CBEg 6162- Advanced Chemical Engineering Thermodynamics

Phase stability of Thermodynamic System

By

Dr. Eng. Shegaw Ahmed

School of Chemical & Bio Engineering
Addis Ababa Institute of Technology
Addis Ababa University

March, 2020

CBEg 6162-ADCHENTD-Outline

CHAPTER-6-Phase stability of Thermodynamic System

- *Criteria for stability of Thermodynamic system*
- *Stability Criteria for Thermodynamic Potentials*
- *Physical Significance of Stability Criteria*
- *Phase Transition*
- *Clapeyron Equation*
- *Gibbs Phase Rule*
- *Phase Diagram*

Stability of TDs

For what condition ***stability occur & its significance?***

What is the criteria for ***stability of thermodynamic system?***

- In order to achieve ***stability criteria maximum entropy and minimum energy principle*** need to be satisfied. Constant : U & V = constant
- Equilibrium criterion:

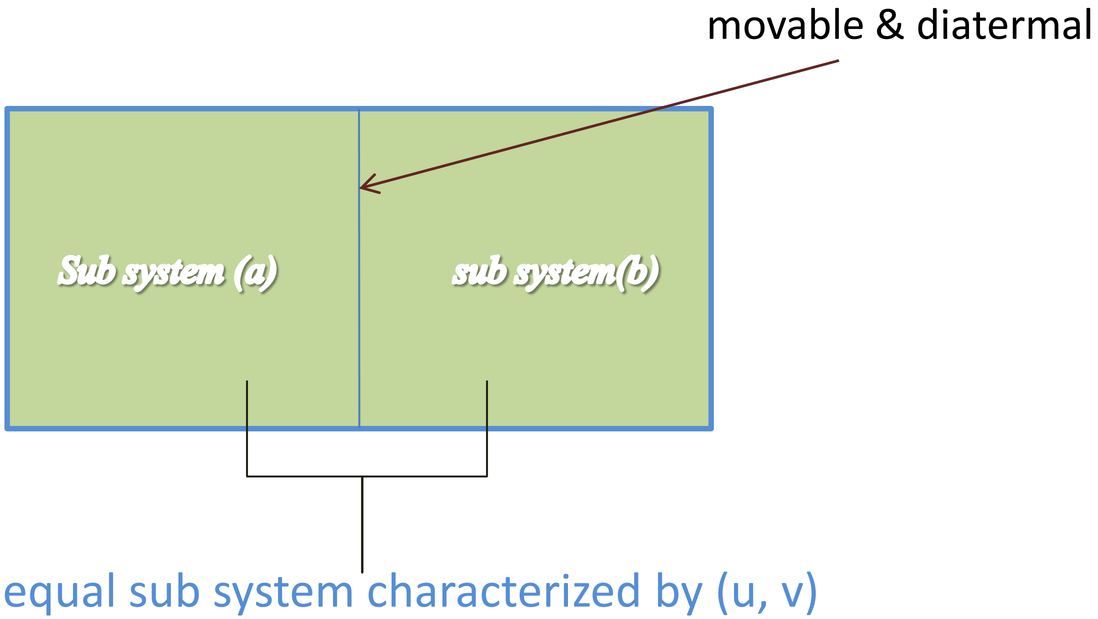
  S = maximum , $ds = 0$

- Stability criterion:

  $d^2S < 0$

- For minimum energy $du = 0$ & $d^2u > 0$ ***@ const*** S

Consider an isolated TDs


movable & diatermal

Sub system (a)

sub system(b)

equal sub system characterized by (u, v)

- Here we are interested to investigate the condition ***under which the system is stable.***
- du^a & dv^a → represent ***virtual change in subsystem a.***
- $-du^b$ & $-dv^b$ → represent ***virtual change in subsystem b***. this virtual change in entropy of composite system expressed by ***tayler series.***
  $\Delta s = ds + d^2s$

Stability criteria

- The thermodynamic system is in ***a state of stable equilibrium*** only if it simultaneously ***satisfies the stability criteria of*** $U_{ss} > 0$ ***and*** $\frac{U_{ss}U_{vv} - U_{sv}^{2}}{U_{ss}} > 0$. These two criteria also imply that $U_{vv} > 0$. These two equations are ***the stability criteria in the energy representation.***
- The ***stability criteria*** state that ***the fundamental surface in the energy representation is convex*** with respect to ***the extensive variables s and v*** or ***u is a convex function of s and v.***

Stability criteria

- The ***stability criteria in the entropy representations*** are given by $S_{uu}<0$ ***and*** $S_{uu}S_{vv}-S_{uu}^2>0$. these criteria also imply that $S_{vv}<0$.
- The ***stability criteria*** state that ***the fundamental surface in the entropy representation is concave with respect to the extensive variables U and V*** or ***S is a concave function of U and V.***

- $ds = ds^a + ds^b$, each of sub system characterized by (u, v)
- $ds = ((1/T^a)-(1/T^b))du^a – ((P/T)^a - (P/T)^b)du^b$

For the condition to satisfy (i.e. ds = 0) it must be

$((1/T^a) = (1/T^b))$ & $((P/T)^a = (P/T)^b)$ 1st criteria

- $d^2s = d^2s^a + d^2s^b$
- Consider: - sub system contain 1mole at constant T° & P.
  - Equality of $s^a = s^b \rightarrow a=b$ d^2s become

$\rightarrow s_{uu}(du)^2 + 2s_{uv}dudv + u_{vv}(dv)^2 < 0$

Let's consider equation of state (1/T) = 1/T (U, V)

$\rightarrow du = (1/s_{uu})(d(1/T) - S_{uv}dv)$

$1/s_{uu}(d(1/T)^2) + (S_{vv} - S^2uv/s_{uu}) (dv)^2 < 0$

$\rightarrow 1/s_{uu} < 0$ or $s_{uu} < 0$ & $Svv - S^2uv/suu) < 0$

That is $s_{uu} < 0$ & $S_{vv} < 0$ ensure ***local stability*** & $s_{uu} <0$, $S_{vv} < 0$ & $S_{vv}S_{uu} - S^2_{uv} >$ ***0 global stability of the system.***

A globally stable system will not be able to change to more phases, while a locally stable system can sometimes split.

Stability criteria of thermodynamic potential (A, H &G)

☐ $a_{TT} =(\partial^2 a/ \partial T^2)_v < 0$ & $a_{vv} =(\partial^2 a/ \partial v^2)_T > 0$

☐ $h_{ss} = (\partial^2 h/\partial s^2)_s > 0$ & $h_{PP} = (\partial^2 h/\partial P^2)_s < 0$

☐ $G_{TP} = (\partial^2 G/\partial T^2)_p < 0$ & $G_{PP} = (\partial^2 G/\partial P^2)_T < 0$

☐ $U_{ss} = = (\partial^2 u/\partial s^2)_v > 0$ & $u_{vv} = (\partial^2 u/\partial v^2)_s > 0$

Physical significance of stability criteria

- addition of energy in the form of heat either at constant volume or const Pressure to stable thermodynamic system ***increase its temperature.***
- either isothermal or isotropic compression of a stable thermodynamic system ***decrease its volume.***
- stability guaranteed only $K \geq K_s > 0$ & $C_p \geq C_v > 0$

Stability criteria of thermodynamic potentials

- The ***stability criteria for thermodynamic potentials a, h and g*** which are the ***partial Legendre transform of U*** are obtained by relating ***the second derivative of a, h and g to the second derivative of U*** through ***Legendre transformation.***
- It was observed that ***the thermodynamic potentials*** are ***convex functions of their extensive parameters*** and ***concave function of their intensive parameters.***

