

PC-1(A): PHASE EQUILIBRIUM: SYNOPSIS

1 **PHASE (P)**-Physically distinct and mechanically separable

2 **COMPONENTS (C)**

Number of chemically independent chemical constituents by means of which the composition of each phase can be expressed. It is the number of **chemical constituents** –number of **relationships** among them

$\text{Ar} = \text{One component}$

$\text{Ar} + \text{Ne} = \text{Two components}$

$\text{N}_2 + \text{H}_2 + \text{NH}_3 = \text{Three components}$

$\text{N}_2 + \text{H}_2 + \text{NH}_3 (773\text{K}) = \text{Two components}$

$\text{A} + \text{B} + \text{C} = \text{Three components}$

$\text{A} + \text{B} + \text{C} ; \text{B} = \text{C} = \text{Two components}$

$\text{N}_2 + \text{H}_2 \rightleftharpoons \text{NH}_3 = \text{Two components} (3-1=2)$; one chemical relation

$\text{CaCO}_3 + \text{CaO} + \text{CO}_2$ at room temperature, three components

$\text{CaCO}_3 + \text{CaO} + \text{CO}_2$ at high temperature, two components

$\text{CaCO}_3 \rightleftharpoons \text{CaO} + \text{CO}_2$ at high temperature, two components $(3-1=2)$

3 **DEGREES OF FREEDOM (F)**: *It is the minimum number of variables like p, T & concentration that must be specified to understand the system completely.*

4 **GIBB'S PHASE RULE, $F = C - P + 2$**

5 **DERIVATION OF THE PHASE RULE.**

All components are distributed in all the phases

Equations:-

$\mu_1(1) = \mu_2(1) = \mu_3(1) = \mu_4(1) \dots\dots = \mu_p(1)$ for the first component

(P-1) equations for each component in a phase

Total equations = **C(P-1)** for all the components in all the phases

Variables:-

Concentration variable for each phase = C-1

Total number of concentration variable for all the phases = P(C-1)

The physical variables = 2 (p & T)

Total number of variables for the system = **P(C-1) + 2**

F = "No of Variables-No of Equations" = P(C-1) + 2 - C (P-1) = C-P + 2

$$F = C - P + 1 \text{ (Reduced Phase rule for two component system)}$$

$$F = C - P \text{ (Reduced Phase rule for three component system)}$$

6 CLAPEYRON EQUATION

$$dG = Vdp - SdT = 0 \text{ for eq process}$$

$$dp/dT = \Delta S / \Delta V = \Delta H / T \Delta V \text{ for any system.}$$

Application to ice water equilibrium

$$\Delta V = V_{\text{water}} - V_{\text{ice}} = -ve$$

$$\Delta H = +ve$$

Hence, $dT/dp = T \Delta V / \Delta H = -ve$ *m.p decreases with pressure*

7 CLAUSIUS-CLAPEYRON EQUATION

$$\Delta V = V_g = RT/p \text{ (For phase eq like L-V, S-V)}$$

$$dp/dT = \Delta H / T \Delta V \text{ for any system}$$

$$\text{Hence, } d(\ln p)/dT = \Delta H_v / RT^2$$

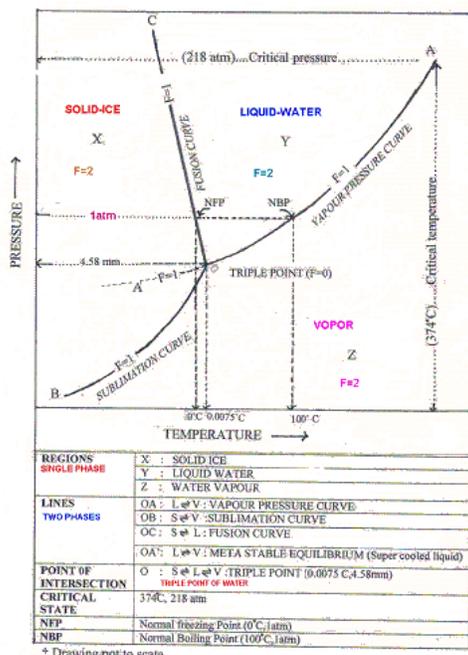
$$\ln p = -\Delta H_v / RT + \text{const}$$

