- They apply equally to reversible and irreversible processes in both closed and open systems, because changes **in state functions** depend only on the initial and final states of the system.
- On the other hand, an equation for Q or W is specific to the process considered in its derivation.
- The work of an irreversible process is calculated by a two-step procedure.
  - ✓ First, W is determined for a mechanically reversible process that accomplishes the same change of state as the actual irreversible process.
  - ✓ Second, this **result is multiplied or divided by an efficiency** to give the actual work.
- If the process **produces work**, the absolute value for the reversible process is **too large** and must be **multiplied** by **an efficiency.**
- If the process **requires work**, the value for the reversible process is **too small** and must be **divided** by **an efficiency.**

Example-1



	Mechanically reversible				Irreversible			
	ΔU	ΔH	Q	W	ΔU	ΔH	Q	W
(*a*)	998	1663	0	998	998	1663	−250	1248
(*b*)	−998	−1663	−1663	665	−998	−1663	−1829	831
(*c*)	0	0	1495	−1495	0	0	1196	−1196
Sum	0	0	−168	168	0	0	−883	883

In conclusion

- The cycle is one which requires work and produce an equal amount of heat.
- The work required for the three irreversible steps is **more than 5X** than the total work required for mechanically reversible processes

5. Cubic Equations of State

- Cubic equations are in fact the **simplest equations** capable of representing both **liquid and vapor behavior and give accurately represent P,V,T characteristics.**
- They compromise between **generality** and **simplicity** that is suitable to many purposes.

The van der Waals Equation of State:

- It the first practical cubic equation of state was proposed by J. D. van der waals in 1873:

$$P = \frac{RT}{V - b} - \frac{a}{V^2} \qquad 1.28$$

- Here, **a and b are positive constants**; when **they are zero**, the **ideal-gas equation** is recovered.
- The constant a and b, can be calculated from critical pressure Pc and critical temperature Tc values that are available in table.(appendix)
- If values of a and b for a particular fluid are given, P as a function of V for various values of T can be calculated.

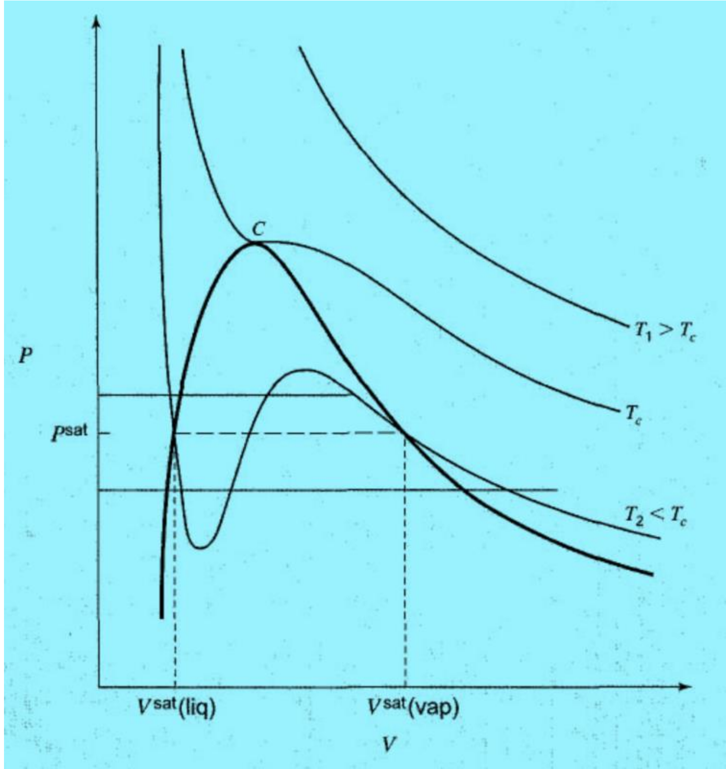
Cubic Equations of State

- The PV diagram shown below has **three isotherms** and the "dome" representing states of saturated liquid and saturated vapor.

  - **For the isotherm:**

- **$T_1 > T_c$:** pressure is a **monotonically decreasing function** with increasing molar volume.
- **T_c (the critical isotherm):** contains the horizontal inflection at C characteristic of the critical point.

- **$T_2 < T_c$**: the pressure decreases rapidly in the sub-cooled liquid region with increasing V; **after crossing** the saturated-liquid line, it goes through a **minimum**, rises to a **maximum**, and then **decreases**, crossing the saturated-vapor line and continuing downward into the superheated-vapor region.



