Physical Chemistry
The second stage

Free energy functions

1. Gibbs free energy (G)

Thermodynamic energy new discovered by Mr. Gibbs describes the state of the system of constant pressure and constant temperature, according to the following.

$\Delta G = \Delta H - T\Delta S$

Changes Gibbs free energy with pressure and temperature

$$G = H - Ts$$
$$H = U + Pv$$
$$G = U + Pv - Ts$$

بالتفاضل

$$dG = \overset{\cancel{Td}s}{\underbrace{dU + Pdv}} + vdp - T\cancel{ds} - sdT$$

$$\because du + pdv = dq$$
$$dq = Tds$$
$$\therefore\ dG = vdp - sdT$$

وبالتفاضل نسبة الى T مع بقاء p ثابت

$$\left(\frac{dG}{dT}\right)_P = -S$$

وبالتفاضل نسبة الى p مع بقاء T ثابت

$$\left(\frac{dG}{dP}\right)_T = V$$

بالتكامل

$$dG = vdp$$

$\because V = \frac{RT}{P}$ لمول واحد

$$\int dG = RT \int \frac{dP}{P}$$

$$G_2 - G_1 = \Delta G = RT\,[\,\mathrm{lin}\,P_2 - \mathrm{lin}\,P_1]$$

$$\Delta G = RT\,\mathrm{lin}\,\frac{P_2}{P_1}$$

$$- RT\mathrm{lin}P_1 - \mathrm{lin}P_2$$

ولكن

$$\Delta G = -W$$

$$G = H - Ts \;,\; G - H = -Ts$$

$$-S = \frac{G - H}{T}$$

$$\left(\frac{dG}{dT}\right)_P = -S$$

وبالتعويض

$$\left(\frac{dG}{dT}\right)_P = \frac{G-H}{T}$$

من خلال هذه المعادلة نستطيع استخراج معادل كبس هلمهولتز بالترتيب الاتي:

$$\Delta G = \Delta H + T\left(\frac{d\Delta G}{dT}\right)_P$$ معادلة كبس هلمهولتز

Or

$$G = H + T\left(\frac{dG}{dT}\right)_P$$ Helmholtz free energy

هذه الحالة تصف النظام عند حجم ثابت ودرجة حرارة ثابتة ويرمز لها بالرمز (A)

$A = U - TS$

$\Delta A = \Delta U - T\Delta S$

Gibbs free energy changes with volume and temperature

$$A = U - TS$$

$$dA = dU - Tds - sdT$$

بالتفاضل

$$\because dU = dq - pdv \quad \because dq = Tds$$

$$\therefore dA = \cancel{Tds} - pdv - \cancel{Tds} - sdT$$

$$dA = -pdv - sdT$$

العلاقة التفاضلية لدالة هلمهولتز

$$dA = -sdT \qquad \text{at constant volume}$$

$$\left(\frac{dA}{dT}\right)_V = -S$$

عند تفاضلها

$$\left(\frac{dA}{dV}\right)_P = -P$$

عند تفاضلها مع T

الحجم وبثبوت

$$\because P = \frac{RT}{V}$$

لمول واحد

$$dA = -\frac{RT}{V}dv$$

بالتكامل

$$\int_{A_1}^{A_2} dA = -RT\int_{V_1}^{V_2}\frac{dV}{V}$$

$$A_2 - A_1 \boxed{= \Delta A = - RT} \text{lin}\frac{V_2}{V_1}$$

$$\Delta A = RT\ \text{lin}\frac{V_1}{V_2}$$

The master equation of closed systems

They are systems that allow the exchange of energy between them with the surrounding with constant mass

$$du = Tdu - pdv$$
$$u = f\,(s.v)$$

u دالة حالة فيكون تفاضلها تام

$$du= \left(\frac{du}{ds}\right)_v ds + \left(\frac{du}{dv}\right)_s$$

$$\left(\frac{du}{ds}\right)_v = T \ldots\ldots\ldots\ldots(1)$$ عند

ثبوت الحجم

$$\left(\frac{du}{dv}\right)_s = -P \dots\dots\dots\dots(2) \qquad T$$

عند ثبوت

تفاضل المعادلة (١) نسبة الى الحجم وتفاضل المعادلة (٢) نسبة الى الانتروبي ونحصل على

$$\left(\frac{du^2}{dvds}\right) = \left(\frac{dT}{dv}\right)_s \dots\dots\dots(3)$$

$$\left(\frac{du^2}{dvdv}\right) = \left(\frac{dP}{ds}\right)_v \dots\dots\dots(4)$$

∵ الطرف الايسر مشابه لكل من المعادلة (٣) و (٤)

$\therefore \boxed{\left(\frac{dT}{dv}\right)_s = -\left(\frac{dP}{ds}\right)_v}$ Maxwell relationship of the internal energy

$$dH = du + P(dv)$$

$$dH = du + Pdv + vdP$$

$$dq = du + pdv \quad , \; dq = Tds$$

$$\boxed{dH = Tds + vdp}$$

$$H = f(s,p)$$

$$dH = \left(\frac{dH}{ds}\right)_P ds + \left(\frac{dH}{dp}\right)_S dp$$

$$\left(\frac{dH}{ds}\right)_P = T \;\ldots\ldots\ldots\ldots'(1)$$

$$\left(\frac{dH}{dp}\right)_S = V \;\ldots\ldots\ldots\ldots'(2)$$

$$\left(\frac{dH^2}{dp\,ds}\right) = \left(\frac{dT}{dp}\right)_S \ldots'(3)$$

$$\left(\frac{dH^2}{dp\,ds}\right) = \left(\frac{dv}{ds}\right)_P \ldots'(4)$$

يتشابه الطرف الايسر للمعادلة (٣) و (٤)

$$\boxed{\left(\frac{dT}{dp}\right)_S = \left(\frac{dv}{ds}\right)_P}$$

علاقة ماكسويل لطاقة الانثالبي

Derivation Maxwell's relationship in relation to the Gibbs

$$G = H - Ts$$

$$H = U + Pv$$

$$G = U + Pv - Ts$$

$$dG = dU + pdv + vdp - Tds - sdT$$

$$\because dq = du + pdv = Tds$$

$$\therefore\ dG = T\cancel{ds} \quad + vdp - T\cancel{ds} - sdT$$

$$dG = vdp - sdT$$

$$G = f(\,p - T)$$

$$dG = \left(\frac{dG}{dp}\right)_T dp + \left(\frac{dG}{dT}\right)_P Dt$$

$$\left(\frac{dG}{dp}\right)_T = V \ ....\text{"}(1)$$

$$\left(\frac{dG}{dT}\right)_P = -\ S \ ....\text{"}(2)$$

$$\left(\frac{d^2G}{dp\,dT}\right) = \left(\frac{dv}{dT}\right)_P \ ....\text{"}(3)$$

$$\left(\frac{d^2G}{dp\,dT}\right) = \left(\frac{ds}{dp}\right)_T \ ....\text{"}(4)$$

$$\boxed{\left(\frac{dv}{dT}\right)_P = \left(\frac{ds}{dp}\right)_T}$$

علاقة ماكسويل لطاقة كبس

Derivation Maxwell's relationship in relation to the Helmholtz function

$$A = U - Ts$$

$$dA = dU - Tds - sdT$$

$$dU = dq - pdv$$

$$\therefore\ dA = T\cancel{ds} - pdv - T\cancel{ds} - sdT$$

$$dA = -\ pdv - sdT$$

$$A = f(\ v - T)$$

$$dA = \left(\frac{dA}{dv}\right)_T dv + \left(\frac{dA}{dT}\right)_V dT$$

$$\left(\frac{dA}{dv}\right)_T = -P \ldots\ldots\ldots\ldots\ldots\text{'''}(1)$$

$$\left(\frac{dA}{dT}\right)_V = -\ S \ldots\ldots\ldots\ldots\ldots\text{'''}(2)$$

$$\left(\frac{d^2A}{dTdv}\right) = -\left(\frac{dp}{dT}\right)_V \ldots\ldots\ldots\text{'''}(3)$$

$$\left(\frac{d^2A}{dTdv}\right) = -\left(\frac{ds}{dv}\right)_T \ldots\ldots\ldots\text{'''}(4)$$

∴ تشابه الطرف الايسر للمعادلة (٢)''' و (٤)'''

علاقة ماكسويل لطاقة هلمهولتز

$$\boxed{\cancel{-}\left(\frac{dp}{dT}\right)_V = \cancel{-}\left(\frac{ds}{dv}\right)_T}$$

The function name	**Symbol**	**The basic equation**	**Differential relationship**	**Maxwell relationship**
Internal energy	U	U=q – w	Du= Tds – pdv	$\left(\frac{dT}{dv}\right)_s = -\left(\frac{dP}{ds}\right)_V$
Enthalpy	H	H= U + pv	dH=Tds + vdp	$\left(\frac{dT}{dp}\right)_s = \left(\frac{dv}{ds}\right)_P$
Helmholtz free energy	A	A= U – Ts	dA= pdv – sdT	$-\left(\frac{dp}{dT}\right)_v = -\left(\frac{ds}{dv}\right)_T$
Gibss free energy	G	G= H – Ts	dG= vdp - sdT	$\left(\frac{dv}{dT}\right)_P = \left(\frac{ds}{dp}\right)_T$

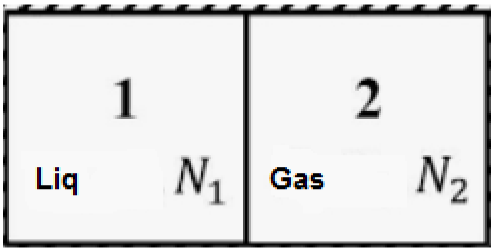
Chemical potential (2 phases) الجهد الكيميائي

(Molar free energy of molecular):Studying multi component system which include chemical reaction, it is necessary to add some limits to the equations of the closed systems of the pure substance or a system that has a chemical structure constant.

دراسة الانظمة المتعددة المكونات والتي تتضمن التفاعلات الكيميائية وعليه من الضروري اضافة بعض الحدود الى المعادلات للانظمة المغلقة للمادة النقية أو النظام الذي يمتلك تركيب كيميائي ثابت

dG = vdp – sdT for closed system

For open system (2 phases)



N= Number of molecules

$$dG = vdp - sdT$$

$n_{1n} \ldots\ldots\ldots n_2 , n_1$

$$dG = vdp - sdT + \left(\frac{dG}{dn_1}\right)_{P_1,T_1,n_1} dn_1 + \left(\frac{dG}{dn_2}\right)_{P_1,T_1,n_1} \cdots \left(\frac{dG}{dn_n}\right)_{p,t,n_n}$$

n_n = الرمز السفلي يدل على الكميات لجميع المكونات ماعدا التي موضحة داخل القوس

$\mu_i = i$ للمكون chemical potential = dni

$$\mu_i = \left(\frac{dG}{dn_i}\right)_{p,t,n_n}$$

حيث تصبح المعادلة لدالة كبس

$$dG = vdp - sdT + \Sigma\, \mu_i dn_i$$

Chemical potential: The rate of change of the Gibbs free energy of system with the number of mole (n_1) and can be considered the driving force for chemical equilibrium system.

يساوي معدل التغير لطاقة كبس الحرة للنظام مع عدد مولات

n_1 ويمكن اعتباره القوة الدافعة للانظمة الكيميائية للاتزان.

وحالة التوازن بين طورين a و b

$$\left(\frac{dG^a}{dn_i^a}\right)_{p,t,n_j} dn_i + \left(\frac{dG^b}{dn_i^b}\right)_{p,t,n_j} dn_i = 0$$

$$\therefore \left(\frac{dG^a}{dn_i^a}\right)_{p,t,n_j} = \left(\frac{dG^b}{dn_i^b}\right)_{p,t,n_j}$$

$$\bar{G}_i^{\,a} = \bar{G}_i^{\,b}$$

Chemical potential of pure materials

الجهد الكيميائي للمواد النقية

$$\mu_i = \left(\frac{dG}{dn_i}\right)_{p,t,n_n} = \bar{G}_i$$

G_i = الطاقة الحرة المولارية الجزيئية للمكون i

$$Vi = \left(\frac{dv}{dn_i}\right)$$ Vi = الحجم المولاري الجزيئي

$$Si = \left(\frac{ds}{dn_i}\right)$$ Si =ا الانتروبي المولاري الجزيئي

Relationship chemical potential with activity

علاقة الجهد الكيميائي مع الفعالية

The chemical potential of a given component in a liquid solution (μ)

$\mu_\iota = \mu^o + RT\ lin\ (p_i/p_i{}^o)$

p_i= vapour pressure of that component

$p_i{}^o$ = pressure of the pure component at the same T and P

If ideal solution → $P_i = x\ P_i{}^o$

$\mu_\iota = \mu^o + RT\ lin\ (x_i)$

For non-ideal solution

$\mu_\iota = \mu^o{}_{(\ell)} + RT\ [lin\ x_i + \alpha\ x_i{}^2 + ß\ x_i^3 + \ldots..)$

$p_i = x_i\ p_i^o\ exp[\alpha\ x_i{}^2 + ß\ x_i^3 + \ldots..] = a_i\ p_i^o$

α and ß constants

a_i= activity

Relationship chemical potential with activity

الجهد $1=a$ $\mu = \mu^o + RT\ lina$

μ^o = القياسي عند

a = الفعالية

$$\Delta G = \ell\ (\mu^o_2 + RT\ lina_L) + m(\mu^o_M + RT\ lina_M) -$$
$$a(\mu^o_A + RT\ lina_P) + b(\mu^o_B + RT\ lina_B)$$

حيث a_A و a_B و a_L و a_M هي فعاليات المواد A و B و L و

M على التوالي في حالة الغازات والظروف القياسية , $273=T$

ولما كانت

$$\Delta G^o = (\ell\mu^o_L + m\ \mu^o_M) - (a\ \mu^o_A + b\ \mu^o_B)$$

ΔG^o = الطاقة الحرة القياسية

$$\Delta G_r = \Delta G^o + RT\ lin \left(\frac{a^\ell_L\ a^m_M}{a^a_A\ a^b_B} \right) \text{eq.}$$ توازن

$$K = \frac{a^\ell_L\ a^m_M}{a^a_A\ a^b_B}$$

$$\because \Delta G = \Delta G^o + RT\ lin\ K$$

عند الاتزان $o=\Delta G$

$$\therefore \Delta G^o = -\ RT\ lin\ K$$

$1=a$

$\Delta G_r = (\ell\mu^o{}_L + m\,\mu^o{}_M) - (a\,\mu^o{}_A + b\,\mu^o{}_B) +$

$(\ell\ RT\ \text{lin}a_L + m\ RT\ \text{lin}a_M) - (a\ RT\ \text{lin}a_A + b$
$RT\ \text{lin}a_B\ )$

ولما كانت

$\Delta G^o = (\ell\mu^o{}_L + m\,\mu^o{}_M) - (a\,\mu^o{}_A + b\,\mu^o{}_B)$

الطاقة الحرة القياسية = ΔG^o

$$\Delta G_r = \Delta G^o + RT\ \text{lin}\left(\frac{a_L^\ell\ a_M^m}{a_A^a\ a_B^b}\right)\text{eq.}$$ توازن

$$K_{th.} = \frac{a_L^\ell\ a_M^m}{a_A^a\ a_B^b}$$

$\because \Delta G = \Delta G^o + RT\ \text{lin}\ K$

عند الاتزان $o = \Delta G$

$\therefore \Delta G^o = -\ RT\ \text{lin}\ K$

Chemical Equilibrium

Heat is energy flowing from a high temperature object to a low temperature object. When the two objects are at the same temperature, there is no net flow of energy or heat. That is why a covered cup of coffee will not be colder than or warmer than the room temperature after it has been in there for a few hours. This phenomenon is known as equilibrium. In this example, we deal with the flow of energy.

Equilibria happen in phase transitions. For example, if the temperature in a system containing a mixture of ice and water is uniformly 273.15 K, the net amount of ice formed and the melt will be zero. The amount of liquid water will also remain constant, if no vapour escape from the system. In this case, three phases, ice (solid) water (liquid), and vapour (gas) are in equilibrium with one another. Similarly, equilibrium can also be established between the vapour phase and the liquid at a particular temperature.

Equilibrium conditions also exist between solid phases and vapour phases. These are phase equilibria.

In Stoichiometry calculations, chemical reactions may not be as complete as we have assumed. For example, the following reactions are far short of completion.

$2\ NO_2 \rightarrow N_2O_4$

$3\ H_2 + N_2 \rightarrow 2\ NH_3$

$H_2O + CO \rightarrow H_2 + CO_2$

Let us consider only the first reaction in this case. At room temperature, it is impossible to have pure NO2 or N2O4. However, in a sealed tube (closed system), the ratio

$$\frac{[N_2O_4]}{[NO_2]^2}$$

Is a constant. This phenomenon is known as chemical equilibrium.