8 APPLICATIONS TO EQUILIBRIUM (S-L, \rightleftharpoons L-V, S-V)

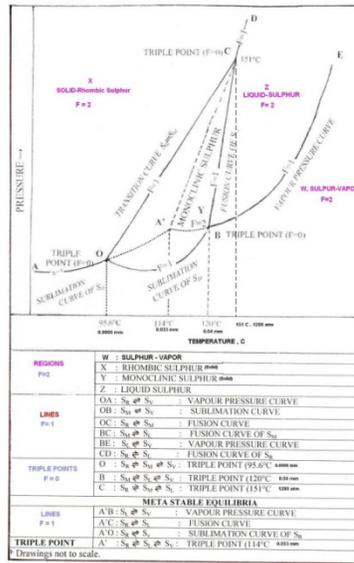
Determination of

ΔH_v by the plot of $\ln p$ vs $1/T$

9 ONE-COMPONENT SYSTEMS: Water system.



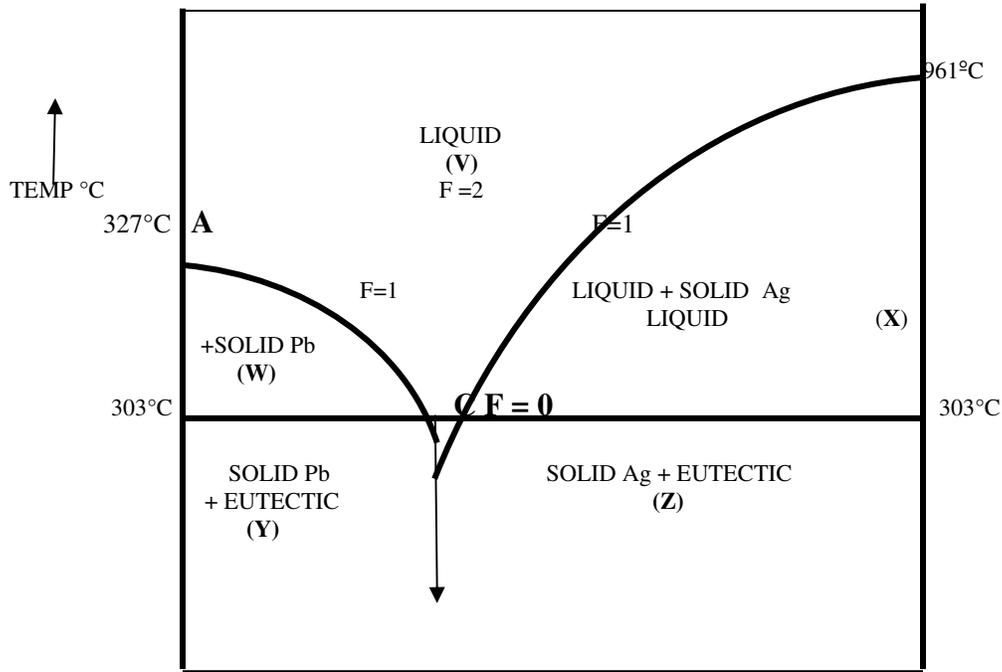
Sulphur system



10 TWO COMPONENT SYSTEMS: $F = C - P + 1$ (Reduced Phase rule for two component system)

(i) Simple eutectic: **Lead-silver system.**

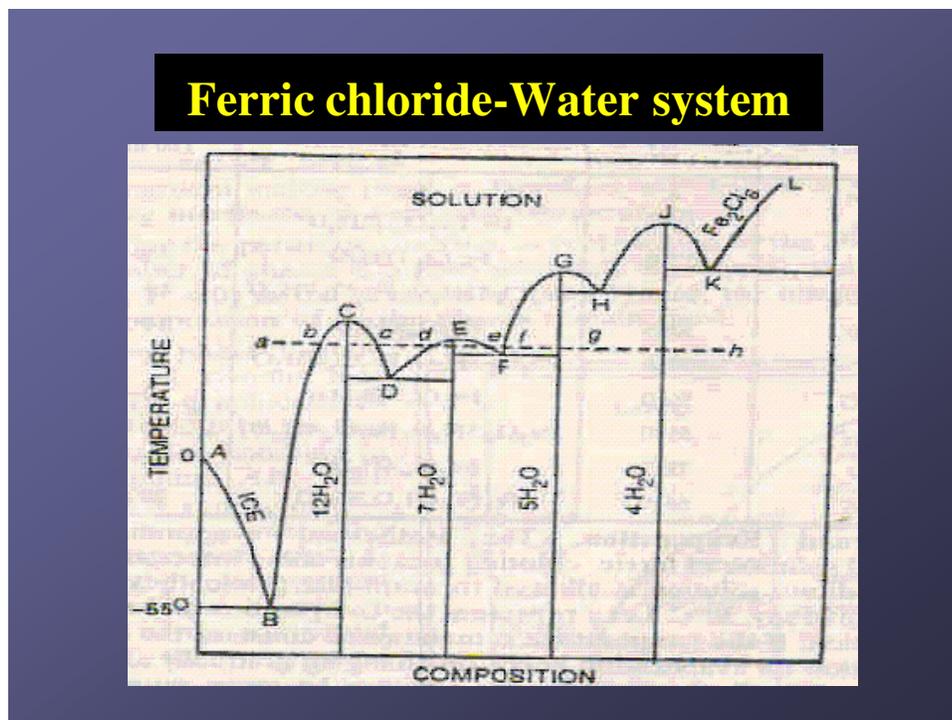
Pb - Ag SYSTEM



$F = C - P + 1$ (Reduced Phase rule)

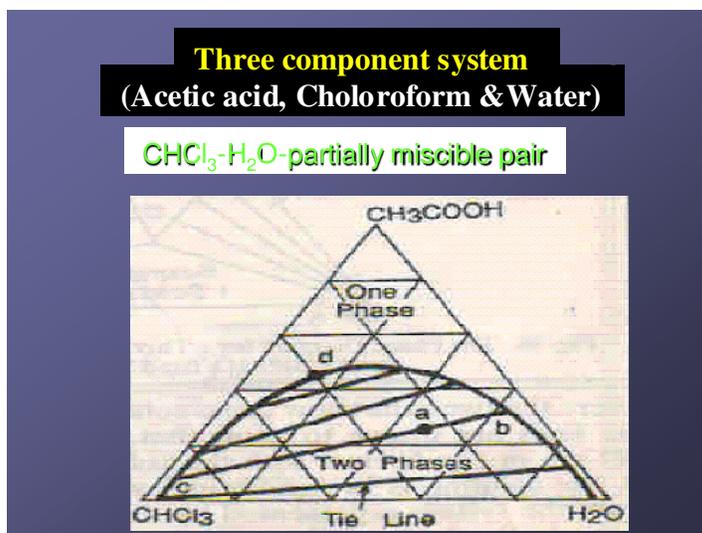
REGIONS	V : Liquid	F = 2
	W : Liquid + Solid Pb	F = 2
	X : Liquid + Solid Ag	F = 2
	Y : Solid Pb + Eutectic	F = 2
	Z : Solid Ag + Eutectic	F = 2
CURVES	AC : Freezing Point Curve of Lead : $Pb_{(l)} \rightleftharpoons Pb_{(s)}$	F = 1
	BC : Freezing Point Curve of Silver : $Ag_{(l)} \rightleftharpoons Ag_{(s)}$	F = 1
POINTS	A :Melting point of pure lead (327°C)	F = 0
	B :Melting point of pure silver (961°)	F = 0
	C :Eutectic Point (2.6% Ag & 303°C)	F = 0

(ii) Formation of compound with congruent m.pt: **Ferric chloride – water system.**