The stability criteria are given by:

$A_{TT} < 0$ *and* $A_{vv} > 0$ *for the potential A*
$H_{ss} > 0$ *and* $H_{pp} < 0$ *for the potential H*
$G_{TT} < 0$ *and* $G_{pp} < 0$ *for the potential G*
$U_{ss} > 0$ *and* $U_{vv} > 0$ *for the potential U*

Physical significance of stability criteria

- The ***stability criteria for the thermodynamic potential*** require that ***C_v, C_p, κ, β and K_s*** of a homogeneous simple system ***must be positive*** i.e. addition of energy in the form of heat either at constant volume or at constant pressure ***must increase the temperature of the system*** and ***isothermal or isentropic compression must decrease the volume of a stable system.***
- The two heat capacities ***Cp and Cv are related by an exact thermodynamic relation.*** Similarly the compressibilitys κ and K_s are also related by an exact thermodynamic relation. Therefore the stability criteria require ***$Cp \geq Cv > 0$ and $\kappa > K_s > 0$***

Physical significance of stability

- Stability criteria for ***internal energy***

$$U_{ss} = \left(\frac{\partial\ u}{\partial s^2}\right)_v = \left(\frac{\partial T}{\partial s}\right)_v = \frac{T}{C_v} > 0 \qquad \text{or} \;\; C_v > 0$$

$$U_{vv} = \left(\frac{\partial\ u}{\partial v^2}\right)_s = \left[\frac{\partial}{\partial v}\left(\frac{\partial u}{\partial v}\right)_s\right]_s = -\left(\frac{\partial P}{\partial v}\right)_s = \frac{1}{vK_s} > 0 \qquad \text{or} \;\; K_s > 0$$

- Stability criteria for ***Helmholtz free energy***

$$a_{TT} = \left(\frac{\partial\ a}{\partial T^2}\right)_v = \left[\frac{\partial}{\partial T}\left(\frac{\partial a}{\partial T}\right)_v\right]_v = -\left(\frac{\partial s}{\partial T}\right)_v = -\frac{C_v}{T} < 0 \qquad or \;\; C_v > 0$$

$$a_{vv} = \left(\frac{\partial\ a}{\partial v^2}\right)_T = \left[\frac{\partial}{\partial v}\left(\frac{\partial a}{\partial v}\right)_T\right]_T = -\left(\frac{\partial P}{\partial v}\right)_T = \frac{1}{v\kappa} > 0 \qquad \text{or} \;\; \kappa > 0$$

Physical significance of stability criteria

- Stability criteria for ***enthalpy***

$$h_{ss} = \left(\frac{\partial^2 h}{\partial s^2}\right)_P = \left[\frac{\partial}{\partial s}\left(\frac{\partial h}{\partial s}\right)_P\right]_P = \left(\frac{\partial T}{\partial s}\right)_P = \frac{T}{C_p} > 0 \ \text{ or } \mathrm{C_p} > 0$$

$$h_{PP} = \left(\frac{\partial^2 h}{\partial P^2}\right)_s = \left[\frac{\partial}{\partial P}\left(\frac{\partial h}{\partial P}\right)_s\right]_s = \left(\frac{\partial v}{\partial P}\right)_s = -vK_s < 0 \ \text{ or } \ \mathrm{K_s} > 0$$

- Stability criteria for ***Gibbs free energy***

$$g_{TT} = \left(\frac{\partial^2 g}{\partial T^2}\right)_P = \left[\frac{\partial}{\partial T}\left(\frac{\partial g}{\partial T}\right)_P\right]_P = -\left(\frac{\partial s}{\partial T}\right)_P = -\frac{C_p}{T} < 0 \ \text{ or } \mathrm{C_p} > 0$$

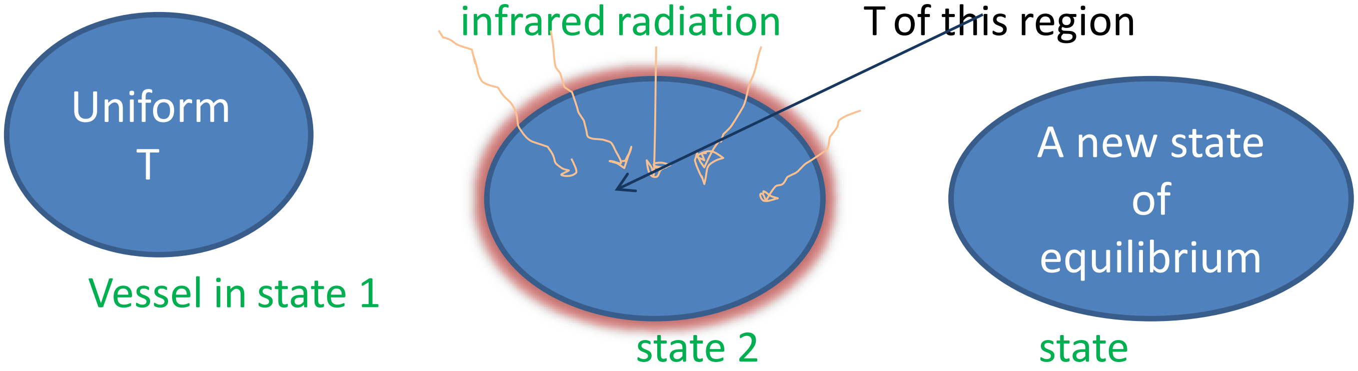
$$g_{PP} = \left(\frac{\partial^2 g}{\partial P^2}\right)_T = \left[\frac{\partial}{\partial P}\left(\frac{\partial g}{\partial P}\right)_T\right]_T = -\left(\frac{\partial v}{\partial P}\right)_T = v\kappa < 0 \ \text{ or } \mathrm{K} > 0$$

Le Chatelier's Principle for Stability Criteria

- The physical content of the stability criteria is embodied in ***the Le chatelier's principle*** which states that ***any disturbance in a homogeneous system*** induces ***spontaneous processes in such a direction as to annul or tend to annual in homogeneity*** and restore the system to ***a new state of equilibrium.***

Le chatelier's principle for stability criteria

- State that any disturbance in any stable system induce in homogeneity heat capacity of a stable system is positive.
- Isothermal compressibility is positive for a homogeneous system. This verified Le chatelier's by example:



infrared radiation

T of this region

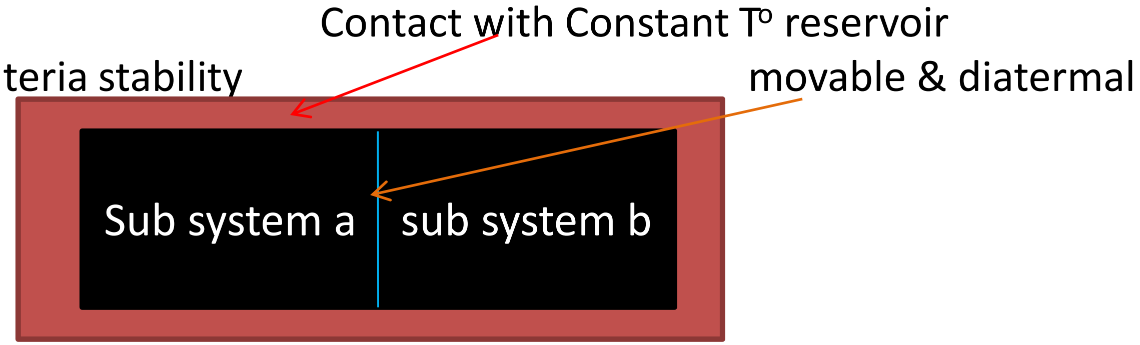
Uniform T

Vessel in state 1

state 2

A new state of equilibrium

state



Contact with Constant T^o reservoir

The 2nd criteria stability

movable & diatermal

Sub system a

sub system b

According to Le chatelier's . ↓V @ const T^o ↑ the P & ↑ V @ const T^o ↓P

Example 1

- Judge whether a thermodynamic system with the fundamental relation ***$S = (CUVN)1/3$ is a stable or not.***