Cubic Equations of State

- The Cubic equations of state have **three volume roots**, of which two may be complex.
- Physically meaningful **values of V are always real, positive, and greater than constant b.**

i. For an isotherm at **$T > T_c$** reference to **Fig. above** shows that solution for V at any positive value of P yields only **one root.**

ii. For the critical isotherm **($T = T_c$),** this is also true, except at the critical pressure, where there are **three roots**, all equal to V_c.

iii. For isotherms at **$T < T_c$,** the equation may exhibit **one or three real roots**, depending on the pressure.

Cubic Equations of State

- Although these roots are real and positive, they are not physically stable states for the portion of an isotherm lying between saturated liquid and saturated vapor (under the "dome").
- Only the roots for $P = P^{Sat}$, namely V^{Sat} (liq) and V^{Sat} (vap), are stable states, connected by the horizontal portion of the true isotherm.
- For other pressures (as indicated by the horizontal lines shown on Fig. above and below P^{Sat}**),** the smallest root is a liquid or "liquid-like" volume, and the largest is a vapor or "vapor-like" volume.
- The third root, lying between the other values, is of no significance.

Cubic Equations of State

Generic Cubic Equation of State

- Since the introduction of the van der Waals equation, scores of cubic equations of state have been proposed.
- **All are special cases of the equation:**

$$\mathbf{P = \frac{RT}{V-b} - \frac{\theta(V-\eta)}{(V-b)(V^2+\kappa V+\lambda)}} \qquad \mathbf{1.29}$$

- Here, b, θ, η, κ and λ are parameters which in general **depend on temperature and (for mixtures) composition.**
- If, η = b, θ = a, and κ = λ = 0; Eq. (1.29) reduces to the van der Waals equation.

$$\mathbf{P = \frac{RT}{V-b} - \frac{a}{V^2}} \qquad \mathbf{1.28}$$

Cubic Equations of State

Generic Cubic Equation of State

- Because of its cubic form, the equation has inherent limitations; hence, an important class of cubic equations results by assigning; $\eta = b$, $\theta = a(T)$, $\kappa = (\epsilon + \sigma)b$ and $\lambda = \epsilon\sigma b^2$:

$$P = \frac{RT}{V - b} - \frac{a(T)}{(V + \epsilon b)(V + \sigma b)} \qquad 1.30$$

- Where: ϵ and σ are **pure numbers**, the **same for all substances,** whereas parameters **a(T) and b are substance dependent.**
- The temperature dependence of a(T) is specific to each equation of state.
- For the **van der Waals** equation, **a(T) = a** is a substance-dependent constant, and **$\epsilon = \sigma = 0$.**

Cubic Equations of State

Determination of Equation-of-State Parameters

- For cubic equations of state, suitable estimates for the parameters are usually found from values for the **critical constants T_c and P_c.**
- Since the critical isotherm exhibits a **horizontal inflection** at the critical point, we may impose the mathematical conditions:

$$\left(\frac{\partial P}{\partial V}\right)_{T;Cr} = \left(\frac{\partial^2 P}{\partial V^2}\right)_{T;Cr} = 0$$

- Where: the subscript **"cr"** denotes the critical point.
- Differentiation of Eq. (1.30) yields expressions for both derivatives, which may be equated to zero for **$P = P_c$, $T = T_c$ and $V = V_c$.**
- The equation of state may itself be written for the critical conditions.

Cubic Equations of State

- These three equations contain five constants: **P_c, V_c, T_c, a(T,), and b.**
- Of the several ways to treat these equations, the most suitable is elimination of V_c to yield expressions relating $a(T_c)$ and b to P_c and T_c.
- The reason is that P_c and T_c are usually more accurately known than V_c.