Chemical equilibrium التوازن الكيميائي

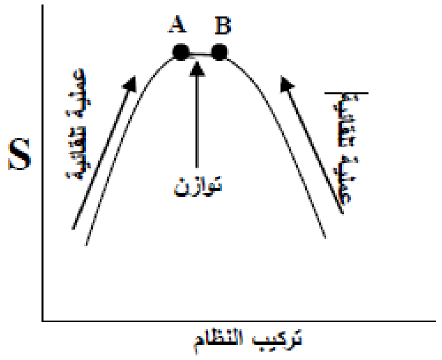
$$A + B \rightleftharpoons C + D$$

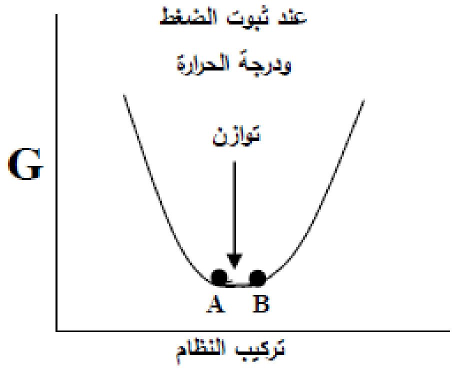
$$R_f = R_r$$

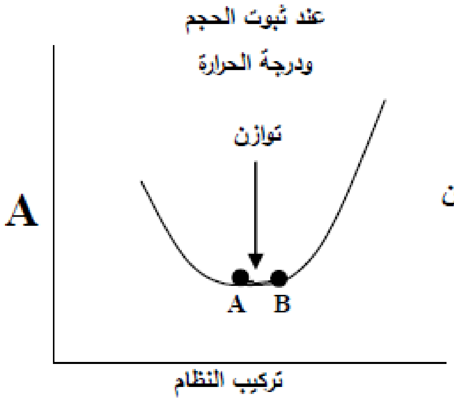
$$R_f = K_F C_A C_B , R_r = K_r C_C C_D$$

$\rightleftharpoons$ يدل على التفاعل عكسي وفي حالة توازن

The reaction rate to the right = there action rate to the left.







مخطط لتوضيح ظروف التوازن

Diagrams to explain equilibrium conditions

The equilibrium between two phases

التوازن بين طورين

$$A \rightleftharpoons B$$

$\Delta G = \Delta G_B - \Delta G_A$

$\Delta G = 0$ at equilibrium

$\Delta G_B = \Delta G_A$

$\therefore$ Gibbs free energy for each of the two phases system be constant.

Clapyeron equation

It is relationship between the variables in the equilibrium between the phases systems mono configuration (e.g. Liquid and vapor, solid and liquid… solid and vapor) and the equilibrium between phases crystalline.

هي العلاقة بين المتغيرات في اتزان مابين اطوار انظمة احادية التكوين مثلاً (سائل – بخار، سائل– صلب، صلب – بخار) والتوازن بين الاطوار البلورية.

$$A \rightleftharpoons B \Rightarrow \Delta G = G_B - G_A \Rightarrow \Delta G = 0 \text{ at equilibrium}$$

$$GB = GA$$

$$dG = vdp - sdT$$

$dG_A = v_A dp - s_A dT$ لـ A

$$dG_B = v_B dp - s_B dT$$

$$\therefore\ V_B dp - S_B dT = V_A dp - S_A dT$$

$$V_B dp - V_A dp = S_B dT - S_A dT$$

$$dp\,(V_B - V_A) = dT\,(S_B - S_A)$$

$$\frac{dp}{dT} = \frac{(S_B - S_A)}{(V_B - V_A)}$$

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

ΔS = تغير الانتروبي في النظام ذي طورين عند تحول مول واحد من A الى B.

ΔV = التغير بالحجم المولي للنظام.

$$\frac{dp}{dT} = \frac{\Delta H}{T\Delta V} = \frac{\Delta H}{T(V_B - V_A)} \qquad \text{(Clapyeron equation)}$$

وكذلك

$$\frac{dp}{dT} = \frac{T(V_B - V_A)}{\Delta H}$$

Application Clapyeron equation

تطبيقات معادلة كلابيرون

1. Solid – liquid equilibrium

$$\underset{(S)}{\text{Solid}} \rightleftharpoons \underset{(\ell)}{\text{liquid}}$$

$$\frac{dp}{dT} = \frac{\Delta H_F}{T_F(V_\ell - V_S)}$$

T_F = درجة حرارة الانصهار والانجماد

2. Equilibrium between two crystalline phases.

$$(\beta) \rightleftharpoons (\alpha)$$

$$\frac{dT}{dp} = \frac{T_{tv}(V_\alpha - V_\beta)}{\Delta H_{tv}}$$

T_{tv}= درجة حرارة التحول

حيث ان ΔH = الحرارة المولية الكامنة

V_A و V_B الحجم المولي للطورين A و B

3. The liquid vapor equilibrium.

$$\text{liquid} \rightleftharpoons \text{vapour}$$

$$\frac{dp}{dT} = \frac{\Delta H_v}{T_b(V_v - V_\ell)} \text{ ، } \frac{dT}{dp} = \frac{T_b(V_v - V_\ell)}{\Delta H_v}$$

ΔH_v = الحرارة الكامنة للتبخر

4. Solid – vapour equilibrium.

$$\text{solid} \rightleftharpoons \text{vapour}$$

$$\frac{dT}{dp} = \frac{T_{sub}(V_v - V_s)}{\Delta H_{sub}}$$

تسامي (sublimation)

T_{sub} = درجة حرارة التسامي

ΔH_{sub} = الحرارة الكامنة للتسامي

Clausius – Clapyeron equation

$$\Delta v = V_g - V_\ell$$

If $V_g >>> V_\ell$

$\therefore V_\ell$ = يهمل

$$\therefore \frac{dp}{dT} = \frac{\Delta H_V}{TV_V}$$

وبأفتراض انه يسلك سلوك الغاز المثالي

$$V_V = \frac{RT}{P}$$

$$\frac{dp}{dT} = \frac{\Delta H_V}{T\frac{RT}{P}}$$

$$\therefore \frac{dp}{dT} = \frac{P\Delta H_V}{RT^2}$$

الصيغة التفاضلية للمعادلة

وبتكامل المعادلة

$$\frac{dp}{dT} = \frac{P\Delta H_V}{RT^2}$$

اجراء التكامل بدون حدود

$$\int \frac{dp}{dT} = \frac{\Delta H_V}{R} \int \frac{dT}{T^2}$$

C = ثابت

$$\text{linp} = \frac{-\Delta H_V}{R} \frac{1}{T} + C$$

التكامل بحدود

$$\text{lin} \frac{P_2}{P_1} = -\frac{\Delta H_V}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

Trouton's Rule قاعدة تروتن

In relation to quite a few of liquid material be entropy of evaporation ΔS_r at boiling point T_b= 21 Cal/mol.K, if the ΔH_rmolar heat of evaporation at boiling point T_b of the

$\frac{\Delta Hr}{T_b}$ = ΔS_r= 21 Cal/ mol. K known Trouton's rule

Used to calculate the vapor pressure

$$\text{Lin p} = \frac{\Delta Hr}{R} \frac{1}{T_b} + C$$

حيث

$R = 1,987$ Cal

$P = 76$ Cm Hg

$C = 4.59$

$$\text{Log } p = -\frac{\Delta H_V}{2.303RT_b} + C \Rightarrow \log p = -\frac{21}{2.303R} + C$$

Henry'S Law

Gas block, which dissolve in given volume of solvent when constant temperature is directly proportional to the gas pressure that remains in the equilibrium with solution.

كتلة الغاز الذي يذوب في حجم معين من مذيب عند ثبوت درجة الحرارة تتناسب مباشرة مع ضغط الغاز الذي يبقى في توازن مع محلوله.

W= dissolved gas black كتلة الغاز الذائب

P = pressure equilibrium ضغط التوازن

K= equilibrium constant

$W = KP$

الكسر المولي $X_2 = KP_2$ if the solution is diluted

Raoult Law

Studying the behavior and solubility of each solute and solvent for ideal solution.

يدرس سلوك وذوبانية كل من المذاب والمذيب بالنسبة لمحلول مثالي.

$P_2 = X_2 P^o$

P_2^o = The vapor pressure of pure solvent

Mixtures of two liquids

المزيجات المكونة من سائلين

A , B = 1, 2

$P_{total} = P_A + P_B$

$\bar{X}_A$ = mole fraction for A

$\bar{X}_B$ = mole fraction for B

$\therefore\ P_A = \bar{X}_A P$

$P_B = \bar{X}_B P$

$P_A = X_A \overset{\circ}{P}_A$ for ideal solution

$P_B = X_B \overset{\circ}{P}_B$

$\overset{\circ}{P}_A$, $\overset{\circ}{P}_B$ = vapor pressure of the components A, B

Example:- Vapor pressure at 25C° for CCl_4 pure 114.9 Mm and $SiCl_4$ 238.3 Mm when ideal behavior. Calculate the vapor pressure for A, B, includes equal weights.

Sol. W_A = weights CCl_4 (153.8 M_{wt})

W_B = weights $SiCl_4$ (169.9 M_{wt})

$$\because X = \frac{n_1}{n_1 + n_2} \quad n = \frac{W}{M_{wt}}$$

$$\therefore X_A = \frac{(W/153.8)}{(W/153.8) + (W/169.9)} = 0.525$$

$$X_B = 1 - X_A = 0.475$$

$$P_A = X_A \overset{o}{P_A} = 0.525 \times 114.9 = 60.3\ M_m$$

$$P_B = X_B \overset{o}{P_B} = 0.475 \times 238.3 = 113.2\ M_m$$

$$P = P_A + P_B$$

$$= 60.3 + 113.2 = 173.5\ M_m$$

Types of chemical equilibrium

1. Homogenous equilibria

One phase = gas or liquid or solid

2. Heterogeneous equilibria

More than phase = solid – gas or liquid – gas or solid – liquid.

Homogeneous Reaction

1. There are no changes in the number of moles.

$H_2 + I_2 \rightarrow 2HI$

g g g

$\Delta_n = 0$

$K_p = K_c\ (RT)^{\Delta n}$

$\therefore\ K_p = K_c$

$$H_2 + I_2 \rightleftharpoons 2HI$$

$C_{H2} = \frac{n_{H_2}}{V}$, $C_{I2} = \frac{n_{I_2}}{V}$

$C_{HI} = \frac{n_{HI}}{V}$

$$K_c = \frac{C_{HI}^2}{C_{H_2} * C_{I_2}}$$

$$K_c = \frac{\left(\frac{n}{v}\right)}{\left(\frac{n}{v}\right) * \left(\frac{n}{v}\right)}$$

$$\begin{array}{lllr} H_2 & + & I_2 \rightleftharpoons & 2HI \\ a & & b & 0 \\ a - x & & b - x & z\ x \end{array}$$

$$K_c = \frac{2X^2}{(a - x)(b - x)}$$

2. Homogeneous in the liquid phase.

$$\begin{array}{lllll} CH_3COOH & + C_2H_5OH & \rightleftharpoons & CH_3COOC_2H_5 & + H_2O \\ a & b & & o & o \\ a-x & b-x & & x & x \end{array}$$

$$K_c = \frac{\frac{x}{v}\frac{x}{v}}{\frac{a-x}{v}\frac{b-x}{v}}$$

$K_p \neq K_c \quad \Delta n \neq o$

3. Homogeneous reaction change the number of moles.

$$\begin{array}{ccc} N_2O_4 & \rightarrow & 2NO_2 \\ g & & g \end{array}$$

$\Delta_n = 2 - 1 = 1$

$K_p = K_c\,(RT)^{\Delta n} = K_cRT$

$$K_p = \frac{P^2_{NO_2}}{P_{N_2O_4}}$$

$$P_{N2O4} = \left(\frac{n_{N_2O_4}}{N}\right)P_{t.}$$

$$P_{total} = P_t$$

$$P_{NO2} = \left(\frac{n_{NO_2}}{N}\right)P_{t.}$$

$$N = n_{N2O4} + n_{NO2}$$

Van't Hoff equation

The equilibrium constant change with temperature

$\Delta G^o = - RT \text{ lin } K_p$ K_p = equilibrium constant

$\Delta G = 0$ at equilibrium

$\Delta G = \Delta G^o + RT \text{ lin } K$ بالتفاضل

$\Delta G^o = - RT \text{ lin } K$

$$\left[\frac{d\Delta G^o}{dT}\right]_p = - R \text{ lin } K_p - RT\left(\frac{d\text{lin}K}{dT}\right)_p$$

وبضرب طرفي المعادلة بـ T

$$T\left[\frac{d\Delta G^{o}}{dT}\right]_{p} = \Delta G^{o} - RT^{2}\left(\frac{dlinK}{dT}\right)_{p}$$

وبالرجوع الى معادلة كبس هلمهولتز

$$\Delta G^{o} = \Delta H^{o} + T\left[\frac{d\Delta G^{o}}{dT}\right]_{p}$$

$$T\left[\frac{d\Delta G^{o}}{dT}\right]_{p} = \Delta G^{o} - RT^{2}\left(\frac{dlinK}{dT}\right)_{p} \;\ldots\ldots\ldots(1)$$

$$T\left[\frac{d\Delta G^{o}}{dT}\right]_{p} = \Delta G^{o} - \Delta H^{o} \;\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$\frac{dlinK}{dT} = \frac{\Delta H^{o}}{RT^{2}}$$

$$d \text{ lin } K = \frac{\Delta H^{o} dT}{RT^{2}}$$

$$\int_{K_1}^{K_2} d\text{lin}K = \frac{\Delta H^{o}}{R} \int_{T_1}^{T_2} \frac{dT}{T^{2}}$$

$$\text{lin } K = - \frac{\Delta H^{o}}{R} \frac{1}{T_2} - \frac{1}{T_1}$$ معادلة فانت هوف

$$\log \frac{(Kp)_2}{(Kp)_1} = - \frac{\Delta H^{o}}{2.303R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

$$= \frac{\Delta H^{o}}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

$(Kp)_1$ = ثابت التوازن بدرجة T_1

$(Kp)_2$ = ثابت التوازن بدرجة T_2

Example :- equilibrium constant Kp of the reaction

$$\underset{(g)}{N_2} + \underset{(g)}{3H_2} \rightleftharpoons \underset{(g)}{2NH_3}$$

1.64×10^{-4} at 400C° and 0.144×10^{-4} at 500C° . Calculate the average temperature of the formation of ammonia gas.

Sol. $T_1 = 400 + 273 = 673$ K

$T_2 = 500 + 273 = 773$ K

$Kp_1 = 1.64 \times 10^{-4}$, $Kp_2 = 0.144 \times 10^{-4}$

$$\log \frac{Kp_2}{Kp_1} = \frac{\Delta H^o}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

$$\log \frac{0.144\times10^{-4}}{1.64\times10^{-4}} = \frac{\Delta H^o}{2.303\times1.987}\left(\frac{773-673}{(773)(673)}\right)$$

ΔH^o = - 25140 Cal

$\Delta H^o = \Delta H_r$ حرارة

التفاعل

$$\frac{1}{2}\underset{g}{N_2} + \frac{3}{2}\underset{g}{H_2} \rightleftharpoons \underset{g}{NH_3} \quad \Delta H_F^o$$ معدل حرارة التكوين

$$\Delta H_F^o = \frac{\Delta H_r^o}{2} = \frac{-2.5140}{2} = -\ 12570 \text{ Cal/ mol}$$

Lowering of the vapor pressure

When dissolve material non-volatile in liquid less vapor pressure, before solvent (state of pure) the quantitative relationship that connects the amount of decrease vapor pressure of the solution and concentration had discovered by the Raoult.

عند اذابة مادة غير متطايرة في محلول يقل ضغط بخار ذلك السائل مقارنةً بحالته قبل الاذابة (حالته النقية) والعلاقة الكمية التي تربط مقدار الانخفاض في ضغط بخار المحلول وتركيزه اكتشفت من قبل راؤولت.

P° = the vapor pressure for pure solvent.

P = the vapor pressure for solution.

$P^{o} - P$ = decrease in the vapor pressure of the solvent.

$$\frac{P^{o} - P}{P^{o}} = \text{Relative lowering of the vapor pressure.}$$

الانخفاض النسبي في ضغط البخار .

$$\therefore X_2 = \frac{n_2}{n_1 + n_2}$$

$$\frac{P^{o} - P}{P^{o}} = X_2 = \frac{n_2}{n_1 + n_2} = \frac{\Delta P}{P^{o}}$$

$$\frac{P^{o} - P}{P^{o}} = \frac{n_2}{n_1} = \frac{W_2 / M_2}{W_1 / M_1} \text{ at diluted solution}$$

يهمل n_2 في المقام

Example:- When dissolve 18.04 gm of sugar alcohol known (mantole) in 100 gm of the water at 20C°, decreased water vapor pressure from 17.535 mm Hg to 17.226 mm Hg in the same temperature. Calculate the molecular mass for alcohol.