PHASE TRASITION

- The fundamental Relation of particular TD system can be obtained by substituting ***equation of state in to Euler relation.***
- Equation of state can be determined from

  -Experimental measurement

  - theoretical models .
- Euler relation

  1. ***Energy Representation***

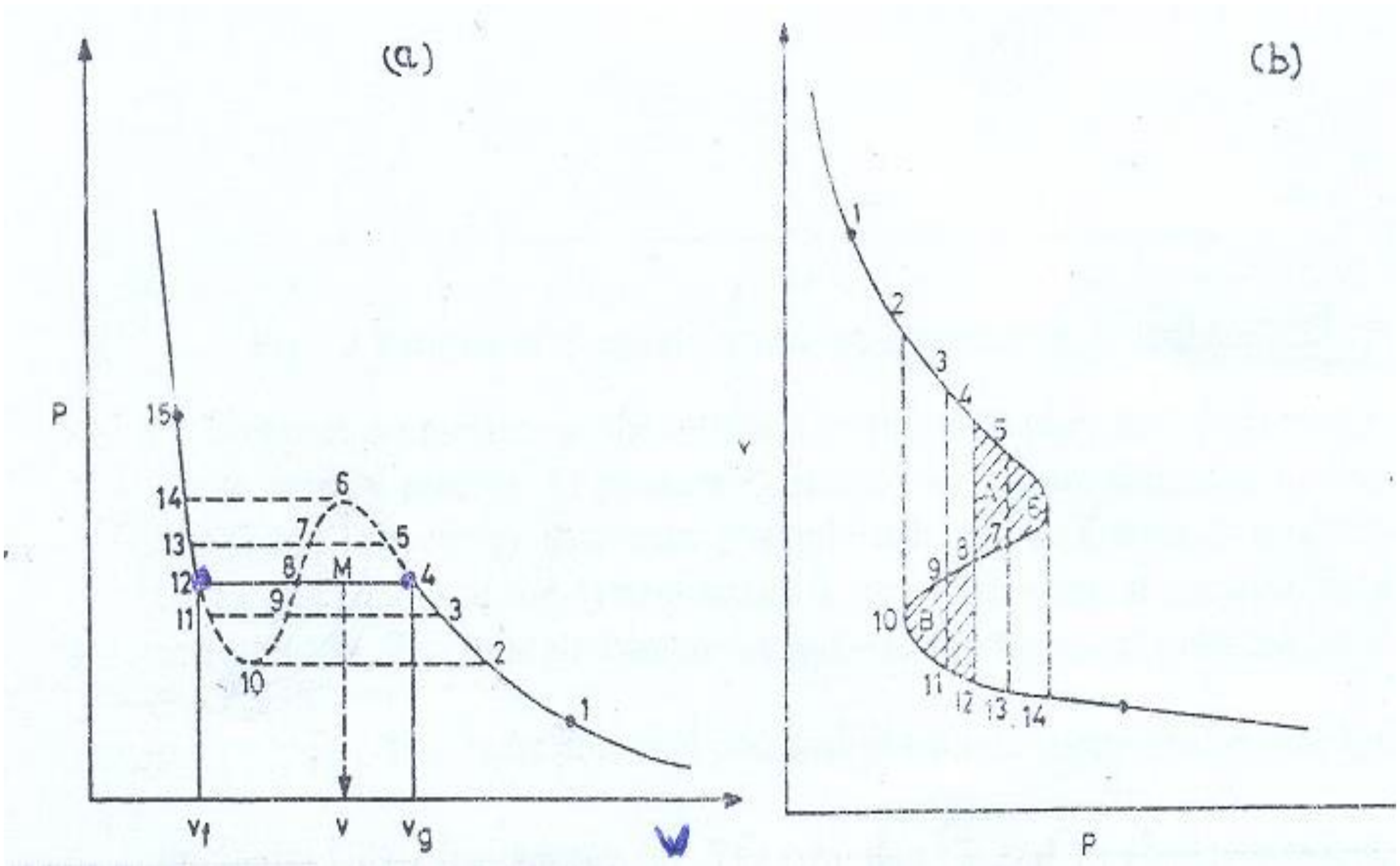
     $(U=TS-PV+\mu N)$

  2. ***Entropy representation***

     $S=1/T\ (U) + (p/T)\ (V)-(\mu/T)N$

- If the ***fundamental relation of a system fails to satisfy the criteria of stability***, the system ***cannot remain homogeneous*** and ***phase transition occurs.*** Suppose the fundamental relation is such that ***it satisfies the stability criteria in a certain rang of parameters only***, and ***fails to satisfy in a different range of parameters.*** Then the system undergoes ***phase transition in the range of parameters over which the fundamental relation fails to satisfy the stability criterion.***
- In order to study ***phase transition*** let us consider a tentative equation of state, say ***cubic question of state.***
- For such equation of state on Isotherm, temperature less than the critical temperature of substance

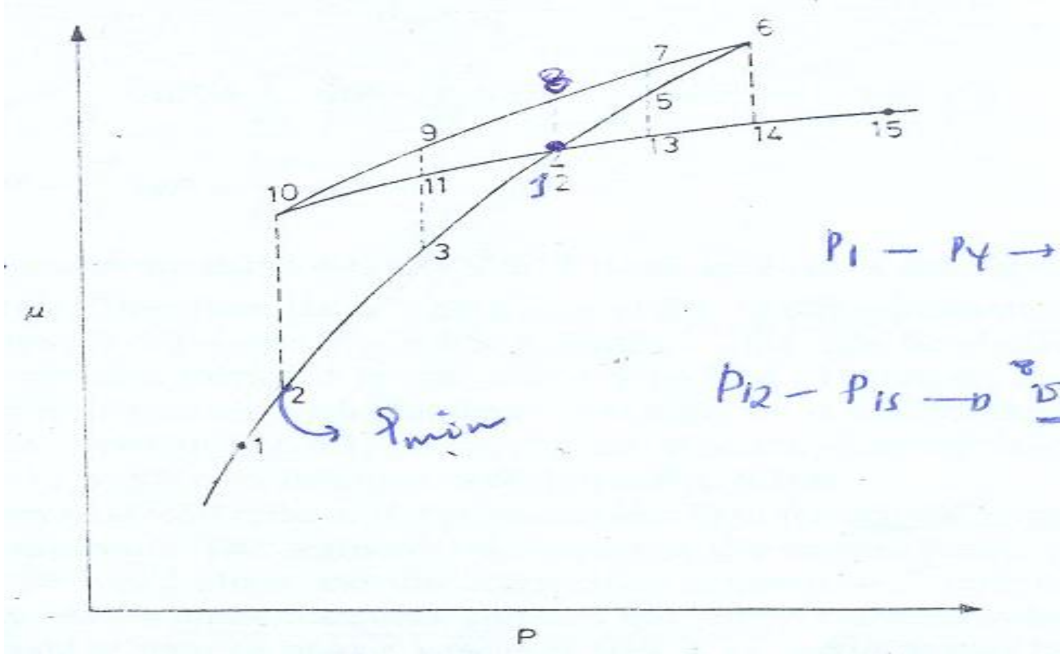
P-v diagram for cubic equation of state



- For single component system the Gibbs duhem relation

  dμ = -sdT + vdp, for a reversible isothermal system

  μ2 =μ1 + vdp this relation uses to convert v-p diagram in to μ-p diagram and, the figure appears below