For the van der Waals equation:

- $$P = \frac{RT}{V-b} - \frac{a}{V^2}$$
- $$\left(\frac{\partial P}{\partial V}\right)_{T:Cr} = \frac{-RT}{(V-b)^2} + \frac{2V}{V^4} = \frac{-RT}{(V-b)^2} + \frac{2a}{V^3} = 0$$
- $$\left(\frac{\partial^2 P}{\partial V^2}\right)_{T:Cr} = \frac{2(V-b)RT}{(V-b)^4} - \frac{3V^2}{V^6} = \frac{2RT}{(V-b)^3} - \frac{6a}{V^4} = 0$$

Therfore; $$P_c = \frac{RT_c}{V_c - b} - \frac{a}{{V_c}^2} ------------------(i)$$

$$\frac{-RT_c}{(V_c - b)^2} - \frac{2a}{{V_c}^3} = 0 ------------------(ii)$$

Cubic Equations of State

- **Alternatively**

➢ $(V - V_c)^3 = 0$

➢ $V^3 - 3V^2V_c + 3VV_c^2 - V_c^3 = 0 ----------------- (A)$

➢ But, $P = \frac{RT}{V-b} - \frac{a}{V^2} \quad \Longrightarrow P\left(V^3 - bV^2\right) = RTV^2 - aV + ab$

➢ $\Longrightarrow V^3 - \left(b + \frac{RT_c}{P_c}\right)V^2 + \frac{a}{P_c}V - \frac{ab}{P_c} = 0 ----------------- (B)$

- Recall that for a particular substance parameter a in the van der Waals equation is a **constant**, independent of temperature.
- **Term-by-term comparison of Eqs. (A) and (B)** provides three equations:

✓ $3V_c = b + \frac{RT_c}{P_c} --- (C)$

✓ $3V_c^2 = \frac{a}{P_c} ----- (D)$

✓ $V_c^3 = \frac{ab}{P_c} ------- (E)$

Solving Eq. (D) for a, combining the result with Eq. (E), and solving for b gives:

$$a = 3P_cV_c^2 \qquad\qquad b = \frac{1}{3}V_c$$

Cubic Equations of State

- Substitution for b in Eq. (C) allows solution for V_c which can then be eliminated from the equations for a and b:

$$\mathbf{V_c = \frac{3}{8}\frac{RT_c}{P_c}} \qquad \mathbf{a = \frac{27}{64}\frac{R^2T_c^2}{P_c}} \qquad \mathbf{b = \frac{1}{8}\frac{RT_c}{P_c}}$$

- Substitution for V, in the equation for the critical compressibility factor reduces it immediately to:

$$\mathbf{Z_c = \frac{P_cV_c}{RT_c} = \frac{3}{8},} \qquad \textbf{a constant}$$

- An analogous procedure may be applied to the generic cubic, Eq. yielding expressions for parameters a(Tc) and b. For the former:

$$\mathbf{a}(T_c) = \psi\frac{R^2T_c^2}{P_c} \tag{1.31}$$

- This result may be extended to temperatures other than the critical by introduction of a dimensionless function **α(Tr)** that becomes unity at the critical temperature. Thus:

Cubic Equations of State

- Function $\alpha(T_r)$ is an empirical expression specific to a particular equation of state

$$a(T_c) = \psi \frac{\alpha(T_r) R^2 T_c^2}{P_c}$$

- **Parameter b** is given by:

$$b = \Omega \frac{RT_c}{P_c} \qquad 1.32$$

- In these equations **Ω and ψ are pure numbers**, independent of substance and determined for a particular equation of state from the values assigned to ϵ and σ.
- The modern development of cubic equations of state was initiated in 1949 by publication of the **Redlic /Kwong (RK) equation**:'

$$P = \frac{RT}{V-b} - \frac{a(T)}{V(V+b)} \qquad 1.33$$

- **Where: $\alpha(T_r) = T_r^{-1/2}$**

Cubic Equations of State

Vapor & Vapor-Like Roots of the Generic Cubic Equation of State

- For vapor or vapor-like volume, Eq. (1.30) is multiplied through by (V-b)/RT. It can then be written:

$$P = \frac{RT}{V-b} - \frac{a(T)}{(V+\epsilon b)(V+\sigma b)} \qquad 1.30$$

$$\Rightarrow V = \frac{RT}{P} + b - \frac{a(T)}{P}\frac{V-b}{(V+\epsilon b)(V+\sigma b)} \qquad 1.34$$

- Solution for V may be by **trial, iteration,** or with the **solve routine of a software package**.
- An **initial estimate for V** is the ideal-gas value **RT/ P.** For iteration, this value is substituted on the right side of Eq. (1.34).
- The resulting value of V on the left is then returned to the right side, and the process continues until the change in V is suitably small.