Sol. $W_1 = 100g \quad W_2 = 18.04$

$M_1 = 18.02$

$P^o = 17.535$ mm Hg ضغط بخار المذيب

النقي

$P = 17.226$ mm Hg ضغط بخار

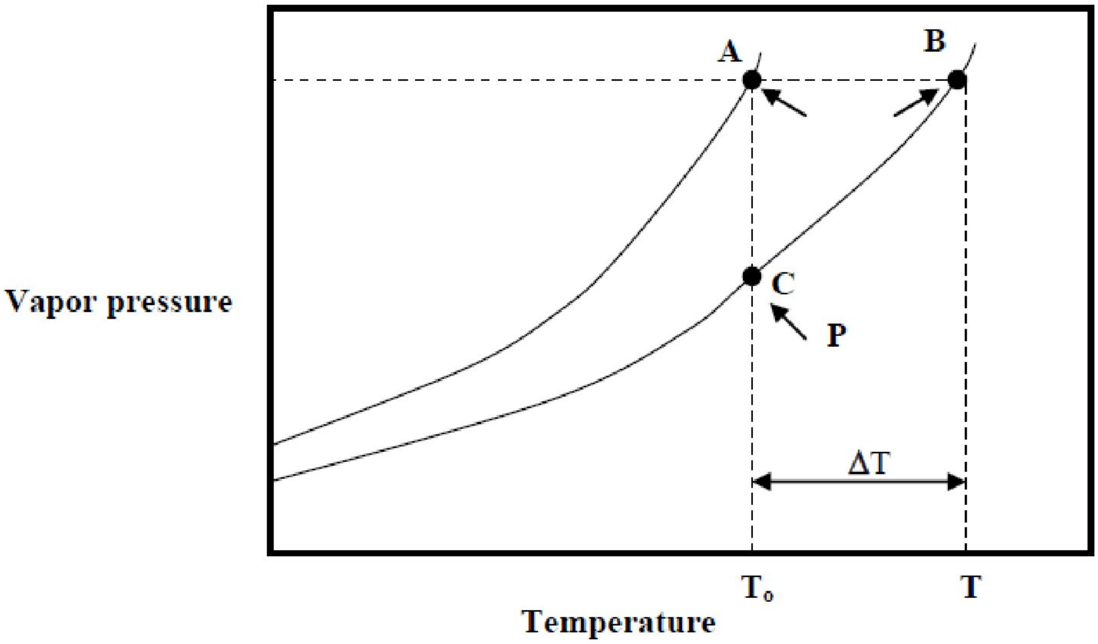
المحلول

$$\frac{P^o - P}{P^o} = \frac{W_2}{M_2} = \frac{M_1}{W_1}$$

$$\frac{17.535 - 17.226}{17.535} = \frac{18.04 \times 18.02}{M_2 \times 100}$$

$M_2 = 181$

Elevation of Boiling point



$\Delta T = T - T_o$

ΔT = The amount of increase in the boiling point

$$K_b = \frac{AB\ Area}{AC\ Area}$$

$A_C = \frac{P^{\circ} - P}{P^{\circ}}$ = Relative lowering of the vapor pressure

A_B = elevation of boiling point

$\Delta T = K_b X_2$

$\frac{d\mathrm{lin}P}{dT} = \frac{1}{P}\frac{dP}{dT} = \frac{\Delta H}{RT^2}$ Clausius – Clapyeron equation

$\Delta H = L_v$

$$\therefore \frac{1}{P}\frac{dP}{dT} = \frac{L_v}{RT^2}$$

$$\frac{1}{P}\frac{\Delta P}{\Delta T} = \frac{L_v}{RT^2}$$

$\frac{1}{P^{\circ}}\frac{\Delta P}{\Delta T} = \frac{L_v}{RT^2}$ when diluted solution

$$\Delta T = \frac{RT^2}{L_v}\frac{\Delta P}{P^{\circ}} = \frac{RT^2}{L_v}\left(\frac{P^{\circ} - P}{P^{\circ}}\right)$$

$\frac{\Delta P}{P^{\circ}}$ = Relative Lowering of the vapor pressure of solution

$$\Delta T = \frac{RT^2}{L_V}\frac{\Delta P}{P^\circ} = \bar{K}_b \frac{\Delta P}{P^\circ}$$

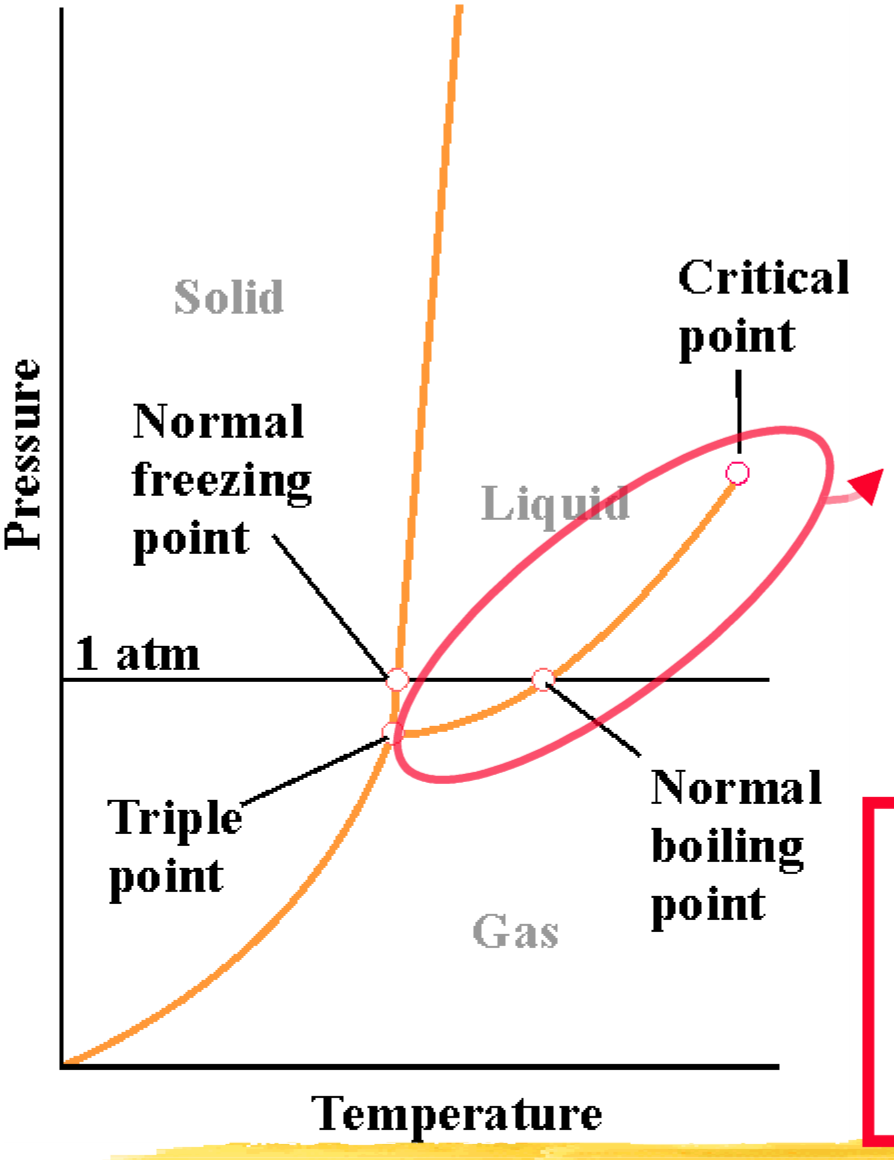
$$\bar{K}_b = \frac{1000K_b}{M_1}$$

$$\therefore \Delta T = \frac{1000K_b}{M_1}\;\frac{\Delta P}{P^\circ}$$

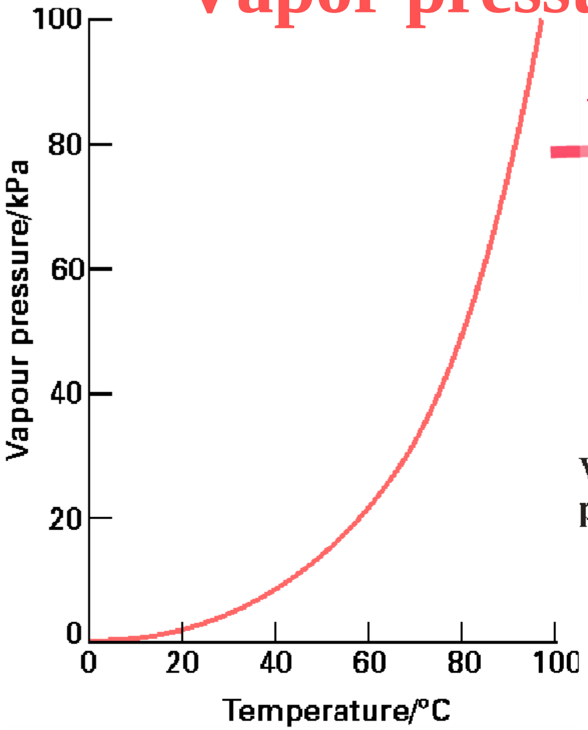
$$\Delta P = P^{O} - P$$

$$\therefore \Delta T = \frac{1000K_b}{M_1}\left(\frac{P^\circ - P}{P^\circ}\right)$$

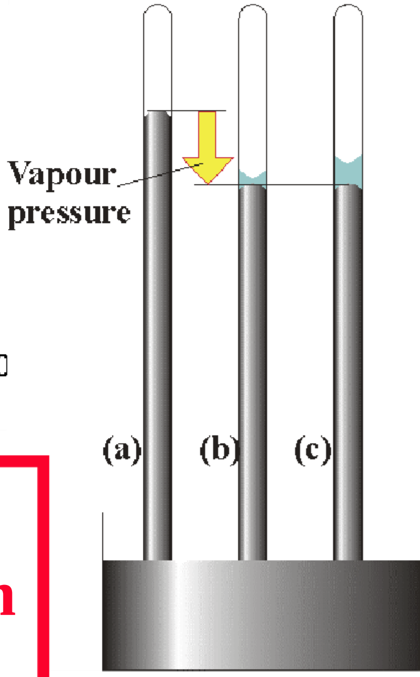
Phase boundaries



Vapor pressure



from



At phase boundary:
<u>Dynamic</u> equilibrium
between two phases
$\Delta G = 0$

Phase boundaries: Where are they?

$$\left.\begin{array}{l}\text{Phase 1: } dG_m(1) = V_m(1)dp - S_m(1)dT \\ \text{Phase 2: } dG_m(2) = V_m(2)dp - S_m(2)dT\end{array}\right\}\ \text{in equilibrium}$$

Along the phase boundary, the molar Gibbs energies stay equal

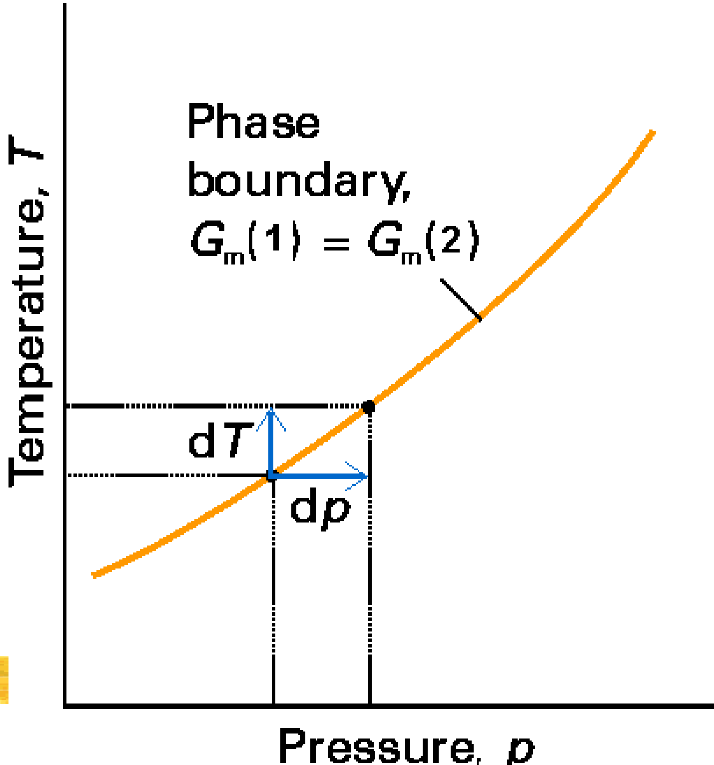
⇒ **the changes in their molar Gibbs energies must be equal**

$$V_m(1)dp - S_m(1)dT = V_m(2)dp - S_m(2)dT$$

$$\Rightarrow \underbrace{[S_m(2) - S_m(1)]}_{\Delta_{trs}S}dT = \underbrace{[V_m(2) - V_m(1)]}_{\Delta_{trs}V}dp$$

$$\Rightarrow \boxed{\frac{dp}{dT} = \frac{\Delta_{trs}S}{\Delta_{trs}V}}$$

Clapeyron equation



Special case: The liquid-vapor boundary

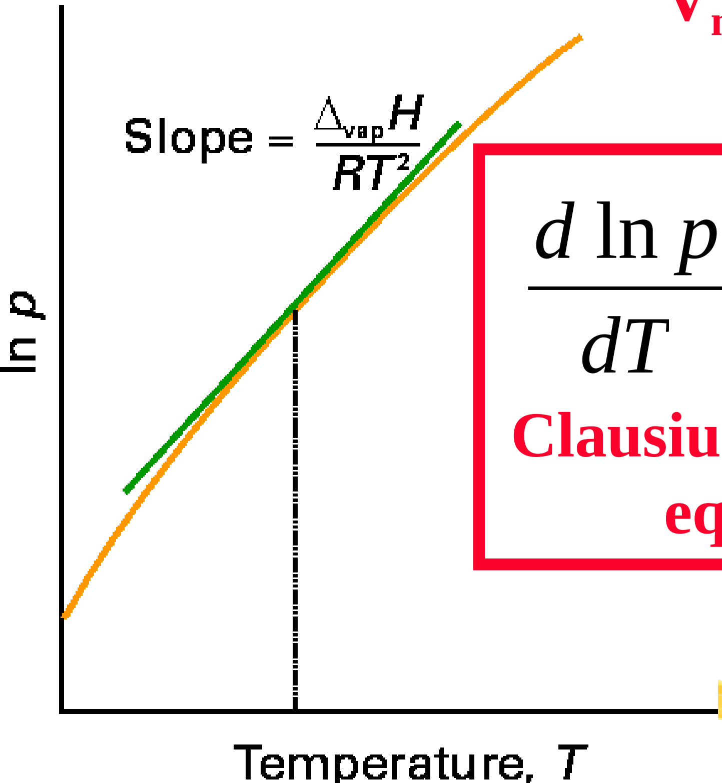
$$\frac{dp}{dT} \underset{\blacktriangle}{=} \frac{\Delta_{vap}S}{\Delta_{vap}V} \underset{\blacktriangle}{=} \frac{\Delta_{vap}H}{T\Delta_{vap}V} \underset{\blacktriangle}{=} \frac{\Delta_{vap}H}{TV_m(g)} \underset{\blacktriangle}{=} \frac{\Delta_{vap}H}{T(RT/p)} = \frac{p\Delta_{vap}H}{RT^2}$$

trs → vap

$\Delta_{vap}S$ $= \Delta_{vap}H/T$

$\Delta_{vap}V$ $\approx V_m(g)$; $V_m(l)$ small

perfect gas approximation



$$\boxed{\frac{d\ln p}{dT} = \frac{\Delta_{vap}H}{RT^2}}$$

Clausius-Clapeyron equation

$$\int_p^{p'} d\ln p = \int_T^{T'} \frac{\Delta_{vap}H}{RT^2}\,dT$$

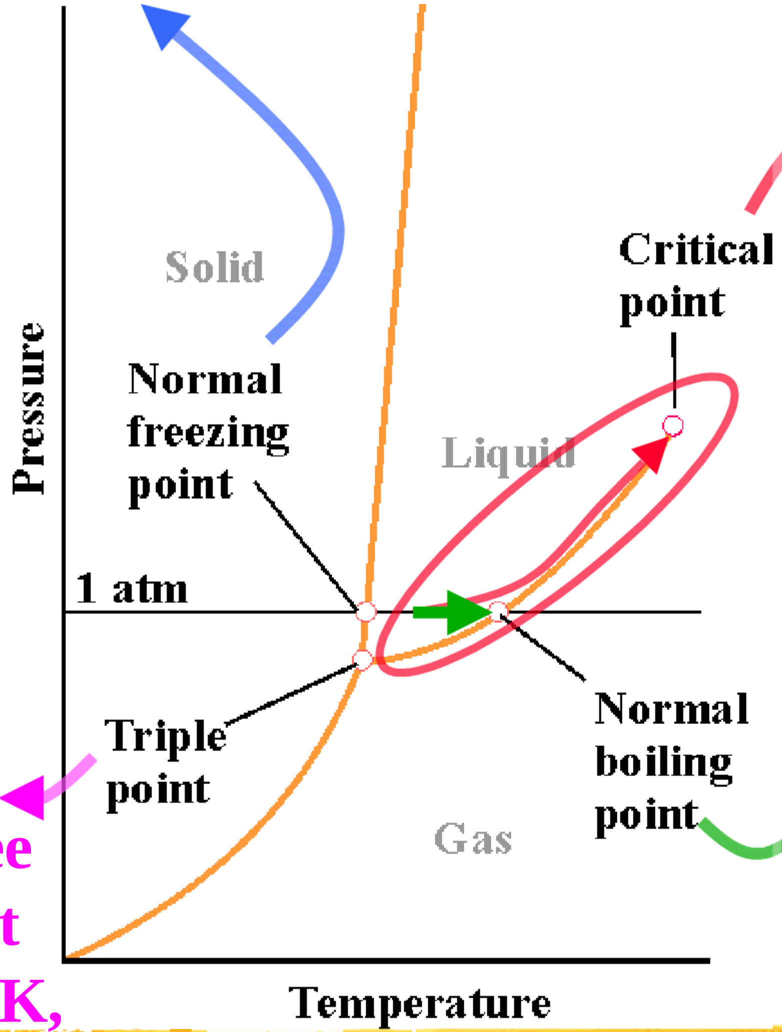
$$* \ln\frac{p'}{p} = \frac{\Delta_{vap}H}{R}\left(\frac{1}{T} - \frac{1}{T'}\right)$$

Characteristic points

Same as melting point;
“normal” = at 1 atm

Highest T for liquid

Closed vessel:
Pressure increases until critical point is reached (T_c, p_c); phase boundary is lost



Lowest T for liquid

Only set of conditions where all three phases coexist (water: 273.16 K, 611 Pa)

Open vessel:
Vapor pressure equals external pressure
⇒ vapor drives back atmosphere: Boiling

How many phases can coexist in equilibrium?