- *P1-P4 = compressible (vapor phase)*
- *P12- P15 = Incompressible (liquid phase)*
- *At P4 = phase transition occurs (from vapor to liquid)*
- *Since chemical potential of both phases are the same*
- *μ4= μ12 – phase transition pressure can be Determined*
- *Each of physical isotherm at temperature less than critical temperature consist of these segments*
- *1-4 - vapor phase*
- *12-15 -liquid phase*
- *4-12 - Represent two phase mixture*

- The molar volume of the mixture can be determined as

v_f = *molar volume of saturated vapor*

v_g = *molar volume of saturated liquid*

Then molar volume of the mixture is

$$V = x_g v_g + v_f x_f$$

$$X_g + X_f = 1$$

- Xg - mole fraction of vapor(some times called quality or dryness fraction)

x_f - *mole fraction of liquid .*

$$V_{fg} = V_g - V_f$$

$$X_g/X_f = (v - v_f)/(v_g - v_f)$$

- ***The internal energy, enthalpy and entropy of mixture*** can be expressed interims of dryness fraction as given below

$$U = X_g U_g + (1 - x_g)U_f = U_f + x_g U_{fg}.$$

$$H = x_g h_g + (1 - x_g)h_f = h_f + x_g h_{fg}$$

$$S = x_g s_g + (1 - x_g)s_f = s_f + x_g s_{fg}$$

Example 2

- A closed rigid, vessel of 1 m3 capacity is filled with steam of quality 0.9 at 0.2 Mpa. After some time, the steam pressure reduced to 0.1 Mpa owing to energy losses as heat to the surroundings. Determine the final quality of steam and energy lost as heat to the surroundings, the properties of steam are:

P (MPa)	*vf (m3/kg)*	*vg (m3/kg)*	*uf (MJ/kg)*	*ug (MJ/kg)*
0.1	*0.001043*	*1.6940*	*0.41736*	*2.5061*
0.2	*0.001061*	*0.8857*	*0.50449*	*2.5295*

Claperon equation

- Phase diagram shows
  1. *pressure vs temperature*
  2. *liquid – vapor*
  3. *liquid – solid*
  4. *vapor -liquid*
- Phase diagram contains
  - ***Fusion curve***
  - ***Vaporization curve***
  - ***Sublimation curve***
- ***Critical point*** is the point at which the liquid and vapor coexist at ***the highest temperature and pressure***

Clapeyron equation

- The Gibbs- Duhem relation for a single- component system is given by dμ= -sdT + vdP. *Then the change in the chemical potential of vapor phase must be identical to the change in the chemical potential of the liquid phase. That is* $d\mu_f = d\mu_g$

$$-s_f dT + v_f dP = -s_g dT + v_g dP$$

or $$\left(\frac{\partial P}{\partial T}\right) = \frac{s_g - s_f}{v_g - v_f} = \frac{h_g - h_f}{(v_g - v_f)T} = \frac{h_{fg}}{T v_{fg}}$$

Clapeyron

- *The Clapeyron equation* can be simplified if the flowing approximations are made. ***At low pressures the vapor may be idealized as an ideal gas*** and ***the molar volume of the liquid phase can be neglected in comparison to the molar volume of the vapor phase.*** Moreover, if ***the latent heat of vaporization hfg*** is assumed to ***be constant over a small range of temperature.***
- With these approximations, the ***Clapeyron equation can be modified to obtain the following form of the Clausius - Clapeyron equation.***

$$\frac{\partial \mathrm{p}}{\partial \mathrm{T}} = \frac{h_{fg}\,p}{RT^2}, \quad \frac{\mathrm{dlnp}}{\mathrm{dT}} = \frac{h_{fg}}{RT^2}$$

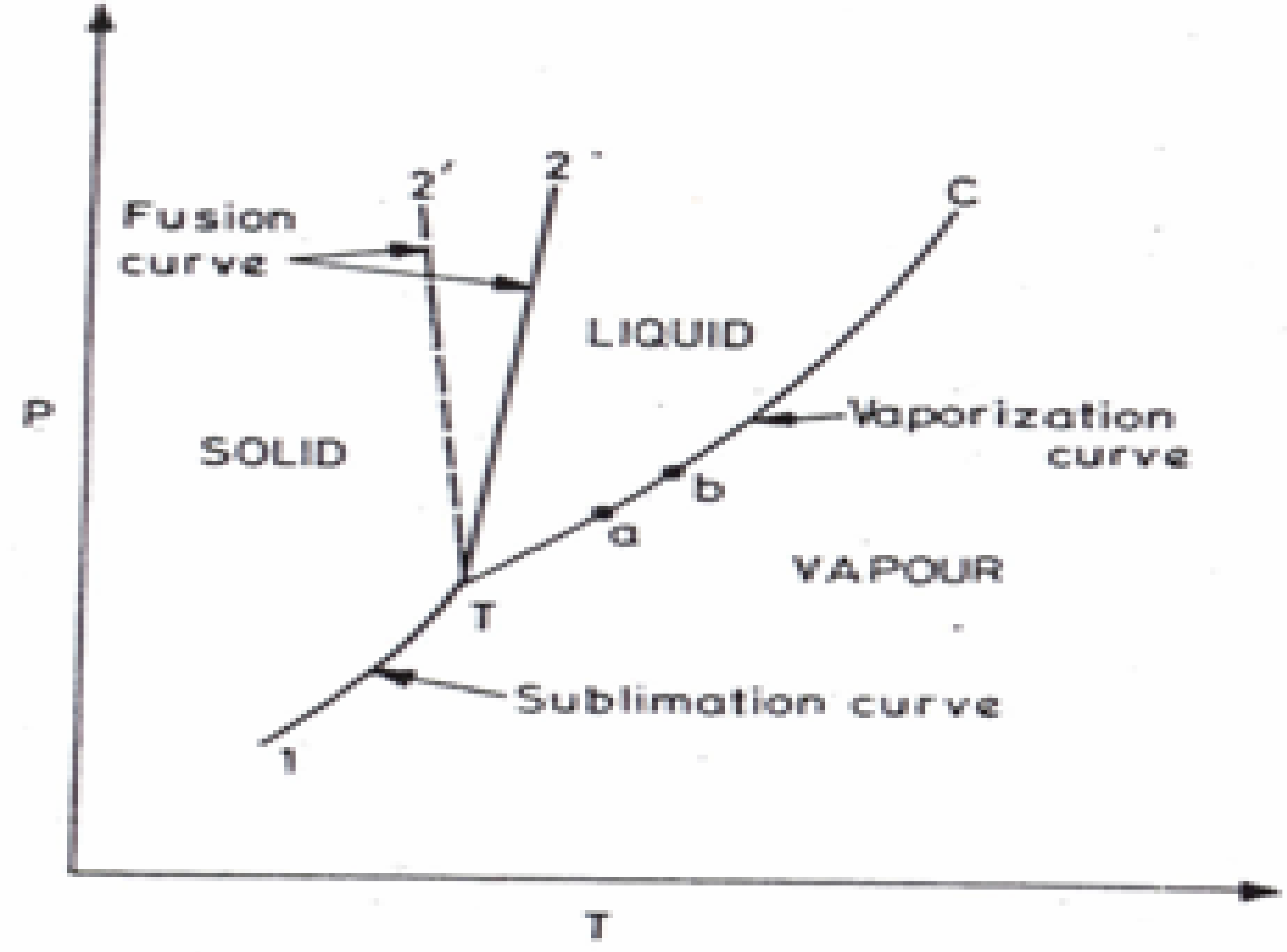
$$\ln P = -\frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{or} \ \ \ln\left(\frac{P_2}{P_1}\right) = \frac{h_{fg}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln P = \frac{-h_{fg}}{R} + Cons\tan t$$