Cubic Equations of State

- An equation for Z equivalent to Eq. (1.31) is obtained through the substitution **V = ZRT/P.**
- In addition, the definition of two **dimensionless quantities** leads to simplification.

$$\beta \equiv \frac{bP}{RT} \qquad 1.35$$

$$q \equiv \frac{a(T)}{bRT} \qquad 1.36$$

- Substitution of Eq. (1.35) and (1.36) to Eq. (1.34) yields:

$$Z = 1 + \beta - q\beta \frac{Z - \beta}{(Z + \epsilon\beta)(Z + \sigma\beta)} \qquad 1.37$$

- Iterative solution of Eq. (1.37) starts with the value Z = 1 substituted on the right side.
- Eq. (1.35) and (1.36) in combination with Eq. (1.31) and (1.32) yield:

$$\beta = \Omega \frac{P_r}{T_r} \qquad 1.38$$

$$q = \frac{\psi\alpha(T_r)}{\Omega T_r} \qquad 1.39$$

$$b = \Omega \frac{RT_c}{P_c}$$

$$a(T) = \psi \frac{\alpha(T_r)R^2T_c^2}{P_c}$$

Cubic Equations of State

Liquid & Liquid -Like Roots of the Generic Cubic Equation of State

- Equation (1.34) may be solved for the V in the numerator of the final fraction to give:

$$\mathbf{V = b(V + \epsilon b)(V + \sigma b)\left[RT + \frac{bP}{a(T)} - VP\right]} \qquad \mathbf{1.40}$$

- This equation with a starting value of $\mathbf{V = b}$ on the right side converges upon iteration to a liquid or liquid-like root.
- An equation for Z equivalent to Eq. (1.40) is obtained when Eq. (1.37) is solved for the Z in the numerator of the final fraction:

$$\mathbf{Z = \beta + (Z + \epsilon\beta)(Z + \sigma\beta)\left(\frac{1 + \beta - Z}{q\beta}\right)} \qquad \mathbf{1.41}$$

- For iteration a starting value of $\mathbf{Z = \beta}$ is substituted on the right side. Once Z is known, the volume root is V = ZRT/ P.

Cubic Equations of State

Theorem of Corresponding States; Acentric Factor

- Experimental observation shows that compressibility factors Z for different fluids exhibit similar behavior when correlated as a function of reduced temperature T_r and reduced pressure **Pr; by definition:

$$T_r = \frac{T}{T_c} \qquad \text{and} \qquad P_r = \frac{P}{P_c}$$

- **Reduced condition** means how far away substances are from the critical conditions.
- **The two-parameter theorem of corresponding states:**
  - ✓ ***All fluids, when compared at the same reduced temperature and reduced pressure, have approximately the same compressibility factor, and all deviate from ideal-gas behavior to about the same degree.***
- Although this theorem is very nearly exact for the **simple fluids(spherical and non polar i.e. argon, krypton, and xenon)** systematic deviations are observed for more complex fluids.

Cubic Equations of State

- Appreciable improvement is obtained by introduction of a third corresponding-states parameter, characteristic of molecular structure; i.e. **"acentric factor ω",** introduced by **K. S. Pitzer and coworkers.**
- The acentric factor for a pure chemical species is defined with reference to its vapor pressure.
- Since the logarithm of the vapor pressure of a pure fluid is approximately linear in the reciprocal of absolute temperature,

$$\frac{\mathbf{d\log P_r^{sat}}}{\mathbf{d(1/T_r)}} = \boldsymbol{S}$$

- Where: P_r^{sat} is the reduced vapor pressure,

  Tr is the reduced temperature, and

  S is the slope of a plot of log P_r^{sat} vs. $1/T_r$.

Note that "log" denotes a logarithm to the base 10.

Cubic Equations of State

- As shown the figure below; Pitzer noted that all vapor-pressure data for the simple fluids (Ar, Kr, Xe) lie on the same line when plotted as log P_r^{sat} vs. $1/T_r$, and that the line passes through **log P_r^{sat} = -1.0 at T_r = 0.7.**

- The acentric factor is defined as this difference evaluated at **T_r = 0.7:**

$$\omega = -1.0 - \log(P_r^{sat})_{T_{r=0.7}}$$

- Therefore ω can be determined for any fluid from Tc, Pc, and a single vapor-pressure measurement made at Tr = 0.7.