Four phases: $G_m(1) = G_m(2)$; $G_m(2) = G_m(3)$; $G_m(3) = G_m(4)$

BUT: Only two unknown parameters (p, T) in a phase diagram

⇒ Four phases cannot coexist in equilibrium!

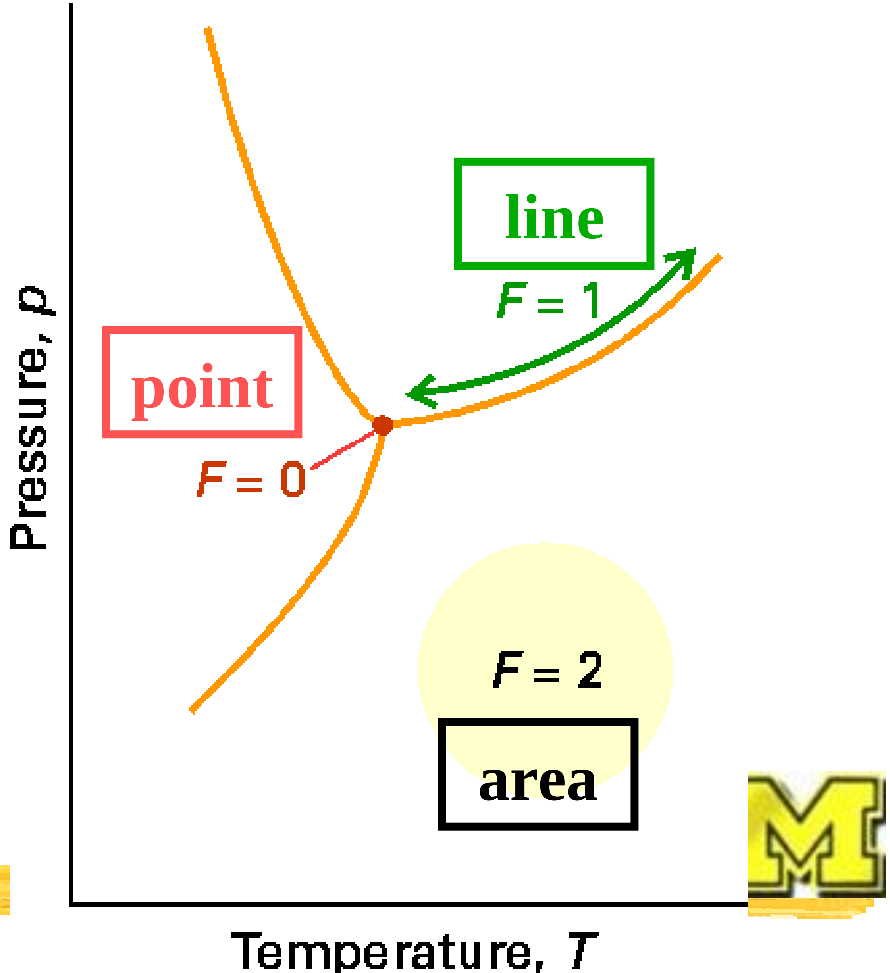
↓

Phase rule: $F = C - P + 2$

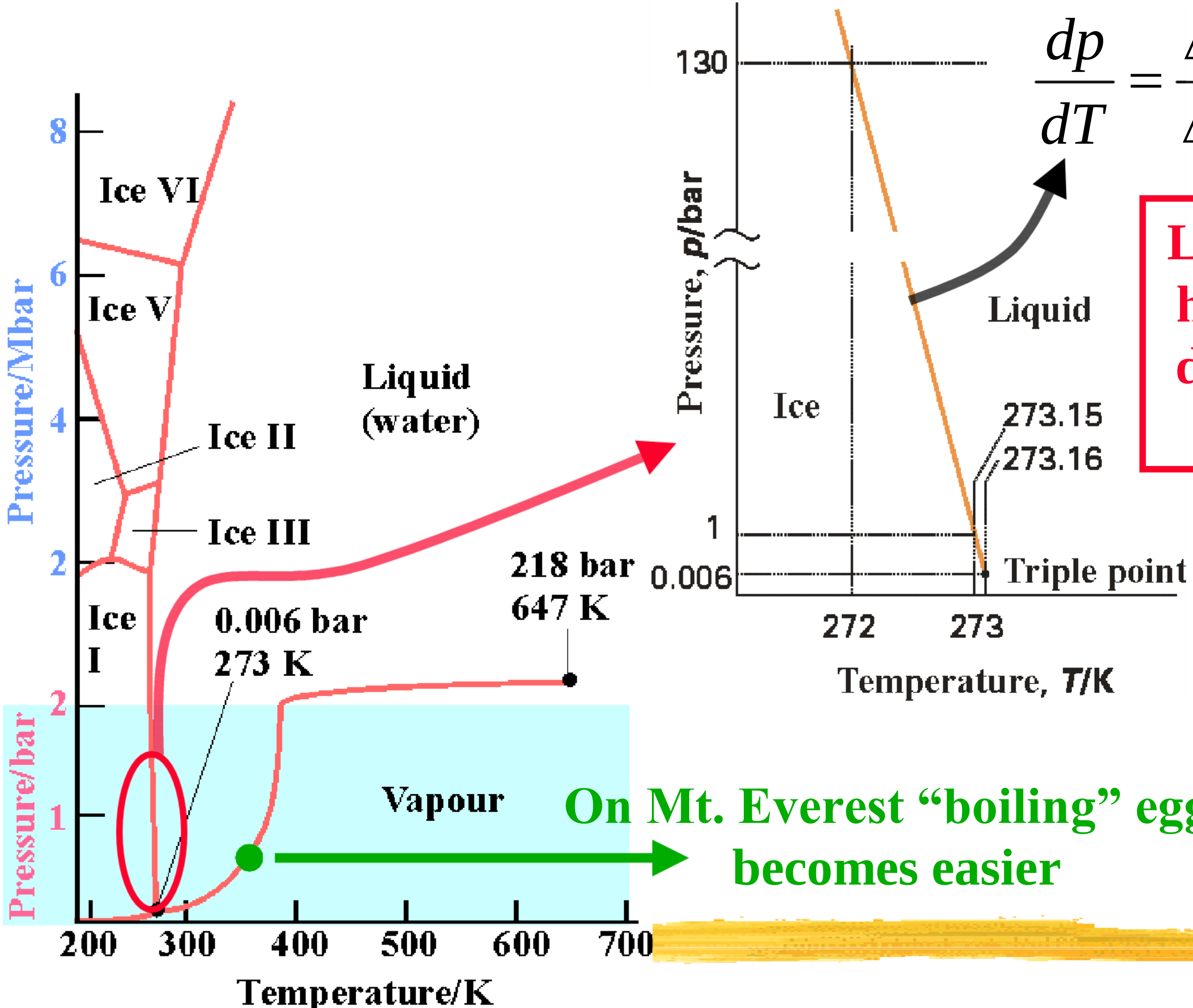
F = Number of degrees of freedom

C = number of components

P = number of phases



Phase diagrams: Water



$$\frac{dp}{dT} = \frac{\Delta_{trs} S}{\Delta_{trs} V}$$

Liquid water has a higher density than water ice

⇓

ice skating! frozen ponds sustain fish!

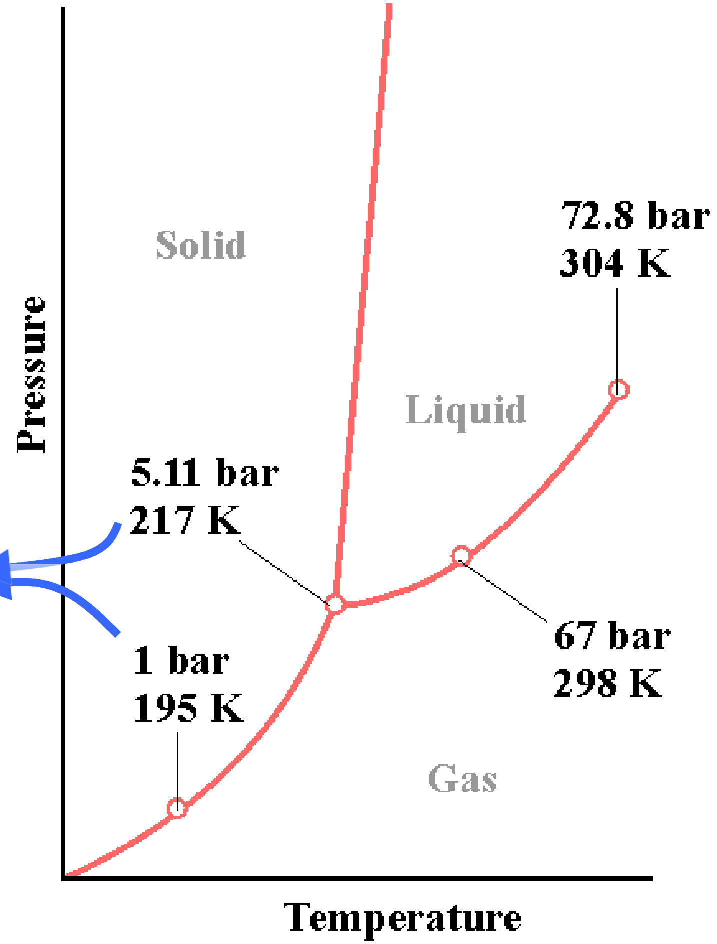
On Mt. Everest "boiling" eggs becomes easier

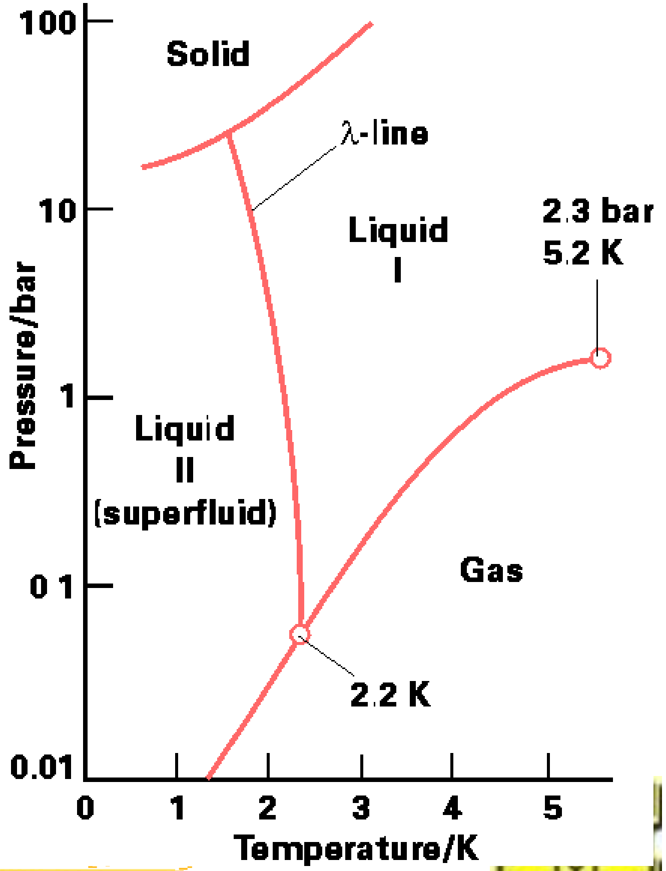
Phase diagrams: CO_2 and Helium

CO_2: quite typical

He: solid and gas are never in equilibrium; He-II is superfluid

Sublimes at 1 atm; exists as a liquid only under pressure





Physical chemistry- 2nd stage

Lecture No. 6
Phase equilibrium

Phase equilibrium

Phase: It is a part of system, uniform through in all chemical compositions and physical properties which is separated from other homogenous parts of the system by boundary surface.

Components:

The number of component is the minimum number of substance of which the composition of each of the phase.

Degrees of freedom (F): The number of intensive parameters that must be specified in order to completely determine the system.

- Intensive variables are pressure, temperature, and composition, that can be changed independently without loss of a phase.

Rule Phase:

This rule was suggested by J.W. Gibbs in 1874, so called Gibb’s rule.

$$\boxed{F = C - P + 2} \quad \text{.....(1)}$$

Josiah Willard Gibbs

Josiah Willard Gibbs (1839 - 1903) has been reckoned as one of the greatest American scientists of the 19th century. He was awarded the first Doctor of Engineering in the U.S., and was appointed Professor of Mathematical Physics at Yale in 1871.
He provided a sound thermo-dynamic foundation to much of Physical Chemistry.

Where:
C is the number of components, usually elements or compounds, in the system.

F is the number of degrees of freedom, or number of variables, such as temperature, pressure, or composition that are allowed to change independently without changing the number of phases in equilibrium.

P is the number of phases present.

In the system may be described separately.

Phase rule

Coexistence of two phases, condition:

$\mu_\alpha(T,P) = \mu_\beta(T,P)$

The two intensive variables are related.

Only one true variable - univariant

Three phases,

$\mu_\alpha(T,P) = \mu_\beta(T,P)$ $\mu_\beta(T,P) = \mu_\gamma(T,P)$

There are two relations and therefore the system is invariant

So for one component, number of variables,

$F = 3 - P$, is the **Phase Rule.**

How about a general rule?

There are several components and several relations between components. At equilibrium, there are relations between chemical potentials.

How many variables to be known?

1. PC - Composition variables for P phases
(In each phase, mole fraction of each component has to be specified. C mole fractions for one phase, PC for P phases.)
2. 2 – Variables corresponding to T and P

Total variables to be known = PC +2

We have also some relations existing.

1. P - P relations of mole fractions

Why: Each phase, there is a relation, $x_1 + x_2 + x_3 + \ldots + x_C = 1$

P phases, P equations

2. C(P-1) - C(P – 1) equations of μ's.

Why: For each component, there are a set of equations:

$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \ldots = \mu_i^P$

(there are P-1 relations in each set, C(P-1) for C components)

Finally the number of variables,

$F = PC + 2 - P - C(P - 1)$

or

$$F = C - P + 2$$

This is the Gibbs phase rule. Can we find out F for a given system?

Reduced Phase Rule

This rule is used, if no vapor phase is found in a system, so the pressure is independent .

$$\boxed{F = C - P + 1}$$

Q/ How Many of C, P, F for the following systems.

② aquoes solution of H_3PO_4

solu.

$$H_3PO_4 \xrightleftharpoons{H_2O} H_2PO_4^- + H^+$$

$$H_2PO_4^- \rightleftharpoons HPO_4^{2-} + H^+$$

$$HPO_4^{2-} \rightleftharpoons PO_4^{3-} + H^+$$

$C = 6$ H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}, H^+, H_2O

There are 3 equilibrium

1 Ionization

∴ $C = 6 - 4 = 2$ $H_2O + H_3PO_4$

$P = 1$ (liquid)

$F = C - P + 1 = 2 - 1 + 1 = 2$ { temp. and Concentration

can be varied

We used a reduced phase rule because no steam system found.