- $d\mu_f = d\mu_g$
- $-S_f\,dT + v_f\,dp = -s_g\,dT + v_g\,dp$
- $V_f\,dp - v_g\,dp = -s_g\,dT + s_f\,dT$
- $dp\,(v_f - v_g) = dT\,(s_f - s_g)$
- $\partial P/\partial T = (S_g - S_f)/v_g - v_f$
- $= (h_g - h_f)/T(V_g - V_f) = h_{fg}/TV_{fg}$
- this is called ***claperon equation –which shows slope of coexistence curves.***

Phase diagram for a single-component simple system



- Application of phase rule gives only one degree of freedom for the system along the coexistence curves.

  only one of the intensive parameters (T or P) specifies the state of the system along the sublimation and fusion curve.

- At the triple point, where ***all the three phase- solid, liquid and vapour coexist,*** the system has no degree of freedom, that is, only at particular value of P & T all the three phases coexist.

Clausius claperon equation

- is a simplification of claperon equation
- at low pressure vapor may be treated as Ideal gas
- then molar volume of liquid phase can be neglected from claperion equation

$\partial p/\partial p = h_{fg/}TV_{fg}$ & $V_{fg} = v_g - V_f$

$\partial p/\partial T = h_{fg}/T(V_g\text{-}V_f) = h_{fg}/TV_g$, *from the simplification* $v_f = 0$

And from ideal gas PV= NRT, V=NRT/P

V = RT/P Then substituting into V_g = RT/P

- ✓ $\partial p/\partial T = h_{fg} / RT^2, \; dlnp/dT = h_{fg}/RT^2$

  $lnp = -(h_{fg}/RT + const)$

  $ln(p_2/p_1) = h_{fg} / R(1/T_1 - 1/T_2)$…………….** Called ***clasious claperoin equation***

- ✓ Used to determine *latent heat of vaporization from knowledge of saturation pressure as a function of temperature.*

Example 3 and 4

Example 3

- Estimate the boiling point of water at 0.2 Mpa given that it boils at 100oC at atmospheric pressure (0.101325 MPa) with a latent heat of vaporization 40.626 kJ/mol. Assume that no other data are available

Example 4

- The vapour pressure of water as reported in the literature is given below:

T (0C)	*P(kPa)*
50	*12.349*
70	*31.19*

- Making use of the above data, estimate the latent heat of vaporization of water.

b) ***two-component systems***

- ***phase diagram of two-component (binary) and multi component system*** are of practical interest to Chemical and Metallurgical Engineers.
- To illustrate the application of phase rule the discussion is limited ***two-component systems only.*** Considering ***liquid-liquid solutions, the two component can be***

1. completely miscible systems

The fundamental relation per mole of a binary mixture in the Gibbs free energy representation can be expressed as

$$g = g\,(T, P, X, Y)$$

where X & Y denote the mole fraction of component 1 in ***the liquid & vapour phase***

- *The Gibbs phase rule tells us*

$$F = c + 2 - p$$

variables from the T, P, X, Y can be arbitrarily assigned.

Where F - degree of freedom

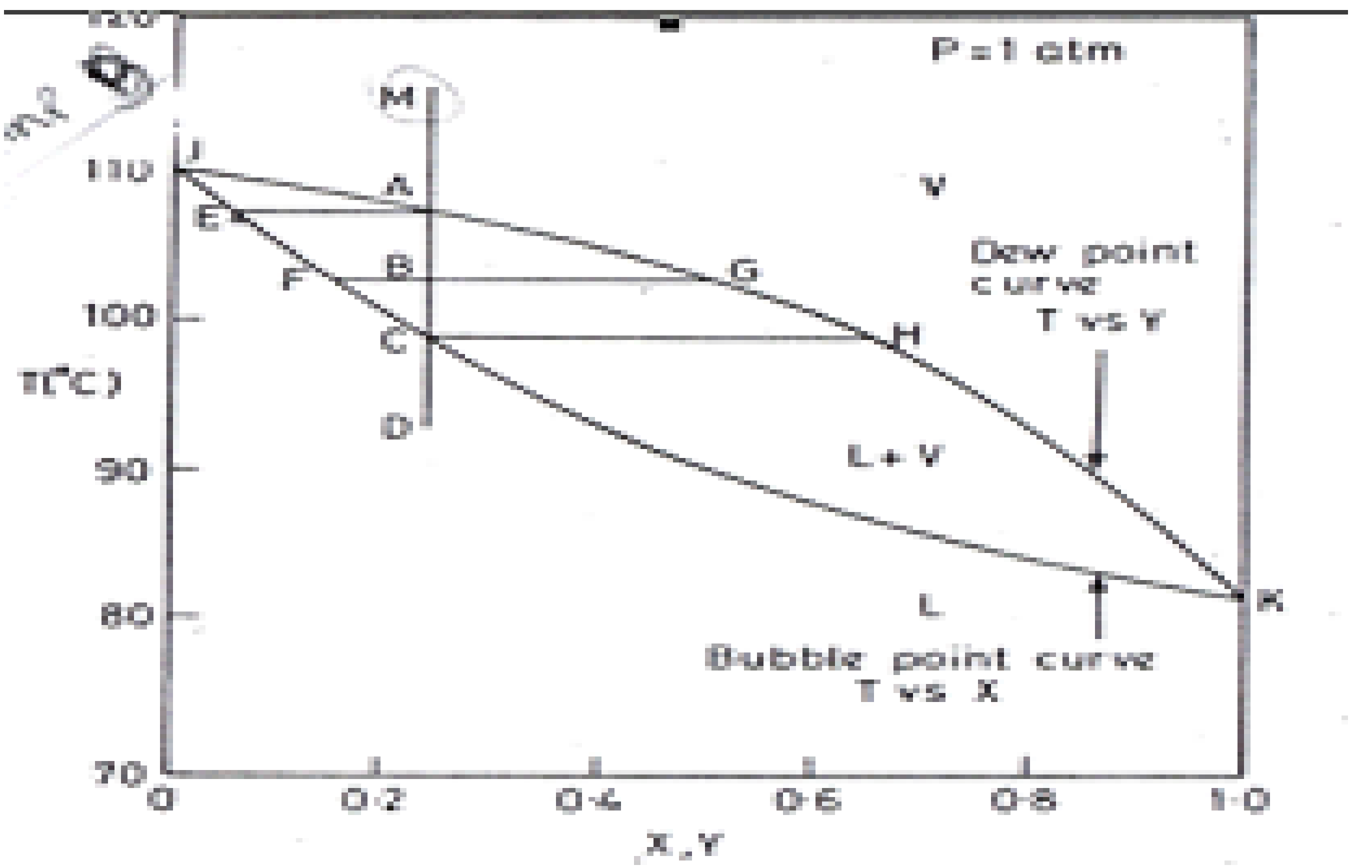
c - no of components

p - no of phases

- The data at ***constant pressure*** gives values of ***T-X-Y*** & the data at ***constant temperature*** gives values of ***P-X-Y***

→*Industrial distillation operations are commonly conducted at constant pressure & hence constant pressure data are of much practical interest.*

T-X-Y diagram of a completely soluble binary system at constant pressure



- *In the liquid or vapour phase regions*

  $p=1$, $c=2$

  hence $F=c+2-p$

  $=2+2-1=3$(degree of freedom) so it is necessary to specify T , P & composition (X or Y) for the description of the state of the system.