- Values of ω and the critical constants Tc, Pc, and Vc for a number of fluids are listed in **App. B.**

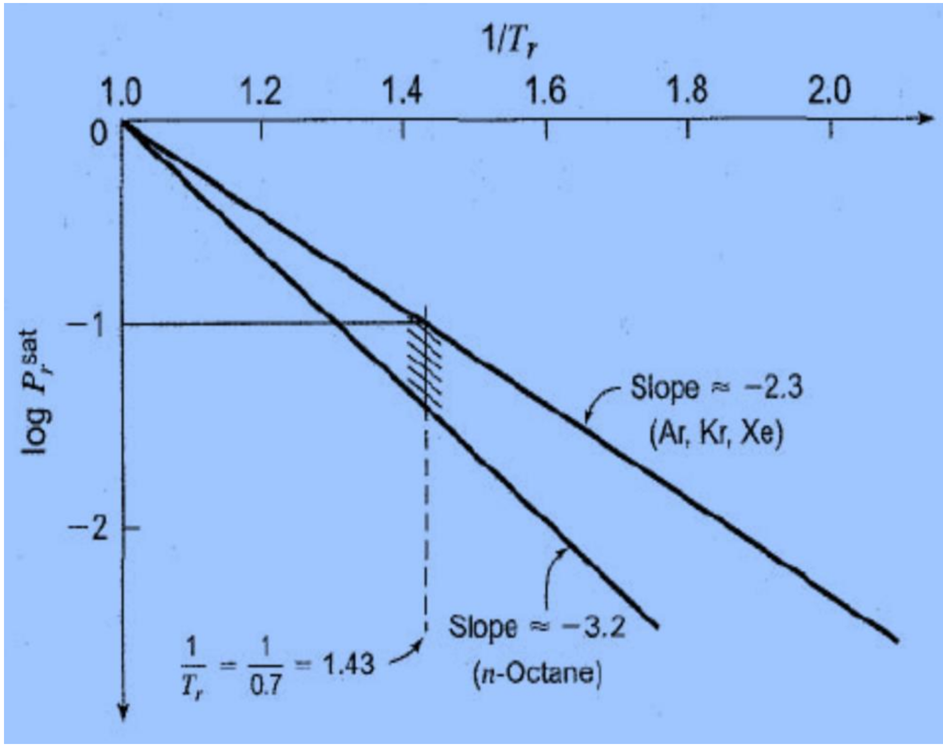


Fig: Approximate temperature dependence of the reduced vapor pressure

Cubic Equations of State

- The definition of **ω** makes its value zero for argon, krypton, and xenon, and experimental data yield compressibility factors for all three fluids that are correlated by the same curves when Z is represented as a function of T_r and P_r.
- This is the basic premise of the following **three-parameter theorem of corresponding states:**
  - ✓ ***All fluids having the same value of ω, when compared at the same T_r and P_r have about the same value of Z, and all deviate from ideal-gas behavior to about the same degree.***

Cubic Equations of State

- Equations of state which express Z as a function of T, and P, are said to be **generalized**, because of their general applicability to all gases and liquids. In General:

i. Express Z as functions of **T_r and P_r** only, yield **2-parameter** corresponding states correlations:
   - ✓ **The van der Waals equation**
   - ✓ **The Redlich/Kwong equation**

ii. The acentric factor enters through function **$\sigma(T_r;\omega)$** as an additional parameter, yield **3-parameter** corresponding state correlations:
   - ✓ **The Soave/Redlich/Kwong(SRK) equation**
   - ✓ **The Peng/Robinson (PR) equation**

Cubic Equations of State

- The numerical assignments for parameters **ϵ, σ, Ω** and **ψ** both for these equations and for the **van der Waals** and **Redlic/Kwong equations** are given in Table below.
- Expressions are also given for **$\alpha(T_r)$** for the **SRK** and **PR** equations.

EOS	$\alpha(T_r)$	σ	ϵ	Ω	ψ	Z_c
Van dar Waals	1	0	0	1/8	27/64	3/8
Redlich-Kwong	$T_r^{-1/2}$	1	0	0.08664	0.42748	1/3
SRK	$\alpha\mathrm{SPK}(T_r;\ \omega)$	1	0	0.08664	0.42748	1/3
(PR)	$\alpha\mathrm{PR}(T_r;\ \omega)$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07779	0.45724	0.30740

- ✓ $\alpha\mathrm{SPK}(T_r;\ \omega) = \left[1 + (0.480 + 1.574\omega - 0.176\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$
- ✓ $\alpha\mathrm{PR}(T_r;\ \omega) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