② Saturated solution of K_2SO_4, boiling in closed container

Soln.

$$K_2SO_{4(s)} + H_2O \longrightarrow Soln._{(l)} + Vapor_{(g)}$$

$C = 2$, $P = 3$ $F = 2 - 3 + 2 = 1$

Conc or P or Tem

③ Solution → $AlCl_3$ in H_2O can be يترسب precipitated as $Al(OH)_3$ without ionization

Soln.

$$AlCl_{3(s)} + 3H_2O_{(l)} \longrightarrow Al(OH)_{3(s)} + 3HCl_{(l)}$$

$C = 4$, $P = 2$ (s, l)

$F = C - P + 1 = 4 - 2 + 1 = 3$ 2 Conc. + Temp.

in general

① One Component system

$$\boxed{C = 1}$$

$$F = C - p + 2$$

$$= 1 - 1 + 2 = 2 \qquad <^{T}_{p} \text{ or } <^{T}_{c} \text{ or } <^{c}_{p}$$

$$= 1 - \cancel{2} + \cancel{2} = 1 \qquad T \text{ or } P \text{ or } c$$

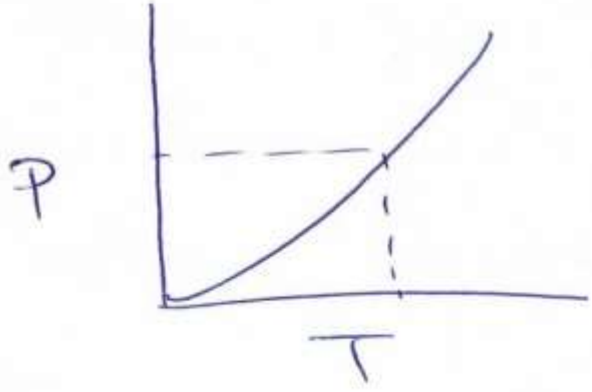
$$= 1 - 3 + 2 = 0$$

μ is same No effect

نقطة ثلاثية (Tripe point)

ثلاث نقاط) الماء يكون في حالة اتزان $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$ عند الثليث

عند رفع درجة الحرارة قليلاً فان
الاتزان سوف يزاح نحو احد
الطورين (اي الطور الغازي)
ويتم الحصول على حالة
الاتزان مرة اخرى.



② Two - Component System

$\boxed{C = 2}$

$F = C - P + 2$

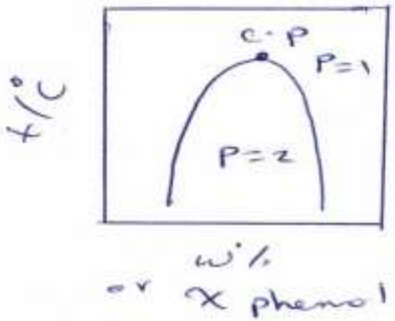
$= 2 - 1 + 2 = 3$ P, T, C

$= \cancel{2} - \cancel{2} + 2 = 2$ P, T or P, C or C, T

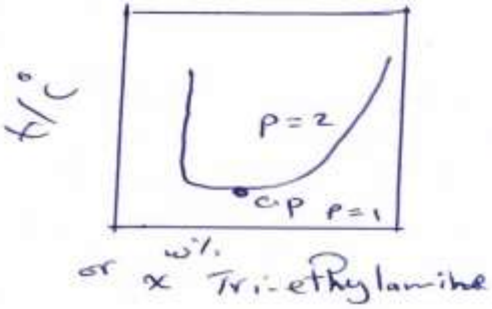
$= 2 - 3 + 2 = 1$ P or T or C

Methods to study this system

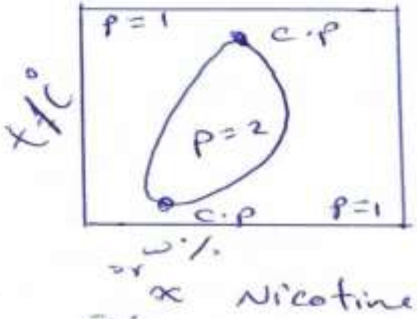
① Solubility method



Solubility curve
a) (up critical point)



Solubility curve
b) (down critical point)



Close
Closed Solubility cur
c) (up-down critica
point)

② Thermal analysis method

This method depended on the rate of cooling in the other word, it is depended on the temp. curve with time that curve called thermal curve, or Cooling curve.

Equilibrium between immiscible liquids

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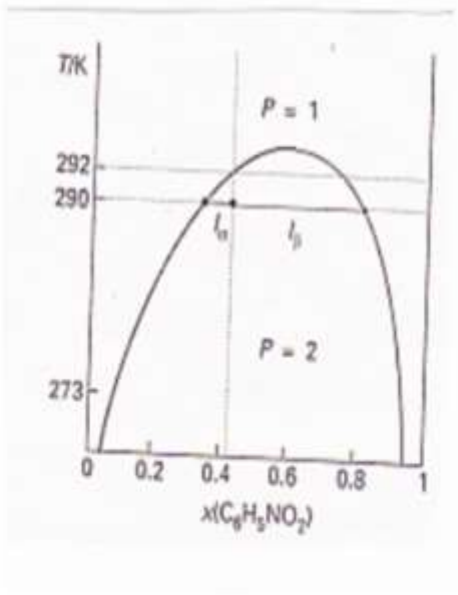

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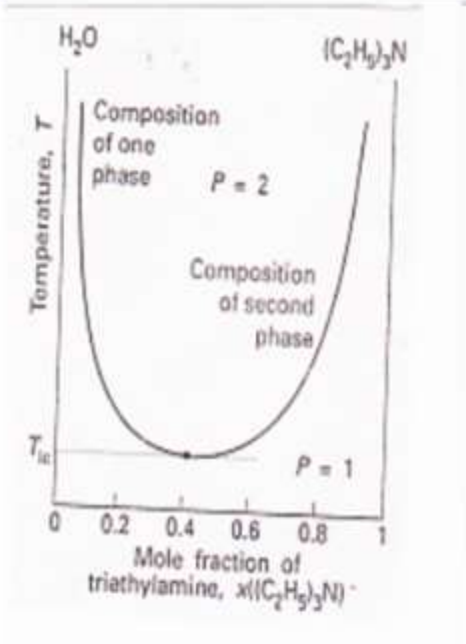

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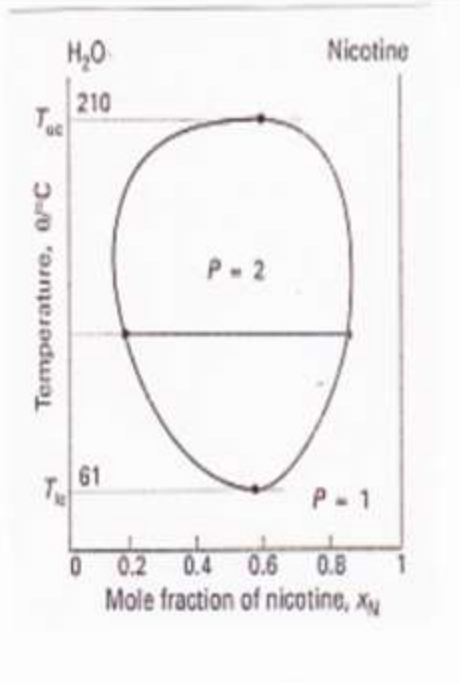

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<tr>
<td>Upper Critical Temperature</td>
<td>Lower Critical Temperature</td>
<td>Double Critical Temperature</td>
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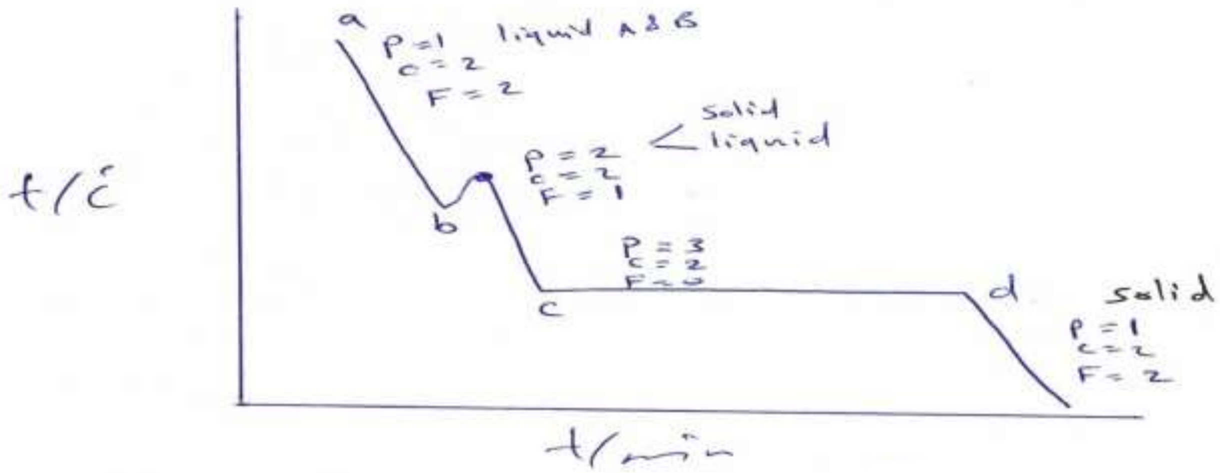


When mixed two components A & B then fused them ;

a-b step refered to Cooling process for liquid A and B, so one of liquid Separated [illegible] as soli phase (freezing) at b point

$$F = C - P + 1$$ reduced Phase rule

$$= 2 - \cancel{1} + \cancel{1} = 2$$ T & C_1 or T & C_2

at b step freezing point $P = 2 <$ liquid, solid

$$F = 2 - 2 + 1 = 1$$ C_1, or C_2, or T

at c-d step the two solid A & B & liquids so them in equilibrium $\boxed{P = 3}$

$$F = 2 - 3 + 1 = 0$$ eutactic

at d step all Components are solid

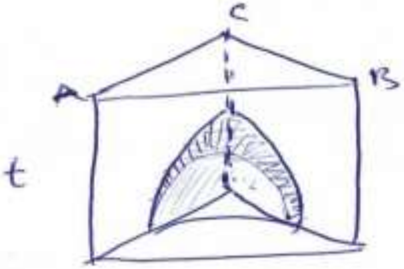
$$F = 2 - \cancel{1} + \cancel{1} = 2$$ T, C_1 or T, C_2

Three Component system

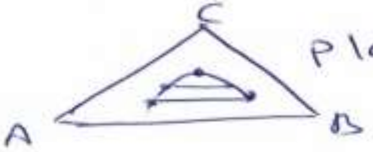
$\boxed{C = 3}$

In this system the phase rule that use is

$$F = C - P \quad .....(7)$$

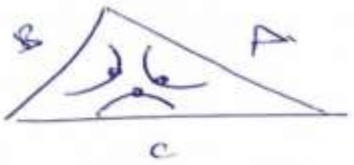


هذا النظام يصبح درجة حرية 4 اذا استخدمت القاعدة العامة ومعناها يحدد النظام بـ T و P وتركيزين وهذا يحتاج الى مخطط رباعي الابعاد والذي يصعب تمثيله عملياً لذا اعتبر الضغط ثابت فيصبح هناك ثلاثة درجات للحرية T وتركيزين لذا نتولد منشور ذي قاعدة مثلثة متساوي الاضلاع حيث تمثل التراكيز للمكونات = على اضلاعه وتمثل الارتفاع العمودي درجة الحرارة لذا اختزلت قاعدة الطور لتصبح $\boxed{F = C - P}$ للنظام ذي مكونات ثلاث ليسهل تمثيله عملياً



plait point نقطة الطية

binodal cure منحني ثنائي العقد



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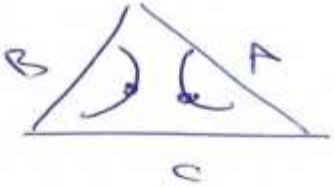

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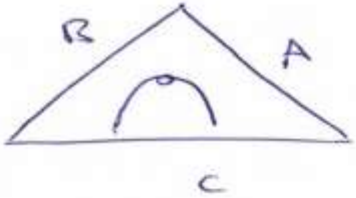
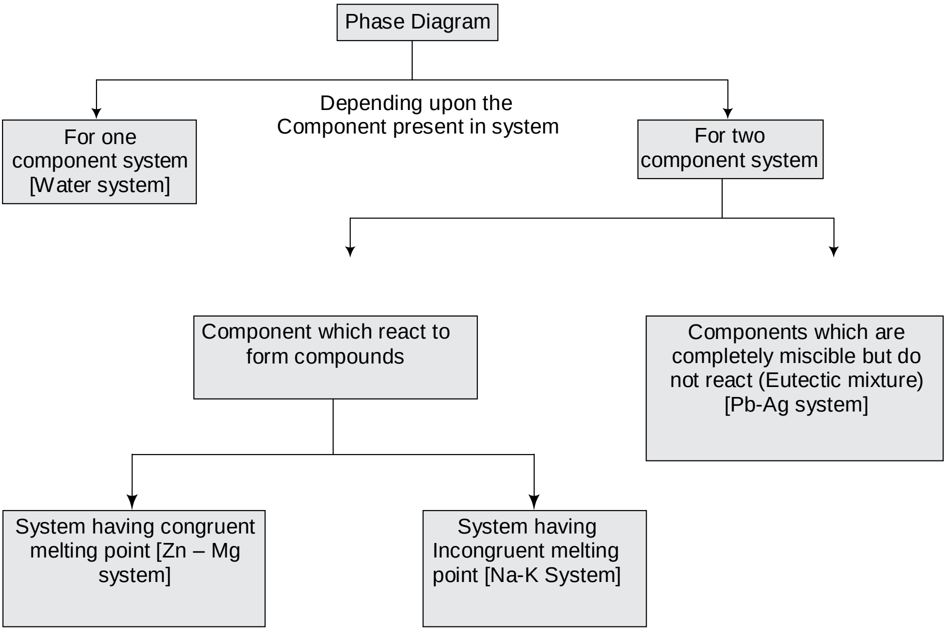


type one

PHASE DIAGRAMS

The graphical presentation giving the conditions of pressure and temperature under which the various phases are existing and transform from one phase to another is known as the phase diagram of the system. A phase diagram consists of areas, curves or lines and points.



4 PHASE RULE FOR ONE-COMPOUNT SYSTEMS

The least number of phases possible in any system is one. So, according to the phase rule equation, a one-component system should have a maximum of two degrees of freedom.

When $C = 1, \; P = 1$

So, $F = C - P + 2 = 1 - 1 + 2 = 2$

Hence, a one-component system requires a maximum of two variables to be fixed in order to define the system completely. The two variables are temperature and pressure. So, phase diagrams for one component system can be obtained by plotting P vs T.

In case of a one-component system, phase diagram consists of areas, curves or lines and points which provide the following information regarding the system:

Point on a phase diagram represents a non-variant system.

Area represents a bivariate system

Curve or a line represents a univariate system.

Water system and the Sulphur system are the example of one component systems.

[1] Water System

Water is a one component system which is chemically a single compound involved in the system. The three possible phases in this system are: ice (solid phase), water (liquid phase) and vapour (gaseous phase).

Hence, water constitutes a three-phase, one-component system.

Since water is a three-phase system, it can have the following equilibria:

ice ⇌ vapour,

ice ⇌ water;

water ⇌ vapour

The existence of these equilibria at a particular stage depends upon the conditions of temperature and pressure, which are the variables of the system. If the values of vapour pressures at different temperatures are plotted against the corresponding temperatures, the phase diagram of the system is obtained.

The phase diagram of the water system is shown in Fig. 2.1. The explanation of the phase diagram of water system is as follows:

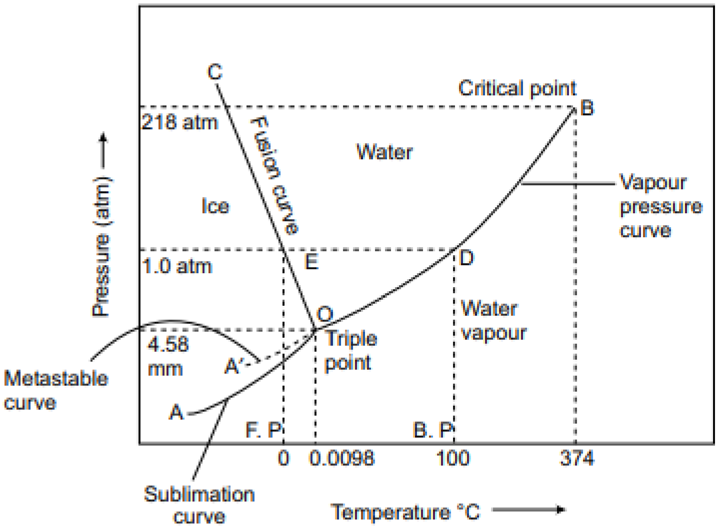


Fig. 2.1 Phase diagram of water system

(a) Curves

The phase diagram of the water system consists of three stable curves and one metastable curve, which are explained as follows:

(i) Curve OB: The curve OB is known as vapour pressure curve of water and tells about the vapour pressure of water at different temperatures. Along this curve, the two phases—water and vapor exists together in equilibrium.

At point D, the vapour pressure of water become equal to the atmospheric pressure (100°C), which represents the boiling point of water. The curve OB finishes at point B (temp. 374°C and pressure 218 atm) where the liquid water and vapour are indistinguishable and the system has only one phase. This point is called the critical point.