  → *In the two phase region $p=2$, $c=2$ hence $F=2$ so it is necessary to specify T & P.*

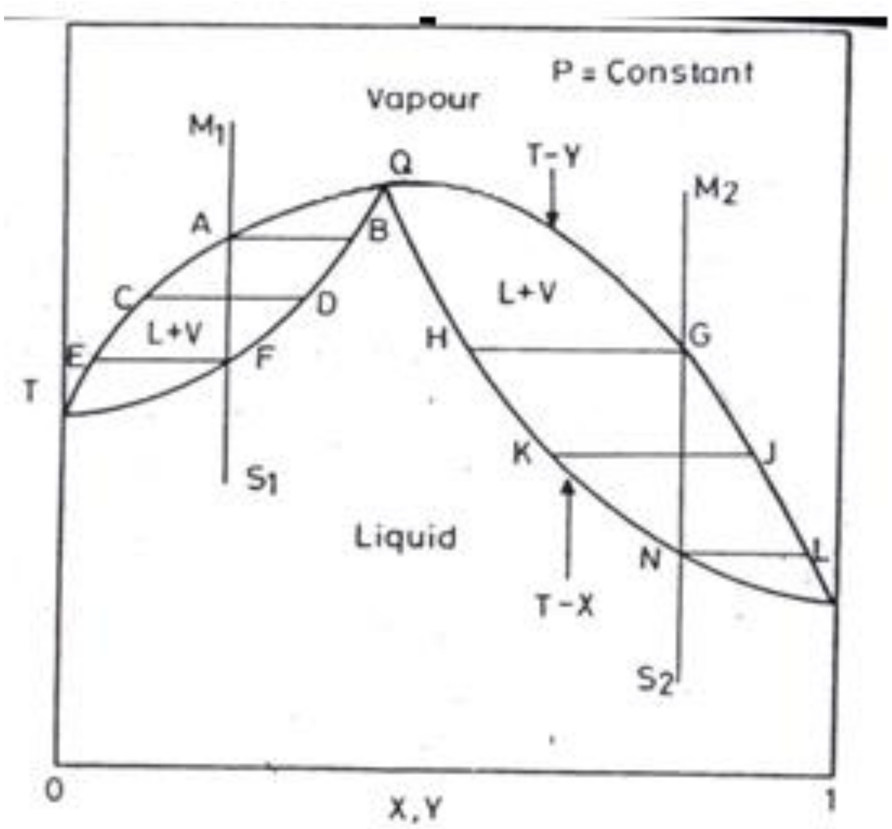
- The horizontal line is called ***tie line*** which indicates the compositions of the two coexisting phase equilibrium. The curve JAGHK is associated with the formation of dew or liquid droplets and is called the ***dew line*****.**

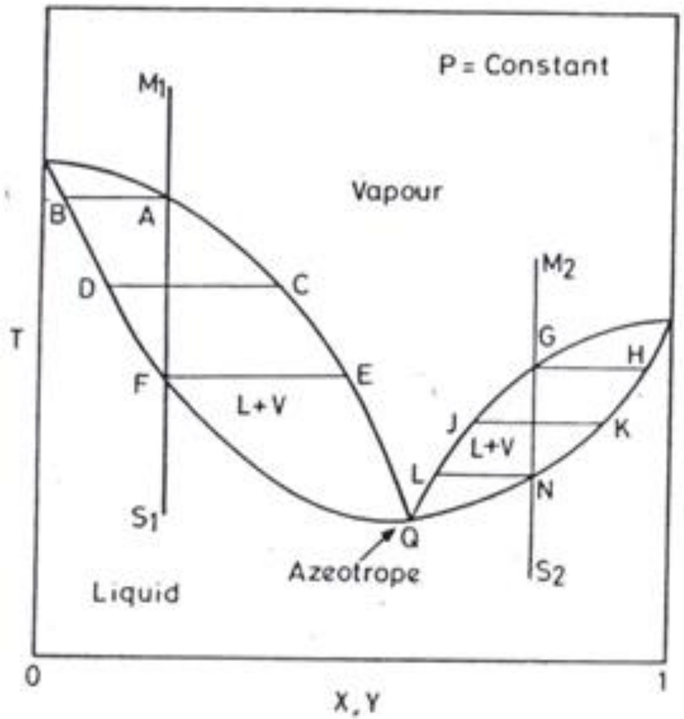
- The curve JEFCK is associated with the formation of vapour and is called the **bubble line.**

- If there is no difference in the composition between the vapour & liquid phases, the components can't be separated by ***distillation & such a mixture is called an azeotrope***. In a maximum boiling azeotrope, at a temperature which is greater than the boiling point of both the components. ***E.g chloroform-tetrahydrofuran***
- If the boiling point of an azeotrope is lower than the boiling point of both the components it is called ***a minimum boiling azeotrope.***