GENERALIZED CORRELATIONS FOR GASES

Pitzer Correlations for the Compressibility Factor:

- Generalized correlations find widespread use;
- In which the most popular are correlations developed by **Pitzer and coworkers** for the compressibility factor Z and for the second virial coefficient B.
- Pitzer Correlations for the Compressibility Factor:

$$\mathbf{Z = Z^0 + \omega Z^1} \qquad \mathbf{1.42}$$

- Where; Z^0 and Z^1 are functions of both T_r and P_r.
- When $\omega = 0$, as is the case for the simple fluids, the second term disappears, and Z^0 becomes identical with Z.
- Thus a generalized correlation for Z as a function of T_r and P_r based on data for just argon, krypton, and xenon provides the relationship:

$$Z^0 = F^0(T_r, P_r).$$

GENERALIZED CORRELATIONS FOR GASES

Pitzer Correlations for the Second Virial Coefficient

- The complexity of the functions Z^0 and Z^1 precludes their accurate representation by simple equations.
- However, we can give approximate analytical expression to these functions for a limited range of pressures.
- The basis for this is the simplest form of the virial equation:
- Thus, Pitzer and coworkers proposed a second correlation, which yields values for BP_c/RT_c:

$$\mathbf{Z = 1 + \frac{BP}{RT}} = 1 + \left(\frac{BPc}{RTc}\right)\frac{Pr}{Tr}$$

$$\frac{BP_c}{RT_c} = B^0 + \omega B^1 \qquad 1.43$$

- Together, these two equations become:

$$Z = 1 + B^0\frac{P_r}{T_r} + \omega B^1\frac{P_r}{T_r} \qquad 1.44$$

GENERALIZED CORRELATIONS FOR GASES

Pitzer Correlations for the Second Virial Coefficient

- Comparison of this equation with Eq. (1.42) provides the following identifications:

$$\mathbf{Z^0 = 1 + B^0 \frac{P_r}{T_r}}; \quad \textbf{And}$$

$$\mathbf{Z^1 = B^1 \frac{P_r}{T_r}} \qquad \mathbf{1.45}$$

- Second virial coefficients are functions of temperature only, and similarly B^0 and B^1 are functions of reduced temperature only. They are well represented by the following equations:

$$\boldsymbol{B^0 = 0.083 - \frac{0.422}{T_r^{1.6}}} \qquad \mathbf{1.46}$$

$$\boldsymbol{B^1 = 0.139 - \frac{0.172}{T_r^{4.2}}} \qquad \mathbf{1.47}$$

Example-2

- Given that the vapor pressure of n-butane at 350 K is 9.4573 bar, find the molar volumes of

A) Saturated vapor

B) Saturated liquid n-butane at these conditions as given by the Redlick/Kwong equation

Values of Tc and Pc for n-butane from App.B are 425.1 k and 37.96 bar respectively.

Example-2

- ☐ Given that the vapor pressure of n-butane at 350 K is 9.4573 bar, find the molar volumes of

  A) Saturated vapor

EOS	$\alpha(T_r)$	σ	ϵ	Ω	ψ	Z_c
Van dar Waals	1	0	0	1/8	27/64	3/8
Redlich-Kwong	$T_r^{-1/2}$	**1**	**0**	**0.08664**	**0.42748**	**1/3**
SRK	$\alpha SPK(T_r;\ \omega)$	1	0	0.08664	0.42748	1/3
(PR)	$\alpha PR(T_r;\ \omega)$	$1+\sqrt{2}$	$1-\sqrt{2}$	0.07779	0.45724	0.30740

- ✓ $\alpha SPK(T_r;\ \omega) = \left[1 + (0.480 + 1.574\omega - 0.176\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$
- ✓ $\alpha PR(T_r;\ \omega) = \left[1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

Values of T_c and P_c for n-butane from App. B yield:

$$T_r = \frac{350}{425.1} = 0.8233 \qquad \text{and} \qquad P_r = \frac{9.4573}{37.96} = 0.2491$$

Parameter q is given by Eq. (3.51) with Ω, Ψ, and $\alpha(T_r)$ for the RK equation from Table 3.1:

$$q = \frac{\Psi T_r^{-1/2}}{\Omega T_r} = \frac{\Psi}{\Omega} T_r^{-3/2} = \frac{0.427\,48}{0.086\,64}(0.8233)^{-3/2} = 6.6048$$