Applying the phase rule on this curve,

$$C = 1 \text{ and } P = 2$$

$$F = C - P + 2 = 1 - 2 + 2 = 1$$

Hence, the curve represents a univariant system. This explains that only one factor (either temperature or pressure) is sufficient to be fixed in order to define the system.

(ii) Curve OA: It is known as sublimation curve of ice and gives the vapour pressure of solid ice at different temperatures. Along sublimation curve, the two phase's ice and vapour exist together in equilibrium. The lower end of the curve OA extends to absolute zero (−273°C) where no vapour exists.

Area	Phase exits	Component
(i) Area AOC	ice	H_2O
(ii) Area COB	water	H_2O
(iii) Area below BOA	vapour	

H_2O Thus, for every area contains

$$C = 1 \text{ and } P =$$

1 Therefore, applying phase rule on areas

$$F = C - P + 2 = 1 - 1 + 2 = 2$$

Hence, each area is a bivariant system. So, it becomes necessary to specify both the temperature and the pressure to define a one phase-system.

Table 2.1: Some salient features of the water system

Curve/ area/ point	Name of the system	Phases in equilibrium	No. of phase (P)	Degree of the freedom (F)
Curve OB	Vapourisation curve	Liquid & vapour	02	01(Univariate)
Curve OA	Sublimation curve	Solid & vapour	02	01(Univariate)
Curve OC	Fusion curve	Solid & liquid	02	01(Univariate)
Curve OA’	Metastable vaporization curve	Liquid & vapour	02	01(Univariate)
Area AOC		Ice	01	02(Bivariate)
Area BOC		Water	01	02(Bivariate)
Area AOB		Vapour	01	02(Bivariate)
Point O		Ice & water & vapour	03	0(Invariant)

5 TWO-COMPOUNT SYSTEMS

When the two independent components are present in a heterogeneous system, the system is referred to as a two-component system. Hence, according to the phase rule, for a two-component system having one phase,

$$F = C - P + 2 = 2 - 1 + 2 = 3$$

Therefore, the two component system having one phase will have three degrees of freedom or three variables would be required to define the system. The three variables are pressure (P), temperature (T) and concentration (C). This will require a three-dimensional phase diagram for the study of a two-component system. However, in order to simplify the study, a two-component system is usually studied in the form of a condensed system. A condensed system can be studied by reducing a comparatively less important variable. This reduces the degree of freedom of the system by 1 and the system can easily be studied with the help of a two-dimensional phase diagram.

It can have a maximum of following four phases:

Solid lead, solid silver, Solution of molten silver & lead and Vapors

The boiling points of silver and lead are considerably high and the vapour pressure of the system is very low. So, the vapour phase can be ignored and the system can be studied as a condensed system. This system thus can be easily studied with the help of a two dimensional T − C diagram and the reduced phase rule equation, F' = C − P + 1, can be used. This system is generally studied at constant pressure (atmospheric). The phase diagram of Lead-Silver system is shown in Fig. 2.2.

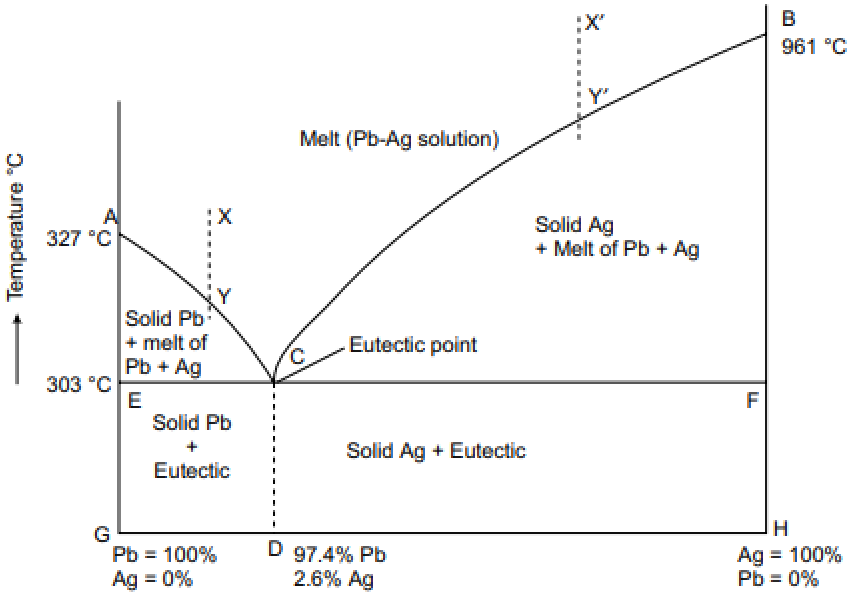


Fig. 2.2 Phase diagram of Pb-Ag system

(a) Curves

The phase diagram of the lead-silver system consists of following curves, which are explained as follows:

(i) Curve AC (Freezing point curve of lead): The AC curve shows the variation of the melting point of lead on addition of silver. The pure lead melts at 327°C (point A). Addition of silver lowers its melting point along curve AC. The added silver dissolves in molten lead to form Ag-Pb solution with the separation of some part of solid lead. Therefore, the two phases, solid lead and Ag-Pb solution remain together in equilibrium along the curve AC.

Hence, P = 2, (solid Pb and melt of Ag-Pb)

C = 2(Pb and Ag)

So, C = 2 and P = 2,

On applying the reduced phase rule

$F' = C - P + 1 = 2 - 2 + 1 = 1$ the system is univariate.

(iii) Area BCF: The area consists of two phases—solid Ag and a solution of Pb and Ag. Hence it is also univariate.

(i) Area DCFH: This area also has the two phases which are solid Ag crystals and solid eutectic crystals. Hence C = 2 and P = 2, the system is univariate.

(ii) Area CEGD: The area also has the solid Pb crystals and solid eutectic crystals phases. The system is univariate.

Table 2.2: Some salient features of the Pb-Ag system.

Curve/ area/ point	Name of the system	Phases in equilibrium	No. of phase (P)	Degree of freedom (F)
Curve AC	Freezing curve of Pb	Pb & Melt (Pb+ Ag Solution Pb & Ag)	02	01(Univariate)
Curve BC	Freezing curve of Ag	Ag & Melt Pb & Ag)	02	01(Univariate)
Area ACE	.....	Pb & melt	02	01(Univariate)
Area BCF	.....	Ag & melt	02	01(Univariate)
Area above ACB	.....	Liquid (melt)	01	02(Bivariate)
Area ECF	.....	Pb & Ag both in solid	02	01(Univariate)
Point O	Eutectic point	Pb, Ag & melt	03	0(invariant)

(B) Systems having Congruent Melting Point

A binary system is said to possess a congruent melting point when it melts at a sharp temperature to give a liquid of the same composition as that of the solid.

The components of a binary mixture at a certain stage enter into chemical combination and form one or more compounds (inter-metallic compounds) in stochiometric proportions. These compounds melt sharply at a constant temperature into a liquid having the same composition as that of the solid. The temperature at which such a compound melts is called the congruent melting point.

Some common examples of this type of system are zinc-magnesium system, mercury-thallium system, gold-tin system and ferric chloride-water system etc.

1 Zn-Mg system

Zn-Mg System is a two-component system and possesses a congruent melting point. The phase diagram of Zn-Mg system is shown in Fig. 2.3. In this system, the two components are zinc and magnesium, which melt at 419°C and 650°C respectively which are represented as point B and A in the phase diagram of the system. Both metals enter into chemical combination and form an intermetallic compound $MgZn_2$ and melts at 590°C to give a liquid of the same composition.

Hence, 590°C is the congruent melting point of the system.

In the reduced form, the system has the following four phases:

Solid magnesium, solid zinc, solid $MgZn_2$ and liquid solution of Zn and Mg.

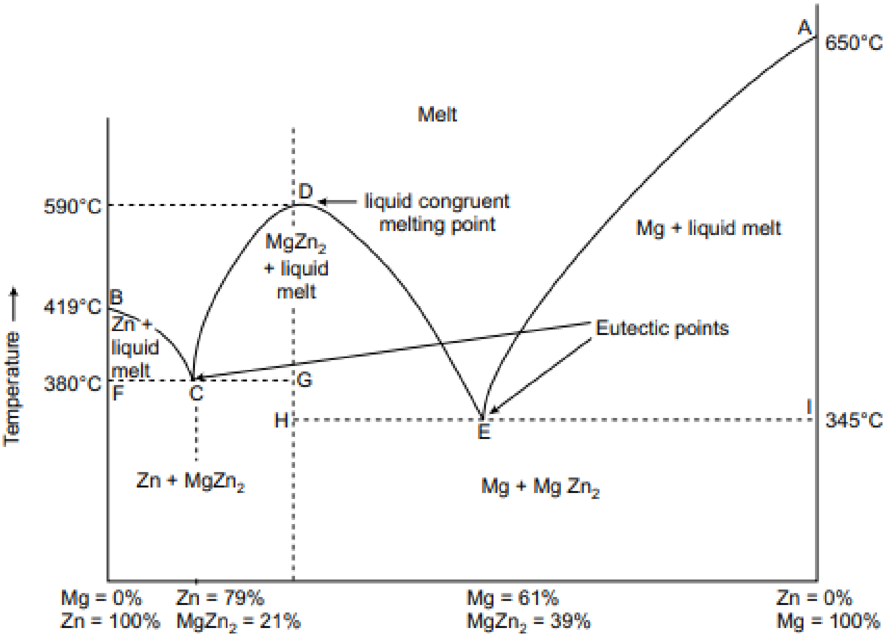


Fig. 2.3 Phase diagram of Zn-Mg system [Congruent melting point system]

On applying the reduced phase rule

$$F' = C - P + I = 1 - 2 + 1 = 0$$

Therefore, at point D constitutes a non-variant system.

(ii) Point E (Eutectic point): Point E represents the eutectic point of the system at a temperature of 345°C which is the least melting point of Mg-$MgZn_2$ system. Here, also three phases existing together in equilibrium at point E are solid Mg, solid $MgZn_2$ and liquid $MgZn_2$.

Hence, $C = 2$ and $P = 3$,

$F' = C - P + 1 = 2 - 3 + 1 = 0$ the system is non-variant.

(iii) Point C (Eutectic point): This point also represents the eutectic point (380°C) which is the least melting point of Zn-$MgZn_2$ system. At this point, the three phases—solid Zn, solid $MgZn_2$ and liquid $MgZn_2$ exist together in equilibrium. Therefore,

$$C = 2 \text{ and } P = 3$$

$$F' = C - P + l = 2 - 3 + 1 = 0$$

Hence, point C represents a non-variant system.

(c) Areas

The phase diagram of zinc-magnesium system consists of many areas. The area above the curve BCDEA constitutes a single phase system. The phase present in this area is a liquid melt consisting of a liquid solution of zinc and magnesium.

Hence C = 2 and P = 1,

$F' = C - P + 1 = 2 - 1 + 1 = 2$ that the system is bivariate.

Most of the other areas of the Zn-Mg system consist of two phases and they are univariate systems as represented in the phase diagram. These areas are explained in detail in table 2.3.

Table 2.3: Some salient features of the Zn-Mg system

Curve/ area/ point	Phases in equilibrium	No. of phase(P)	Degree of the freedom (F)
Curve BC (Freezing curve of Zn)	Zn & Melt (Containing Zn & $MgZn_2$)	02	01(Univariant)
Curve AE (Freezing curve of Mg)	Mg & Melt (Containing Zn & $MgZn_2$)	02	01(Univariant)
Curve CD	$MgZn_2$ & melt (Containing Mg & $MgZn_2$)	02	01(Univariant)
Curve DE	$MgZn_2$ & melt (Containing Zn & $MgZn_2$)	02	01(Univariant)
Curve CDE	$MgZn_2$ & melt	02	01(Univariant)
Area above BCDEA	Liquid (Melt of Zn, Mg & $MgZn_2$)	01	02(Bivariant)

Area BCF	Zn & Melt(Containing Zn & $MgZn_2$)	02	01(Univariant)
Area DCG	$MgZn_2$ & Melt(Containing Zn & $MgZn_2$)	02	01(Univariant)
Area DEH	$MgZn_2$ & Melt(Containing Mg & $MgZn_2$)	02	01(Univariant)
Area AEI	Mg & melt (containing Mg + $MgZn_2$)	02	01(Univariant)
Area below line FCG	Zn & $MgZn_2$ (both solid)	02	01(Univariant)
Area below line HEI	Mg & $MgZn_2$ (Both solid)	02	01(Univariant)
Point C (Eutectic)	Zn, $MgZn_2$ & Melt(Containing Zn & $MgZn_2$)	03	0(invariant)
Point E (Eutectic)	Mg, $MgZn_2$ & Melt(Containing Mg & $MgZn_2$)	03	0(invariant)

(C) Incongruent Melting Point System

There are several systems in which components combine together to form one or more compounds which are unstable and do not possess congruent melting points. A system (compound) is said to possess incongruent melting point, if on heating it decomposes much below its melting point and forms a new solid phase and a solution having different composition from the corresponding solid state. It has no sharp melting point. The decomposition at this temperature is known as transition or meritectic or peritectic rection and the temperature (the incongruent melting point) is known as transition or meritectic or peritectic temperature.

$$\text{Original solid} \rightleftharpoons \text{new solid} + \text{solution (melt)}$$

Examples: Following are some examples of the binary systems which possess incongruent melting point:

(i) Gold-antimony system

(ii) Sodium-bismuth system

(iii) Sodium-potassium system

(iv) Sodium sulphate-water system

(v) Potassium chloride-copper chloride system

Problem 1

The vapor pressure of a substance is 21 torr at 200 K. Calculate the vapor pressure at 310 K if the enthalpy of vaporization is 24 $kJ.mol^{-1}$.

Hint: $\Delta H = 24 \times 10^3$ $j.mol^{-1}$, $P_1 = 21$ torr, $T_1 = 300$ K and $T_2 = 310$

Solution 1

$$P_2 = P_1\, e^{-\Delta H_{vap}/R(1/T_2 - 1/T_1)}$$

$$P_2 = 21 \text{ torr} \times e^{-24000\ J.mol^{-1}/8.314\ J.K^{-1}.\ mol^{-1}(1/310\ K\ -\ 1/300\ K)}$$

$$P_2 = 28.6 \text{ torr}$$

Problem 2

The vapor pressure of a substance is 30 torr at 250 K. At what temperature will the substance have a vapor pressure of 150 torr? The enthalpy of vaporization is 45 $kJ.mol^{-1}$?

Hint: $\Delta H = 45 \times 10^3$ $j.mol^{-1}$, $P_1 = 30$ torr, $P_2 = 150$ torr $T_1 = 250$ K

Solution 2

$T_2 = [\ 1/T_1 - R \ln (p_2/p_1)/\Delta H_{vap}]^{-1}$

$T_2 = [1/250\ K - 8.314\ J.mol^{-1}.K^{-1} \ln (150\ torr/30\ torr)/\ 45 \times 10^3$

$J/mol^{-1}]^{-1}$ $T_2 = [4 \times 10^{-3} - 2.9737 \times 10^{-3}]^{-1}$

$T_2 = [3.7026 \times 10^{-3}\ K^{-}$

$^{1}]^{-1}$ $T_2 = 270.1$ K

Problem 3

A liquid has v. p. of 2.02×10^3 $N.m^{-2}$ at 293 K and heat of vaporization 41 $kJ.mol^{-1}$. The boiling point of liquid (in kelvin) is?

Hint: $\Delta H = 41 \times 10^3$ $j.mol^{-1}$, $P_2 = 2.02 \times 10^3$, $T_2 = 293$ K and $P_1 =$

Solution 2

$\log p_2/p_1 = \Delta H_{vap}/R\ (1/T_1 - 1/T_2)$

Problems about Clausius Clapeyron equation

$\log (2.02 \times 10^3)/(1.01 \times 10^5) = 41 \times 10^3/2.303 \times 8.314 \times (1/T_1 - 1/293)$

$-1.699 = 2.143 \times 10^3 (1/T_1 - 1/293)$

$-1.699/2.143 \times 10^3 = 1/T_1 - 1/293$

$-7.93 \times 10^{-4} = 1/T_1 - 1/293$

$1/T_1 = 2.62 \times 10^{-3}$

$T_1 = 381.7$ K

Example 1: For water at 0 °C, the standard volume of transition of ice to liquid is (−1.6 cm^3 mol^{-1}), and the corresponding standard entropy of transition is (+22 J K^{-1} mol^{-1}). Calculate the slope of the solid–liquid phase boundary at that temperature?