  E.g Ethanol-toluene

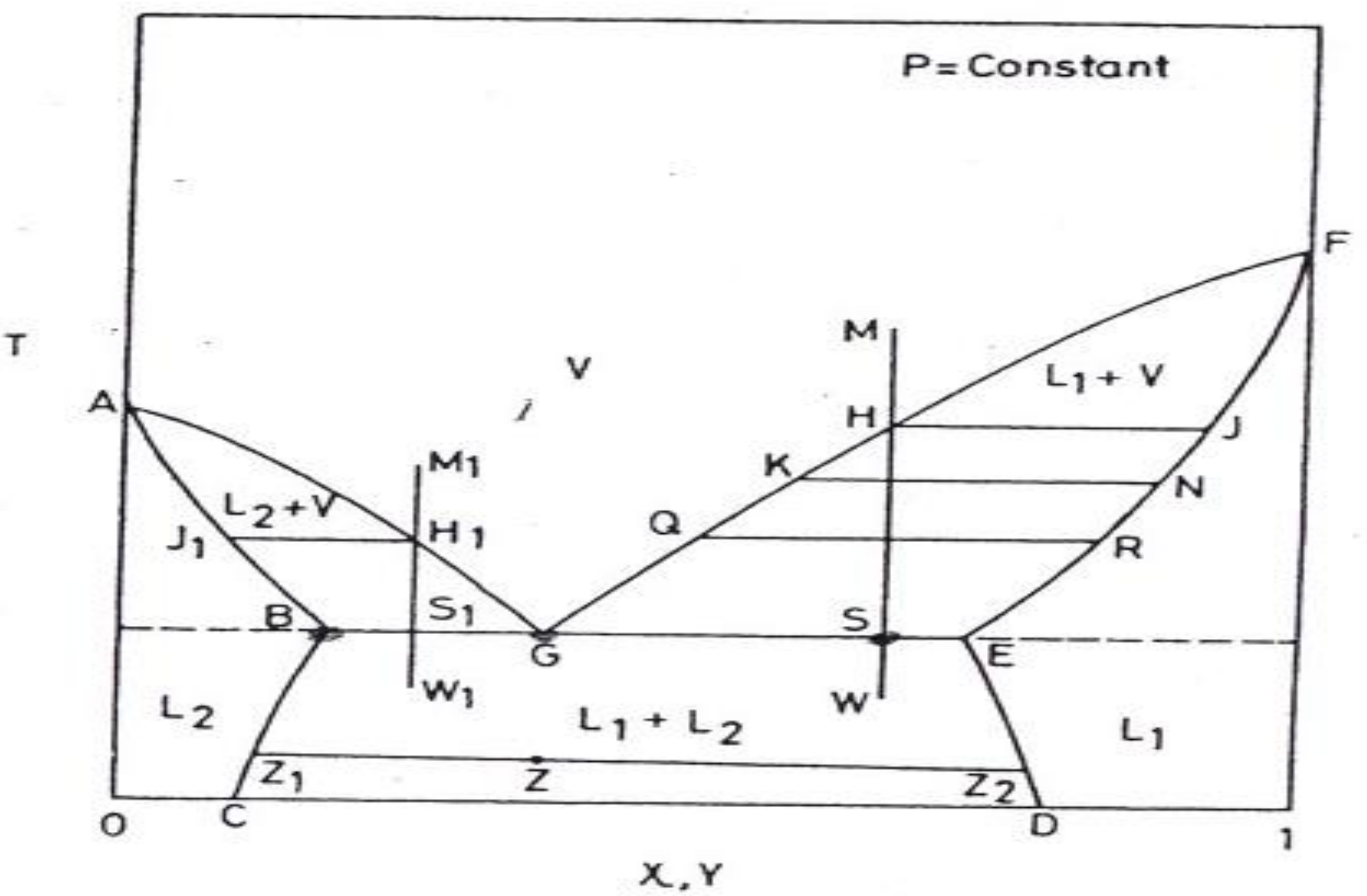
T-X-Y DIAGIARM OF MAXIMUM AND MINIMUM BOILING AZEOTROPE





2, partially miscible systems

- A system with ***limited miscibity*** are important in the field of ***solvent extraction.***
- X and Y denote the mole fractions of component 1 in the liquid phase and vapour phase respectively.
- L_1 and L_2 denote the liquid phases which are in component 1 and component 2 respectively.



T-X-Y diagram for a partially miscible binary system @ const P.

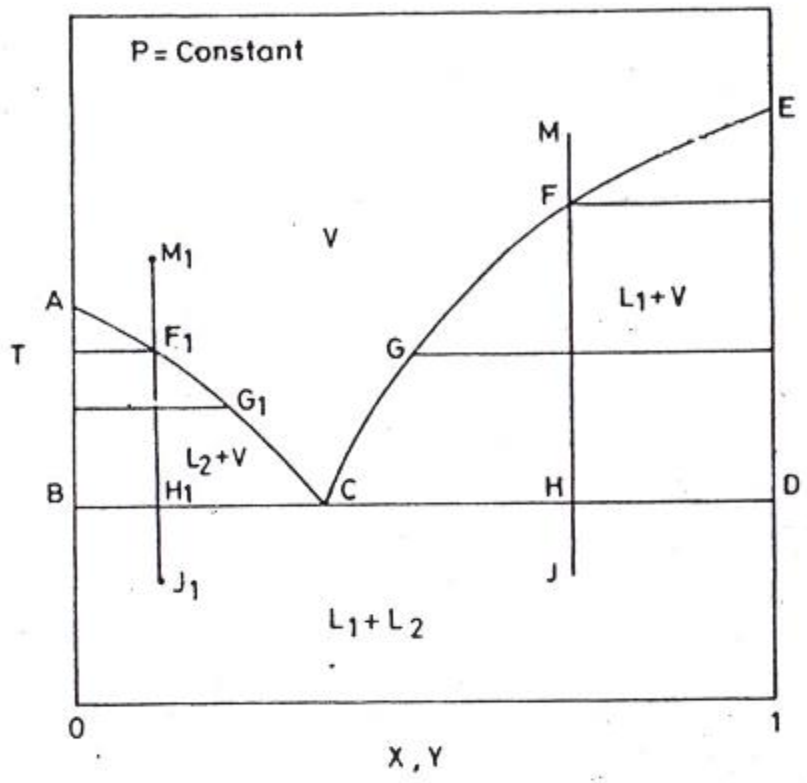
- In a single-phase regions denoted by ***L_1*, *L_2*, and V** there are ***three degree of freedom.***
- Hence ***P, T, X for liquid phases L_1 and L_2 and P, T, Y*** for the vapour phase can be arbitrarily assigned.
- In the two-phase regions marked ***L_1 + V and L_2 +V***, the system has ***two degrees of freedom.*** That is, one can arbitrarily assign values for T and P.
- In the two phase region marked *L_1 + L_2 the number of degree of freedom of the system is again two.*

- The two liquid phases L_1, L_2 and the vapour phase coexist along the line BGE and ***the system has only one degree of freedom.***
- If pressure is specified we can get temperature, composition of the liquid and vapour phase.
- If the temperature increased above three-phase equilibrium temperature, ***one of the liquid phases disappears.***

Completely immiscible systems

- In the region marked V, vapour phase exists and the application of the phase rule yields three degree of freedom.
- That is, P, T and Y can be arbitrarily assigned to the vapour.
- In the region marked $L_1 + L_2$ two liquid phases L_1 (pure component 1) and L_2 (pure component 2) exist.
- *Application of the phase rule to the two-liquid phase region yields two degrees of freedom*

T-X-Y for completely immiscible binary system @ const P.



Solid-solid binary mixture

- Phase diagrams of solid-solid binary systems are of considerable interest and importance to Metallurgical Engineers.
- The solid solutions are also classified in to