POSITIONS	PHASE (S) at Equilibrium	C	P	Temp	F
A	Ice _(s)	1	2	0°C	0
Curve-AB	Ice _(s) + Solution of Fe ₂ Cl ₆	2	2		1
B	Ice _(s) + Solution of Fe ₂ Cl ₆ + Fe ₂ Cl ₆ .12H ₂ O _(s)	2	3	-55°C	0
Curve-BC	Solution of Fe ₂ Cl ₆ + Fe ₂ Cl ₆ .12H ₂ O _(s)	2	2		1
C	Fe ₂ Cl ₆ .12H ₂ O _(s) + Solution of Fe ₂ Cl ₆	1	2	37°C	0
Curve-CD	Fe ₂ Cl ₆ .12H ₂ O _(s) + Solution of Fe ₂ Cl ₆	2	2		1
D	Fe ₂ Cl ₆ .12H ₂ O _(s) + Solution of Fe ₂ Cl ₆ + Fe ₂ Cl ₆ .7H ₂ O _(s)	2	3	26°C	0
Curve-DE	Solution of Fe ₂ Cl ₆ + Fe ₂ Cl ₆ .7H ₂ O _(s)	2	2		1
E	Fe ₂ Cl ₆ .7H ₂ O _(s) + Solution of Fe ₂ Cl ₆	1	2	32.5°C	0
Curve-EF	Fe ₂ Cl ₆ .7H ₂ O _(s) + Solution of Fe ₂ Cl ₆	2	2		1
F	Fe ₂ Cl ₆ .7H ₂ O _(s) + Solution of Fe ₂ Cl ₆ + Fe ₂ Cl ₆ .5H ₂ O _(s)	2	3	30°C	0
Curve-FG	Solution of Fe ₂ Cl ₆ + Fe ₂ Cl ₆ .5H ₂ O _(s)	2	2		1
G	Fe ₂ Cl ₆ .5H ₂ O _(s) + Solution of Fe ₂ Cl ₆	1	2	56°C	0
Curve- GH	Fe ₂ Cl ₆ .5H ₂ O _(s) + Solution of Fe ₂ Cl ₆	2	2		1
H	Fe ₂ Cl ₆ .5H ₂ O _(s) + Solution of Fe ₂ Cl ₆ + Fe ₂ Cl ₆ .4H ₂ O _(s)	2	3	55°C	0
Curve-HJ	Solution of Fe ₂ Cl ₆ + Fe ₂ Cl ₆ .4H ₂ O _(s)	2	2		1
J	Fe ₂ Cl ₆ .4H ₂ O _(s) + Solution of Fe ₂ Cl ₆	1	2	73.5°C	0
Curve-JK	Fe ₂ Cl ₆ .4H ₂ O _(s) + Solution of Fe ₂ Cl ₆	2	2		1
K	Fe ₂ Cl ₆ .4H ₂ O _(s) + Solution of Fe ₂ Cl ₆ + Fe ₂ Cl _{6(s)}	2	3	66°C	0
Curve- KL	Solution of Fe ₂ Cl ₆ + Fe ₂ Cl _{6(s)}	2	2		1

11 THREE COMPONENT SYSTEMS: F = C-P (Reduced Phase rule for three component system)



Three component systems having one partially miscible pairs.

12 FORMATION OF COMPOUND WITH INCONGRUENT MELTING POINT. (*Peritectic Change*): NaCl-H₂O System ; Na₂SO₄ - H₂O (Na₂SO₄ .10H₂O , 7H₂O , 4H₂O- Application to freeing mixture.

SOLUTIONS

1 **IDEAL SOLUTIONS:** (*Vapor pressure- Composition diagram*).

Follows Raoult's Law.

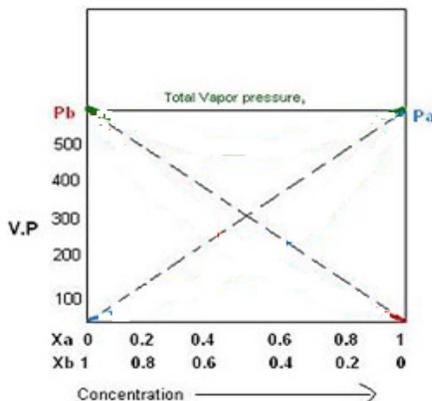


Fig-1: Ideal behavior (Type-I)

Examples (**Type-I**):

- (i) Benzene-Toluene ; (ii) Benzene-Xylene ; (iii) n-Hexane-n-Heptane

2 **REAL SOLUTIONS:** (*Vapor pressure-Composition diagram*).