Solution: $\Delta_{trs}V = -1.6\ cm^3\ mol^{-1}$ and $\Delta_{trs}S = +\ 22\ J\ K^{-1}\ mol^{-1}$

$$\frac{dp}{dT} = \frac{\Delta_{trs}S_m}{\Delta_{trs}V_m}$$

وعند قلب المعادلة (أي تغيير البسط الى مقام والعكس صحيح) نحصل على التالي:

$$\frac{dT}{dp} = \frac{-1.6\ x\ 10^{-6}\ m^3 \cancel{mol^{-1}}}{22\ J\ K^{-1} \cancel{mol^{-1}}}$$

$$\frac{dT}{dp} = -7.3\ \frac{K}{J\ m^{-3}} = -\ 0.073\ x\ 10^{-8}\ K\ Pa^{-1}$$

$$bar\ =\ 10^5 Pa$$

$$\frac{dT}{dp} = -7.3\ x\ 10^{-\cancel{8}}\ K\ \cancel{10^5}\ bar^{-1}$$

$$\frac{dT}{dp} = -7.3\ x\ 10^{-3}\ K\ bar^{-1}\ =\ -7.3\ mK\ bar^{-1}$$

ملاحظة: النتيجة أعلاه تبين أنَّ الزيادة في الضغط بمقدار 100 bar يؤدي إلى انخفاض درجة انجماد الماء بمقدار 0.73 K.

Example 2: What is the expected boiling point of water at 98.7 kPa (approximately 740 torr, a typical barometric pressure at 275 m altitude)? The heat of vaporization is 2258 J g^{-1}, the molar volume of liquid water is 18.87 cm^3 mol^{-1}, and the molar volume of steam is 30.199 dm3.mole^{-1}, all values referring to 373.15 K and 101.325 kPa (1 atm).

Solution: $\Delta_{vap}H$ = 2258 J g-1, $V_m(l)$ = 18.87 cm3 mol-1, $V_m(g)$ = 30.199 dm^3 mol^{-1}, T = 373.15 K and p = 101.325 kPa (1 atm).

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T_b[V_m(v) - V_m(l)]} \qquad (1\text{-}20)$$

$$\frac{dp}{dT} = \frac{2258\,(J\,\cancel{g^{-1}})\ x\ 18(\cancel{g}\ \cancel{mol^{-1}})}{373.15\,K\,[30.199\,(dm^3\cancel{mol^{-1}}) - 0.019\,(dm^3\cancel{mol^{-1}})]}$$

$$\frac{dp}{dT} = 3.611\,J\,K^{-1}\,dm^{-3} = 3.611\ x\ 10^3\ J\,m^{-3}K^{-1}$$

$$\frac{dp}{dT} = 3.611\ x\ 10^3 K^{-1}Pa$$

For a decrease of **101.325 kPa –98.7 kPa = 2.625 kPa**, there is a decrease in temperature of **2.77 x 10-4 K Pa^{-1} x 2625 Pa = 0.73 K**.

Therefore, the new boiling point is **373.15 K – 0.73 K = 372.42 K**.

Example 3: What is the rate of change per pascal in the boiling point of water at a 100 °C in atmospheric pressure? The enthalpy of vaporization is 40.69 kJ mol^{-1}, the molar volume of liquid water is 0.019 x 10^{-3} m^3 mol^{-1}, and the molar volume of steam is 30.199 x 10^{-3} m^3 mole^{-1}. All values are given at 100 °C, and 1.01325 bar.

Solution: $\Delta_{vap}H$ = 40.69 kJ mol-1, Vm(l) = 0.019 x 10^{-3} m^3 mol^{-1}, Vm(g) = 30.199 x 10^{-3} m^3 mol^{-1}, T = 373.15 K

$$\frac{dp}{dT} = \frac{\Delta_{vap}H}{T_b[V_m(v) - V_m(l)]}$$

$$\frac{dp}{dT} = \frac{40.69\ x\ 10^3\ (J\ \cancel{mol^{-1}})}{373.15\ K\ [30.199\ x\ 10^{-3}\ (m^3\cancel{mol^{-1}})\ - 0.019\ x\ 10^{-3}\ (m^3\cancel{mol^{-1}})]}$$

$$\frac{dp}{dT} = 3613\ K^{-1}Pa$$

$$\frac{dT}{dp} = \frac{1}{3613\ K^{-1}Pa} = 2.76\ x\ 10^{-4} K\ Pa^{-1}$$

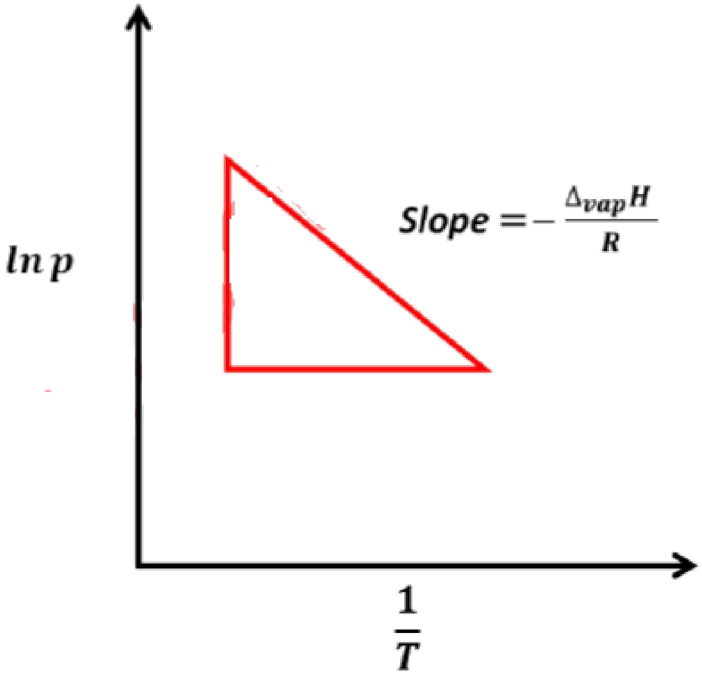
Example 4: Water has $\Delta_{vap}H$ = 41 kJ mol^{-1} vapour pressure at 373 K is 101.325 kPa. What is the vapour pressure at 298 K?

Solution: $\Delta_{vap}H$ = 41 kJ mol-1, Ti = 373.15 K, T2 = 298.15 K,

pi = 101.325 kPa and pf =?

ولغرض رسم معادلة كلاوسيوس- كلابيرون نفترض ان المعادلة خطية من الدرجة الأولى وكما هو موضح في المعادلة والشكل الاتي:

$$\ln p = -\frac{\Delta_{vap}H}{RT} + C \tag{1-28}$$



A. Objective types questions:

1. The degree of freedom at a triple point unary diagram for water ____________

(a) 0 (b) 1 (c) 2 (c) 3

2. Following is wrong about the phase diagram

(a) It gives information on transformation rate.

(b) Relative amount of different phases can be found under given equilibrium conditions.

(c) It indicates the temperature at which the different phases start to melt.

(d) Solid solubility limits are depicted by it.

3. Pick the odd one of the following:

(a) Isomorphous alloy (b) Terminal Solid Solution

(c) Intermediate Solid Solution (d) Compound

4. The boundary line between (Liquid + Solid) and (Solid) regions must be part of _____

(a) Solvus (b) Solidus (c) Liquidus (d) Tie- Line

5. An invariant reaction that produces a solid up on cooling two liquids:

(a) Eutectic (b) Peritectic (c) Monotechtic (d) Syntectic

6. A Liquid Phase produces two solid phases during _________ reaction up on cooling.

(a) Eutectic (b) Eutectoid (c) Peritectic (d) Peritectoid

7. On heating one solid phase results in another solid phase plus one liquid phase during

----------- Reaction.

(a)Eutectic (b) Peritectic (c) Monotechtic (d) Syntectic

8. In a one component system the maximum number of phases that can co-exists in

Equilibrium is:

(a) 1 (b) 2 (c) 3 (d) 4

9. In terms of number of phases (P), components (C) and degrees of Freedom (F), the

Phase rule is expressed as:

(a) P + C = F + 2 (b) F= P + C – 2

(c) P + F = C + 2 (d) P- F = C + 2

10. In the phase diagram of the benzene- naphthalene system, the point C is called the:

(a) Eutectic Point (b) Congruent Point (c) Triple Point (d) Critical Point.

11. Lowest temperature is reached by using:

(a) $CaCl_{22}H_{2O}$ (b) Acetone with dry ice (c) NH_4Cl (d) Ether + Dry Ice

12. A compound with an incongruent melting point decomposes on heating into:

(a) A liquid of the same composition as the solid.

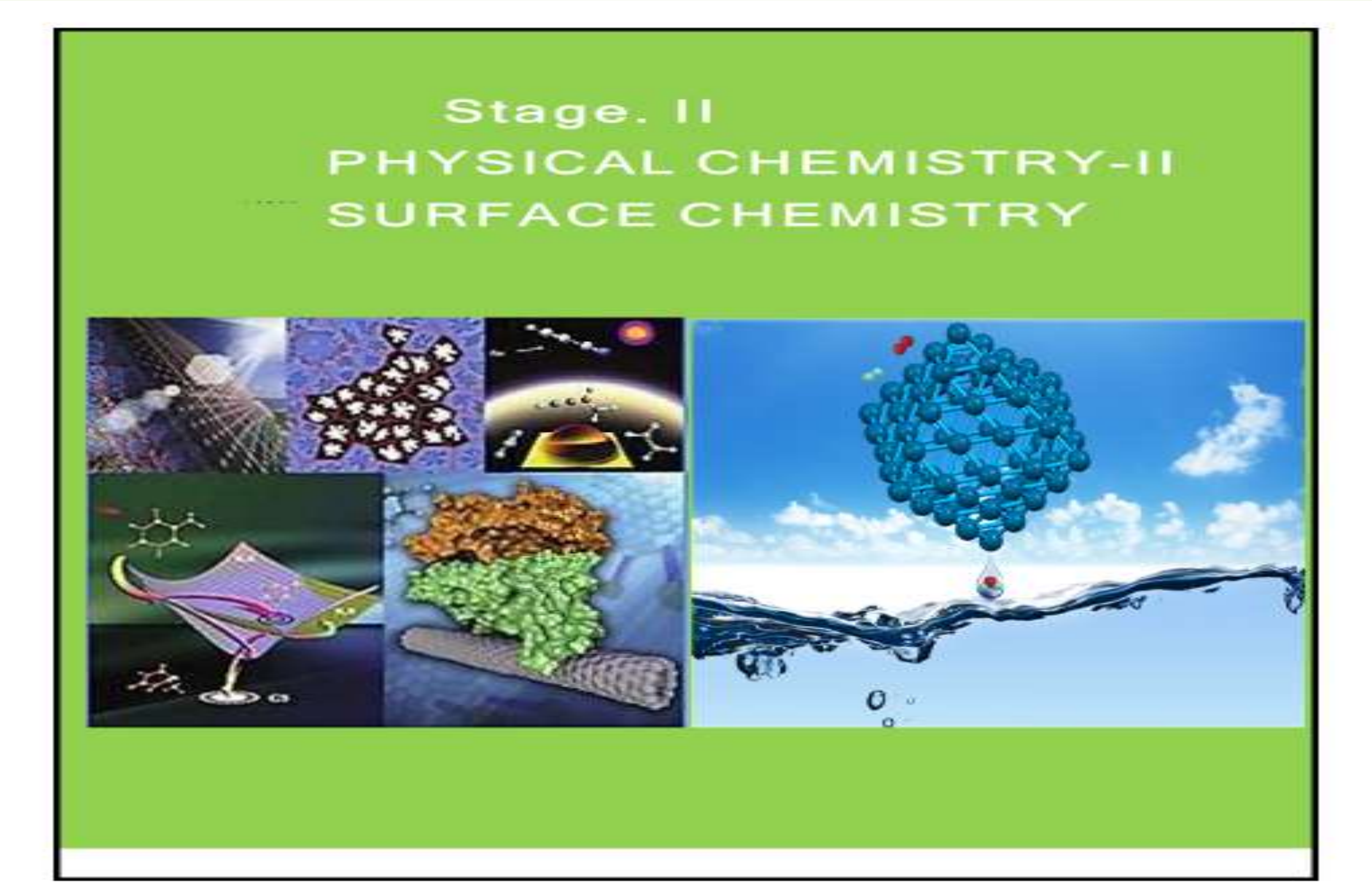
(b) A new solid phase and a solution with a composition different from that of the solid Phase.

(c) A new and a solution with the same composition as that of the solid Phase.

(d) A solution of fixed composition.

B. Short Answer Questions:

1. Define the terms :- Phase, Components and degree of freedom



Stage. II

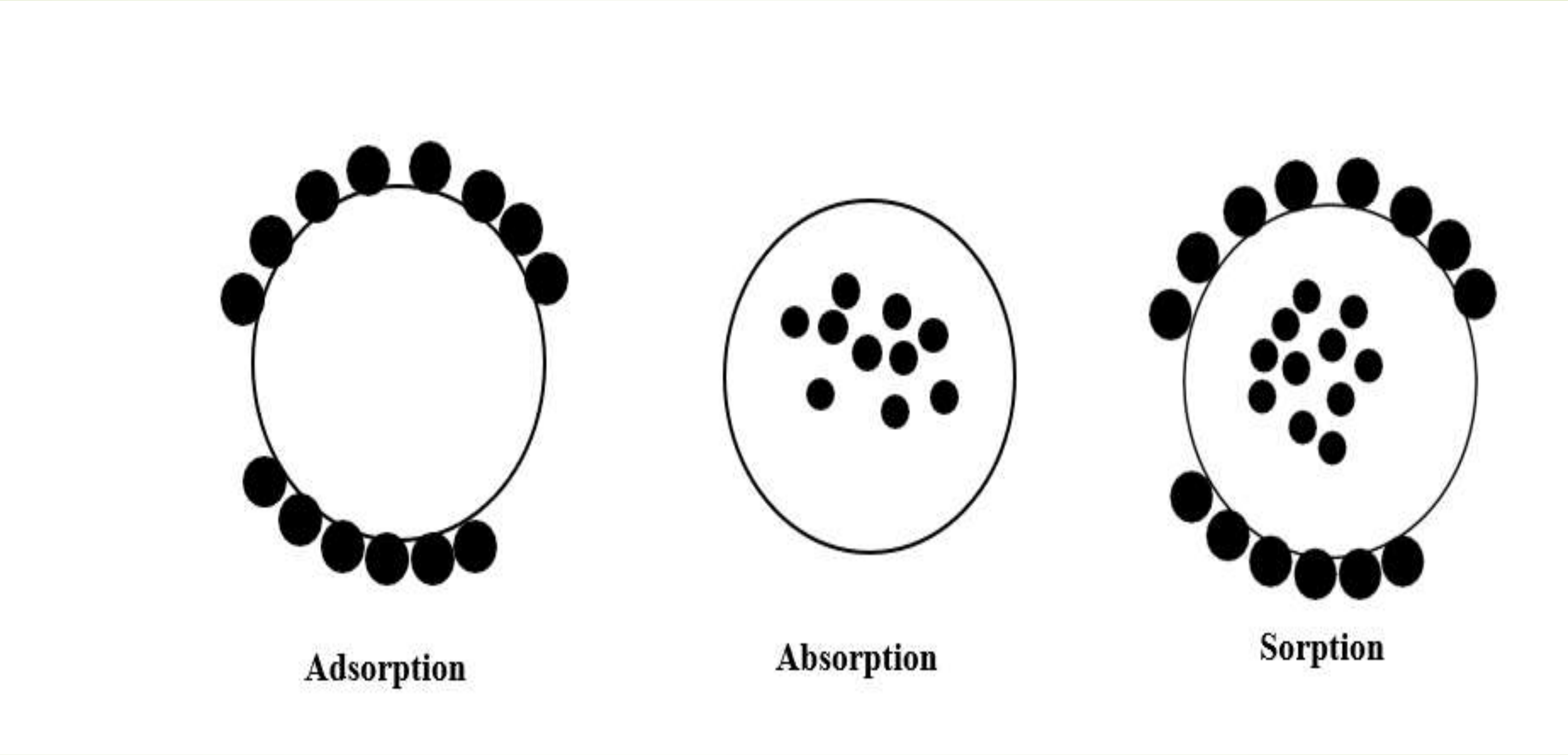
PHYSICAL CHEMISTRY-II
SURFACE CHEMISTRY

INTRODUCTION

Surface chemistry is the branch of Physical Chemistry that occurs at the surfaces or interfaces. The interface or surface is represented by separating the bulk phases by a hyphen or a slash. For example, the interface between a solid and a gas may be represented by solid-gas or solid/gas. Due to complete miscibility, there is no interface between the gases. The bulk phases that we come across in surface chemistry may be pure compounds or solutions. The interface is normally a few molecules thick but its area depends on the size of the particles of bulk phases. Many important phenomena, noticeable amongst these being corrosion, electrode processes, heterogeneous catalysis, dissolution and crystallization occur at interfaces. The subject of surface chemistry finds many applications in industry, analytical work and daily life situations.