Table 3.1 Parameter Assignments for Equations of State

For use with Eqs. (3.46) through (3.53)

Eq. of State	$\alpha(T_r)$	σ	ϵ	Ω	Ψ	Z_c
vdW (1873)	1	0	0	1/8	27/64	3/8
RK (1949)	$T_r^{-1/2}$	1	0	0.086 64	0.427 48	1/3
SRK (1972)	$\alpha_{\mathrm{SRK}}(T_r;\omega)$[†]	1	0	0.086 64	0.427 48	1/3
PR (1976)	$\alpha_{\mathrm{PR}}(T_r;\omega)$[‡]	$1+\sqrt{2}$	$1-\sqrt{2}$	0.077 79	0.457 24	0.307 40

[†] $\alpha_{\mathrm{SRK}}(T_r;\omega) = \left[1 + (0.480 + 1.574\,\omega - 0.176\,\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

[‡] $\alpha_{\mathrm{PR}}(T_r;\omega) = \left[1 + (0.374\,64 + 1.542\,26\,\omega - 0.269\,92\,\omega^2)\left(1 - T_r^{1/2}\right)\right]^2$

Parameter β is found from Eq. (3.50):

$$\beta = \Omega \frac{P_r}{T_r} = \frac{(0.086\,64)(0.2491)}{0.8233} = 0.026\,214$$

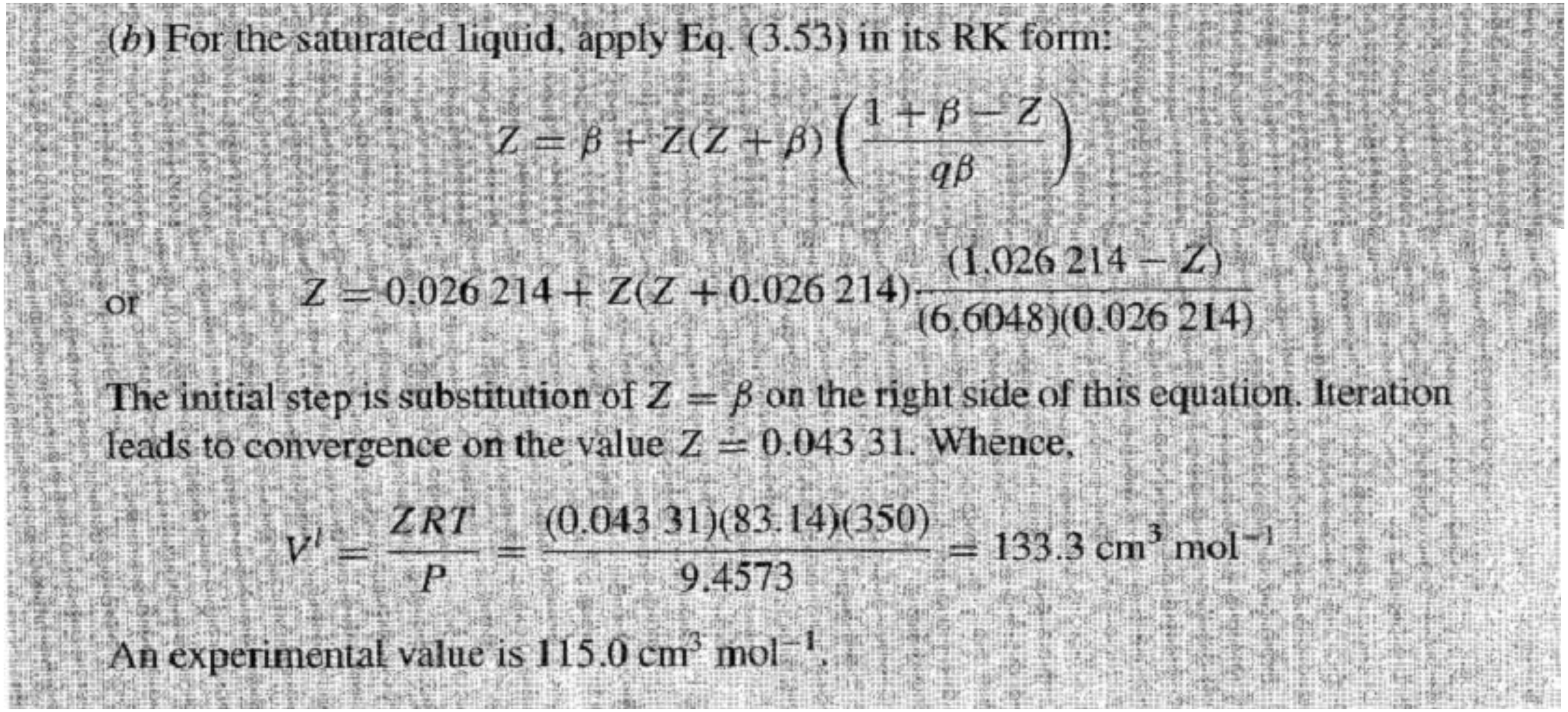
(*a*) For the saturated vapor, write the RK form of Eq. (3.49) which results upon substitution of appropriate values for ϵ and σ from Table 3.1:

$$Z = 1 + \beta - q\beta \frac{(Z - \beta)}{Z(Z + \beta)}$$

Iteration with an initial value $Z = 1$ converges on $Z = 0.8305$. Thus,

$$V^v = \frac{ZRT}{P} = \frac{(0.8305)(83.14)(350)}{9.4573} = 2555 \text{ cm}^3 \text{ mol}^{-1}$$

An experimental value is 2482 cm^3 mol^{-1}.



(*b*) For the saturated liquid, apply Eq. (3.53) in its RK form:

$$Z = \beta + Z(Z + \beta)\left(\frac{1 + \beta - Z}{q\beta}\right)$$

or
$$Z = 0.026\,214 + Z(Z + 0.026\,214)\frac{(1.026\,214 - Z)}{(6.6048)(0.026\,214)}$$

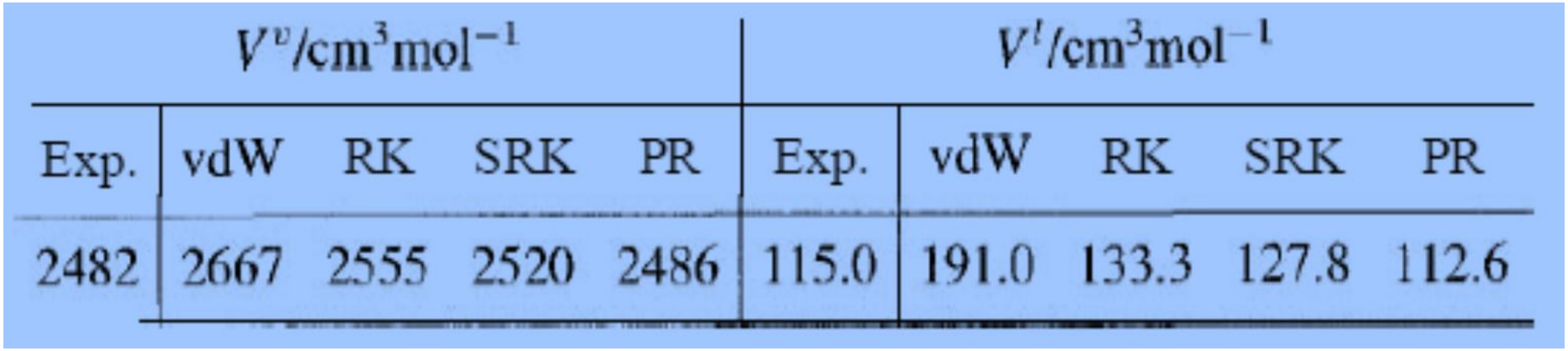
The initial step is substitution of $Z = \beta$ on the right side of this equation. Iteration leads to convergence on the value $Z = 0.043\,31$. Whence,

$$V^l = \frac{ZRT}{P} = \frac{(0.043\,31)(83.14)(350)}{9.4573} = 133.3\ \mathrm{cm^3\,mol^{-1}}$$

An experimental value is 115.0 $\mathrm{cm^3\,mol^{-1}}$.

Example-2

- For comparison, values of **V^v and V^l** calculated for the same conditions by all four cubic equations of state are:



$V^v/\text{cm}^3\text{mol}^{-1}$					$V^l/\text{cm}^3\text{mol}^{-1}$				
Exp.	vdW	RK	SRK	PR	Exp.	vdW	RK	SRK	PR
2482	2667	2555	2520	2486	115.0	191.0	133.3	127.8	112.6