(a) **Positive deviations from Raoult's law-(Type-II)**

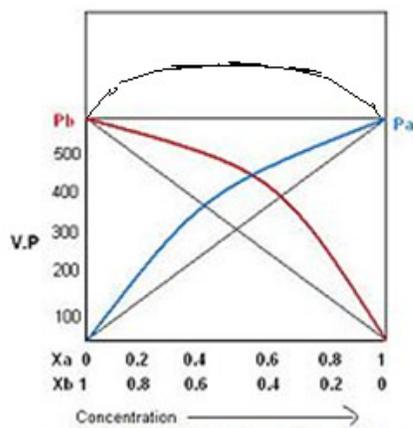


Fig-2: Positive deviation from ideal behavior (Type-II)

The **adhesive** forces between unlike molecules are **weaker** than the cohesive forces, between like molecules. This will lead both components to escape solution more easily.

Examples for Positive Deviation (Minimum BP) (Type-II)

(i) $\text{H}_2\text{O}-\text{CHCl}_3$; (ii) $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$; (iii) $\text{C}_2\text{H}_5\text{OH}-\text{CHCl}_3$

(b) Negative deviations from Raoult's law. (Type-III)

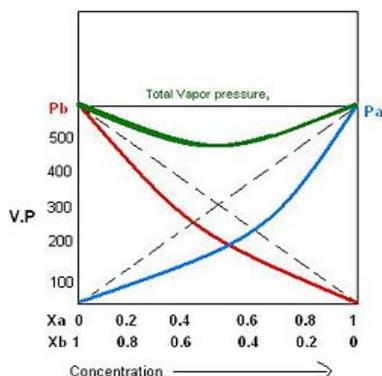


Fig-3: Negative deviation from ideal behavior (Type-III)

The **adhesive** forces between molecules of A & B are **stronger** than the cohesive forces between A & A or B & B. The vapor pressure of the solution is less than the expected vapor pressure from Raoult's law.

Examples for Negative Deviation: (Maximum BP) (Type-III)

(i) $\text{CHCl}_3-\text{CH}_3\text{COCH}_3$; (ii) $\text{CHCl}_3-\text{CH}_3\text{COOCH}_3$; (iii) $\text{H}_2\text{O}-\text{HCl}$

3 IDEAL & REAL SOLUTIONS:(v.p -Composition diagram).- A comparison

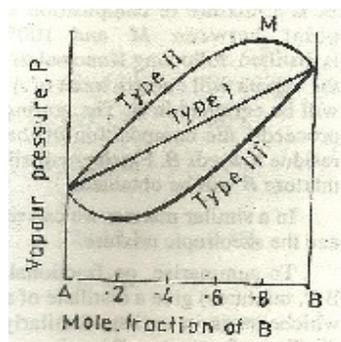


Fig-4: Ideal (I), Positive (II) & Negative (III) Deviations (Types-I, II & III)

4 **FRACTIONAL DISTILLATION** (Binary systems)-**IDEAL SOLUTION: Type-I**

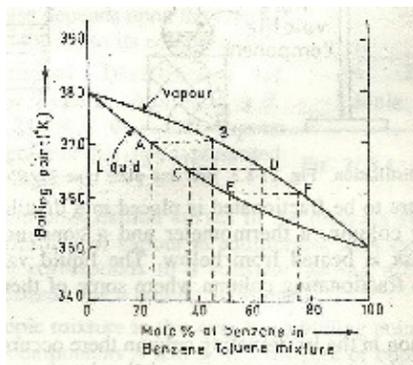


Fig-5: Distillation of Ideal Solution (Type-I)

- The composition of **VAPOR (distillate)** Tends to **Pure A or B (Low bp)**
- The composition of **LIQUID (residue)** Tends to **Pure A or B (High bp)**

5 **BP-COMPOSITION** (Azeotropic distillation)- **(Min bp)-Positive Deviation- Type-II**

- (i) $\text{H}_2\text{O}(373 \text{ K})\text{-CHCl}_3(334 \text{ K})$; Azeotrope (329 K , 2. 8% H_2O)
- (ii) $\text{H}_2\text{O}(373 \text{ K})\text{-C}_2\text{H}_5\text{OH}(351.3 \text{ K})$; Azeotrope (351.2 K , 4% H_2O)
- (iii) $\text{CHCl}_3(334 \text{ K})\text{-CH}_3\text{OH} (337.7 \text{ K})$; Azeotrope (326 K , 87.4% CHCl_3)