  1. *completely miscible systems*

     e.g copper-nickel

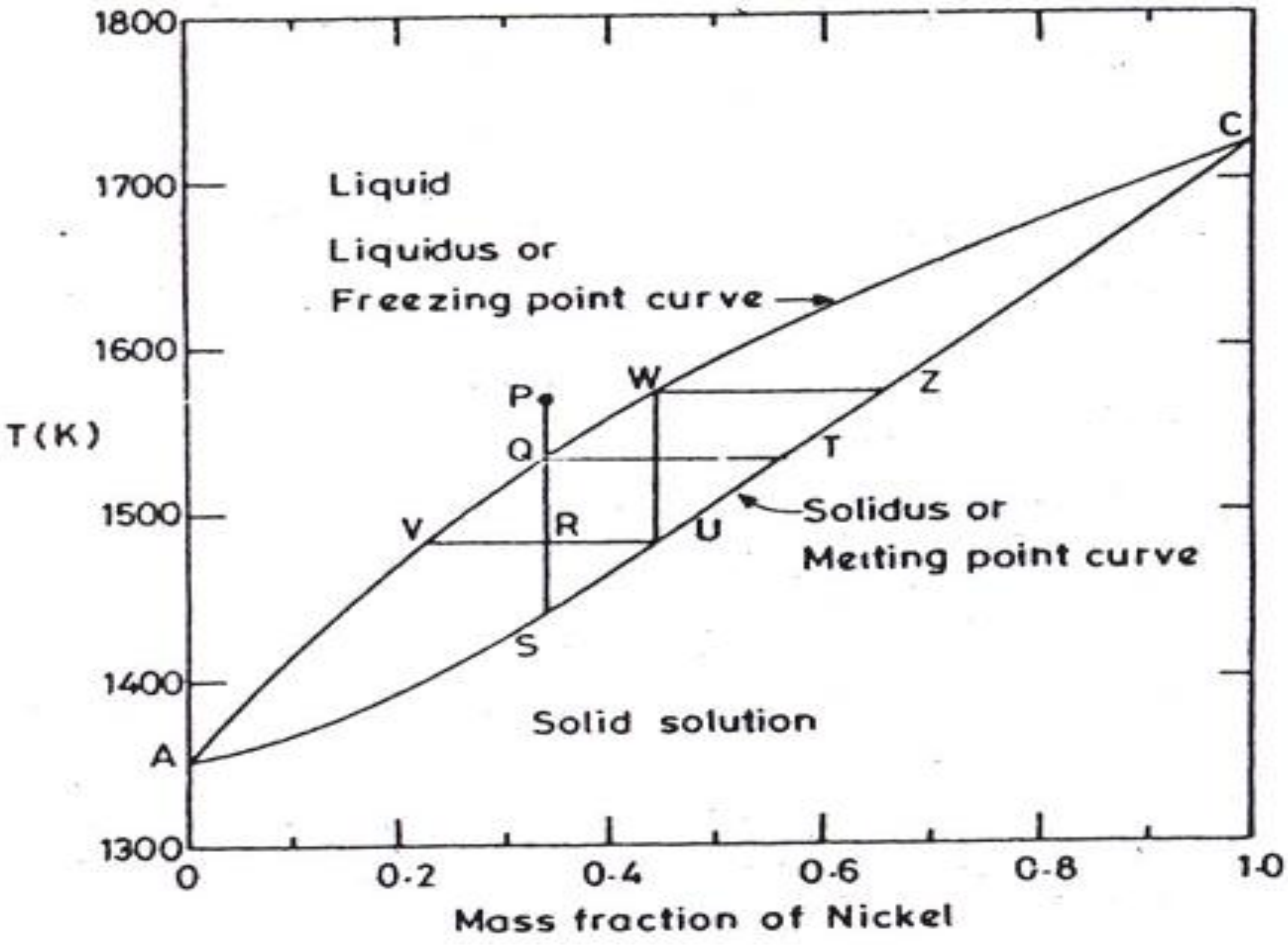
  2. *partially miscible solid solution and*

     e.g silver-copper

  3. *completely immiscible systems*

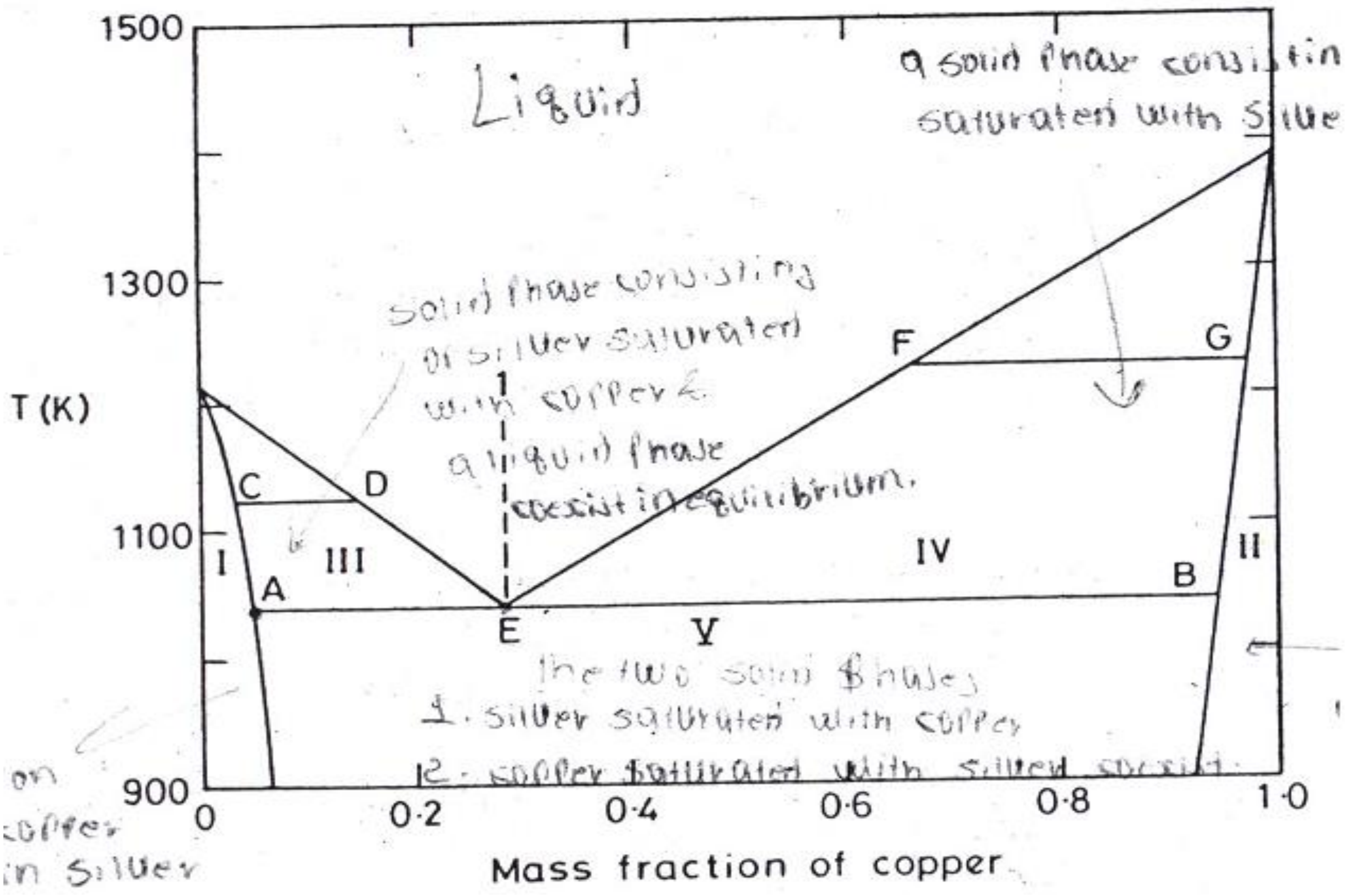
     e.g zinc-cadmium

phase diagram Nickel- copper at0.1 MPa



- The temperature at which solid begins to deposit from the liquid solution is represented by curve AVQC & usually called the *liquidus or freezing point curve.*
- The temperature at which liquefaction begins is represented by the curve ASUTC & usually called the *solidus or melting point curve.*

Phase diagram for silver-copper system at 0.1MPa



a solid phase consistin saturated with silve

solid phase consisting of silver saturated with copper & a liquid phase coexist in equilibrium.

The two solid phases
1. silver saturated with copper
2. copper saturated with silver coexist.

on copper in silver

- At point E, two solid phases of composition A and B and a liquid phase of composition E coexist. This point is called the *eutectic point.*
- At the eutectic point the system has only one degree of freedom.
- Therefore, at a given pressure, the eutectic temperature and the compositions of the coexisting liquid and solid are fixed.

Phase diagram for zink-cadmium system at 0.1 MPa pressure