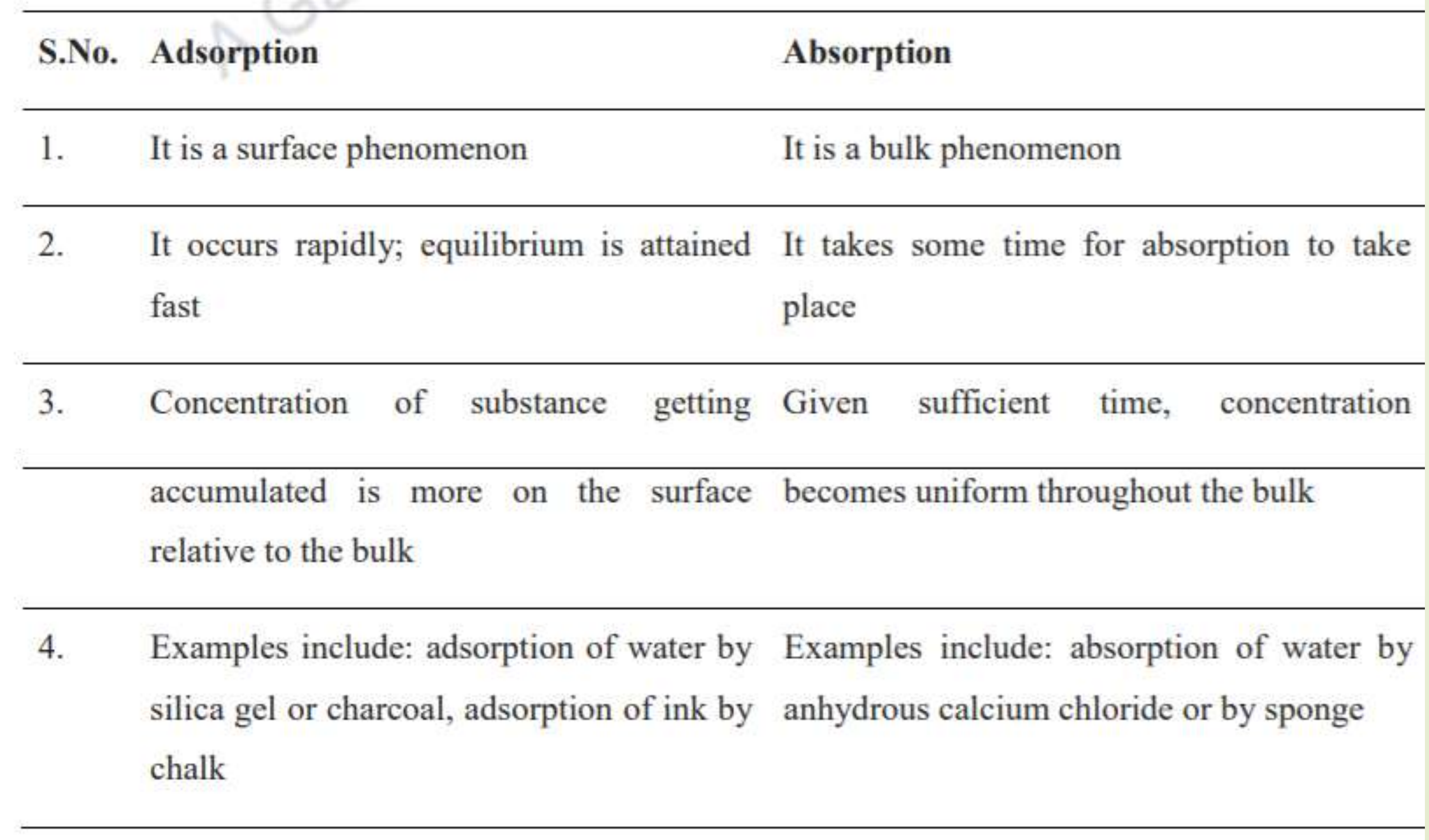
SOME COMMON TERMS USED IN SURFACE CHEMISTRY

1. **Adsorption:** As like to the liquid surface, there occur certain unbalance residual forces at the surface molecules of the solid substances. Thus the tendency of the surface molecules of the solid substances to attract the molecules of the other substances at the surface to minimize the unbalanced residual forces is known as adsorption phenomena. Example : When the gases like NH_3, Cl_2, SO_2 etc. comes in the contact of charcoal then there occurs the adsorption of the gases at the charcoal surface.
2. **Absorption:** The process of attracting the molecules of the other substance in the inner bulk is known as absorption phenomena. Example: When the NH_3ngas comes in the contact of H_2O then the NH_3 is absorbed by the H_2O to form the NH_4OH.
3. **Sorption:** When both the adsorption and absorption phenomena take simultaneously, than such type of the process is known as sorption. Representation of the adsorption, absorption and sorption process can be given as:


Adsorption
Absorption
Sorption

Adsorption and Absorption

Differences between adsorption and absorption



S.No.	Adsorption	Absorption
1.	It is a surface phenomenon	It is a bulk phenomenon
2.	It occurs rapidly; equilibrium is attained fast	It takes some time for absorption to take place
3.	Concentration of substance getting accumulated is more on the surface relative to the bulk	Given sufficient time, concentration becomes uniform throughout the bulk
4.	Examples include: adsorption of water by silica gel or charcoal, adsorption of ink by chalk	Examples include: absorption of water by anhydrous calcium chloride or by sponge

In the adsorption phenomena two types of the species are involved:

A. **Adsorbent:** That substance which attracts the molecules of the other substance at its own surface will be called as adsorbent. **Generally** solid substance can be used as a adsorbent in the adsorption phenomena.

B. **Adsorbate:** That substances of which molecule are adsorbed at the surface of the adsorbent will be called as adsorbate.

Mostly gaseous molecule can behave as an adsorbate in the adsorption phenomena.

TYPES OF ADSORPTION

Depending on the force of attraction between the adsorbate and adsorbent surface the adsorption can be divided in to two different types, which are given below:

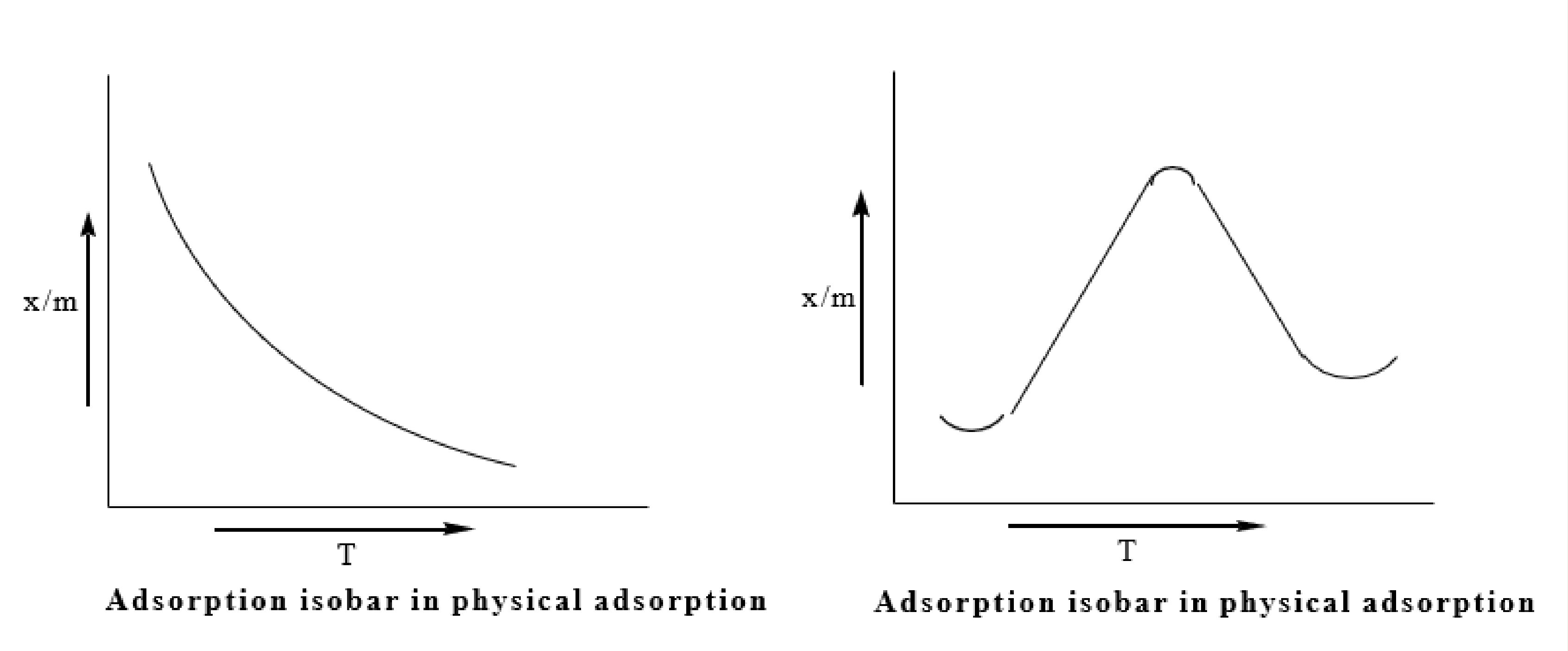
1. **Physical adsorption:** Such type of the adsorption phenomena in which there occur a weak Van der Waal attraction force between adsorbate and adsorbent surface is known as physical adsorption.
2. **Chemical adsorption:** Such type of the adsorption phenomena in which there occur a strong chemical bonding between the adsorbate and adsorbent surface is known as chemical adsorption.

DIFFERENCE BETWEEN THE PHYSICAL AND CHEMICAL ADSORPTION

Properties	**Physical adsorption**	**Chemical adsorption**
Specificity	Physical adsorption does not having the specificity	Chemical adsorption has specificity
Force of attraction	In the physical adsorption there occur weak Vander waal force of attraction between the adsorbate and adsorbent	In the chemical adsorption there occur strong chemical bonding between the adsorbate and adsorbent.
Enthalpy of adsorption	In the physical adsorption there occur very low enthalpy of adsorption(4-40KJ/mol)	In the chemical adsorption there occurs very high enthalpy of adsorption (40-400KJ/mol).
Activation energy	Physical adsorption required negligible activation energy value.	Chemical adsorption requires certain activation energy value.
Reversibility	Due to the weak Van der waal force of attraction between the adsorbate and adsorbent, the physical adsorption having reversible nature	Due to the stronger chemical bonding between the adsorbate and adsorbent the chemical adsorption having irreversible nature.
Effect of temperature	With the increase in the temperature, the extent of physical adsorption is decreases	With the increase in the temperature, the extent of chemical adsorption is initially

ADSORPTION ISOBAR

At a constant pressure the graph plotted between the x/m (extent of adsorption) and temperature T or (the amount of the gas adsorbed per gram of the adsorbent (x/m)) is known as adsorption isobar. For the physical and chemical adsorption, the adsorption isobar can be represented as:



Adsorption isobar in physical adsorption

Adsorption isobar in physical adsorption

Where χ = Amount of the adsorbate at the adsorbent or m = Surface mass of the adsorbent.

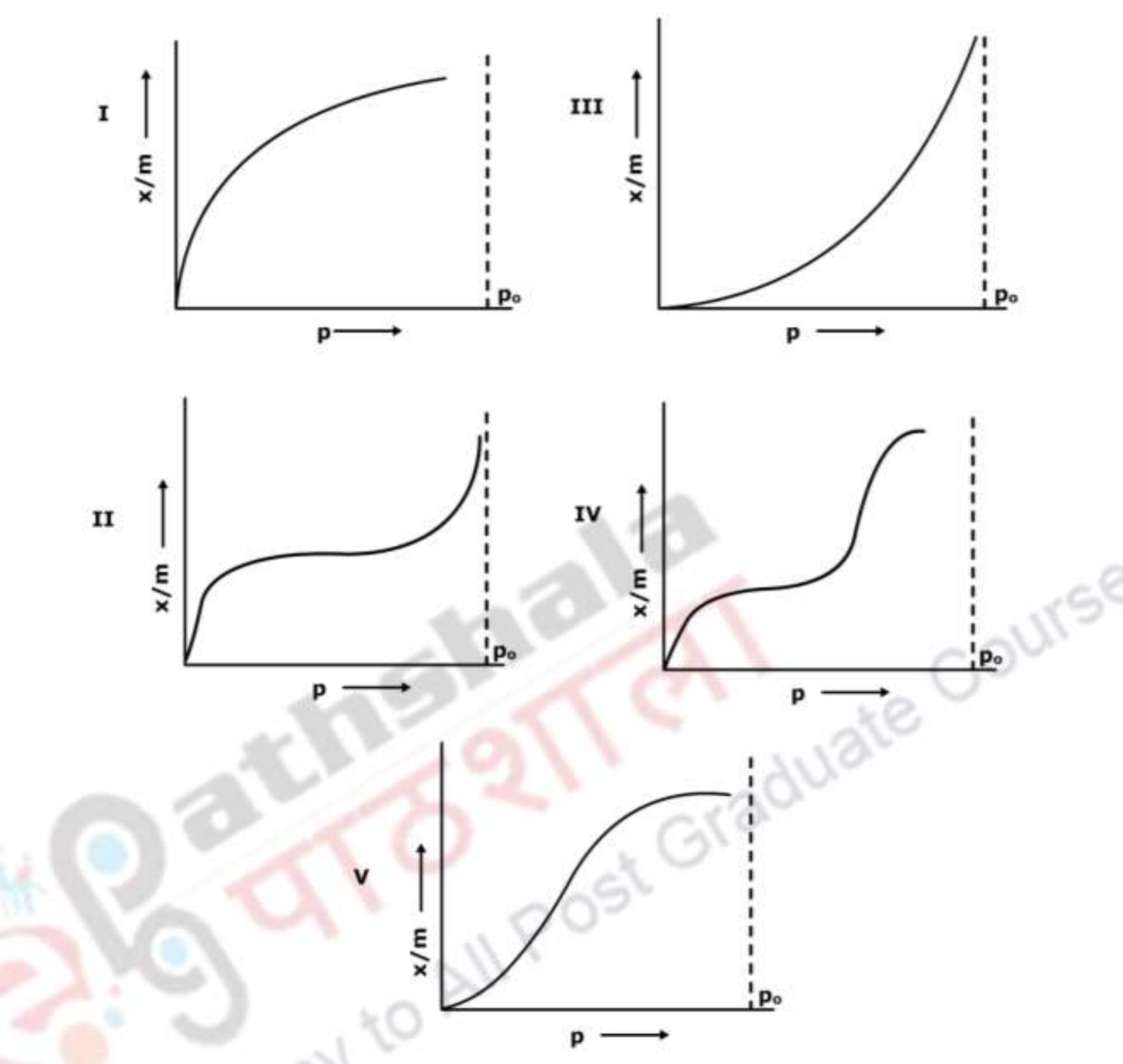
ADSORPTION ISOTHERM

At the constant temperature the graph plotted between the extents of adsorption (x/m) and pressure (P) is known as adsorption isotherm.

There are some different types of the adsorption isotherm which can be defined as:

- Type I: This type of behaviour is shown by gases in which, the extent of adsorption initially increases with the increase in pressure, and thereafter approaches a saturation limit, much before the saturation pressure is reached.
- Type II: This type of behaviour is similar to type I adsorption isotherm, where the extent of adsorption increases with the increase in pressure till the monolayer formation is complete. After the monolayer formation, multilayer adsorption starts which increases with increase in the pressure. This type of behaviour can be explained by van der waals forces operating between the consecutive layers
- Type III: This type of behaviour occurs when multilayer adsorption starts even before the monolayer formation is complete
- Type IV: This is the duplication of type II adsorption isotherm. First the monolayer formation starts, then it completes, and then the multilayer formation starts and thereafter it gets completed
- Type V: This behaviour is erratic and does not fall in any category, and therefore is separately classified as type V adsorption isotherm.

Five main categories of adsorption isotherms showing the amount of gas (x) adsorbed on a definite mass of adsorbent (m); p0 is the saturation pressure



Criteria of Adsorption

- We all know that adsorption is a spontaneous process. Thus, the free energy change of the system (ΔG) is negative. When the adsorbate is adsorbed onto a surface, the translational freedom of the latter gets reduced, making entropy change for the adsorption process a negative quantity. This makes the enthalpy change negative for adsorption, with the condition that $|\Delta H| > |T\Delta S|$.
- Thus, the adsorption process is exothermic in nature. This can also be explained by the fact that adsorption process involves attraction between the adsorbate and adsorbent molecules and there occurs a decrease in the residual forces acting along the surface of the adsorbent. Consequently, there occurs a decrease in the surface energy, which appears as heat. The amount of heat evolved when one mole of gas or vapour is adsorbed on a solid is called as molar enthalpy of adsorption. As adsorption proceeds, this molar enthalpy of adsorption of the adsorbate goes on decreasing, becoming less and less negative, and ultimately becoming equal to TΔS, when ΔG becomes equal to zero. At this state, the system attains equilibrium.
- There are certain exceptions to the fact that enthalpy change for the adsorption process is always negative. This occurs when dissociation of the adsorbate takes place and the latter has high translational mobility on the surface. Example includes endothermic adsorption of hydrogen gas on the glass surface. Hydrogen molecules dissociate into atoms on the glass surface, where they move freely. This is accompanied by a large increase in the translational entropy, which is sufficient to overcome the small positive enthalpy change.