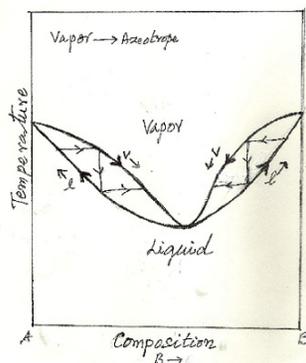


Fig-6: Distillation of Solution showing Positive Deviation (Type-II)

- The composition of **VAPOR (distillate)** Tends to **Azeotrope**
- The composition of **LIQUID (residue)** Tends to **Pure A or B**

6 **BP-COMPOSITION**(Azeotropic distillation)- (Max bp)-Negative Deviation- Type-III

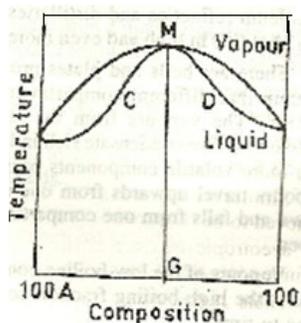


Fig-7: Distillation of Solution showing Negative Deviation (Type-III)

- The composition of **VAPOR (distillate)** Tends to **Pure A or B**
- The composition of **LIQUID (residue)** Tends to **Azeotrope**

Example:

- (i) CHCl_3 (334 K) - CH_3COCH_3 (330 K) ; **Azeotrope** (338K , 80% CHCl_3)
- (ii) CHCl_3 (334 K)- $\text{CH}_3\text{COOCH}_3$ (330 K) ; **Azeotrope** (338K , 77% CHCl_3)

NB: (i) Azeotrope is a mixture

(ii) It is standard solution

(iii) It can be further purified by some other methods

7 **Steam** distillation.

$$P_1 + P_w = \text{Atmospheric pressure}$$

Requirements for Steam distillation: Immiscible & No reaction with water

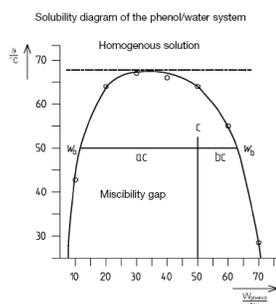
Examples: Aniline, Benaldehyde, nitrobenzene

Advantage(s) of steam distillation: Boiling at low b.p

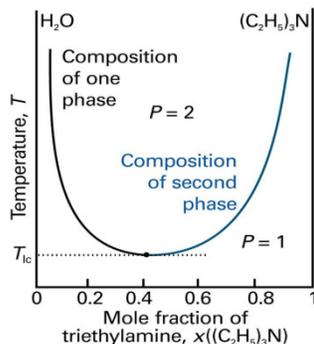
8 **PARTIALLY MISCIBLE BINARY SYSTEMS** (CST-UCST, LCST, and both UCST and LCST).

Miscibility temperature & Critical solution temperature (CST)

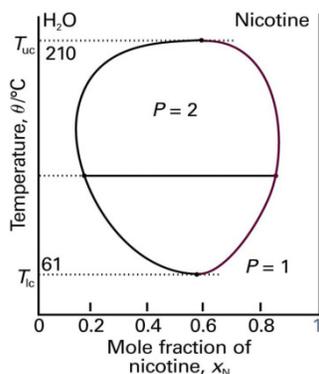
UCST: Phenol-Water (UCST: 338.9K, 36% Phenol)



LCST: *Triethylamine-Water* (LCST: 291.5K, 50% each)



UCST & LCST: *Nicotine-Water* (LCST:483K, 32% Nicotine ; UCST: 334K, 22% Nicotine)



9 **EFFECT OF SOLUTE on CST.** Phenol-Water (NaCl). Determination of conc of NaCl

10 **SOLUBILITY OF GASES in liquids;** Henry's law: $m \propto p$

Relationship with Raoult's law. **Solvent** (Raoult's law); **Solute** (Henry's law)

COLLIGATIVE PROPERTIES

Lowering of vapor pressure is the cause for all colligative properties

11 **LOWERING OF VAPOR PRESSURE & Relative Lowering of vapor pressure**

(RLP):

$$\text{RLP} = \frac{P^0 - P}{P} = x_2 = \frac{n_2}{n_1 + n_2} = \frac{n_2}{n_1} = \frac{w_2 M_1}{M_2 w_1}$$

12 **ELEVATION OF BOILING POINT** (BP temperature at which $vp = \text{atmospheric pressure}$)

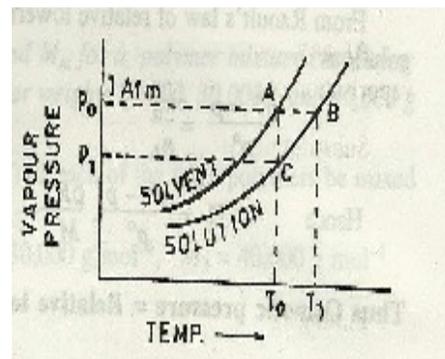


Fig-8: Vapor pressure-Temperature (Boiling)

$$\Delta T_b = K_b m = K_b 1000 \frac{w_2}{M_2 w_1}$$

13 DEPRESSION OF FREEZING POINT (Temperature at which *vp* of solid = *vp* of liquid)

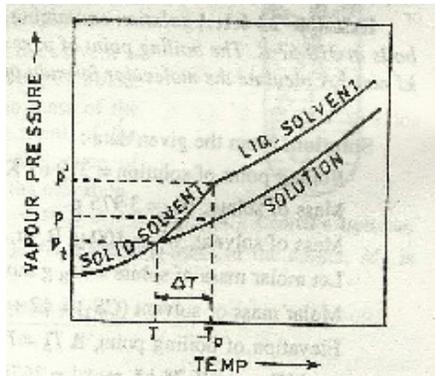


Fig-9: Vapor pressure-Temperature (Freezing)

$$\Delta T_f = K_f m = K_f 1000 \frac{w_2}{M_2 w_1}$$

14 OSMOTIC PRESSURE (Semi permeable membrane-Osmosis-Osmotic pressure)

$$\pi V = nRT$$

$$\pi = \frac{nRT}{V} = \frac{w_2}{M_2 V} RT = CRT$$

Vant Hoff's theory of dilute solutions. Vant Hoff's factor, *i*

$$i = \frac{\text{Observed colligative properties}}{\text{Theoretical colligative properties}} = \frac{\text{Theoretical molecular weight}}{\text{Observed molecular weight}}$$

Vant Hoff's factor, *i* must be 1 if there is no dissociation or association

Expected *i* values for different solutes:

$$\text{Glucose} = 1, \text{NaCl} = 2 ; \text{Al}_2(\text{SO}_4)_3 = 5 ; \text{CH}_3\text{COOH} = 0.5$$

The *i* values may differ from the expected values due to incomplete dissociation or association:

$$\text{Glucose} = 1, \text{NaCl} = 1 \text{ to } 2 ; \text{Al}_2(\text{SO}_4)_3 = 1 \text{ to } 5 ; \text{CH}_3\text{COOH} = 1 \text{ to } 0.5$$

$$\alpha = \frac{i-1}{n-1}$$

Analogy between solute particles and gas molecules.

15 DISTRIBUTION LAW: Nernst Distribution Law: Statement....!!!

Thermodynamic derivation

$$\mu_1 = \mu_1^\circ + RT \ln a_1 \quad (\text{For solvent-1})$$

$$\mu_2 = \mu_2^\circ + RT \ln a_2 \quad (\text{For solvent-2})$$

$$\mu_1 = \mu_2$$

$$\text{i.e., } \mu_1^\circ + RT \ln a_1 = \mu_2^\circ + RT \ln a_2$$

$$RT \ln(a_1/a_2) = \mu_2^\circ - \mu_1^\circ$$

$$\frac{a_1}{a_2} = \exp \left\{ \frac{\mu_2^\circ - \mu_1^\circ}{RT} \right\} = \text{Constant}$$

Limitations of the law:

1. Temperature must be constant
2. The concentration of the solute must very low
3. The solute must be in the same state in both solvent
4. The solute should not increase the mutual solubility of the immiscible solvents.
5. Soluble impurities should not react with the solute (KI & I₂ ; Cu²⁺ & NH₃)

Applications: Study of association, dissociation and solvation

S.No	Solvent-I	Solvent-II	Relationship	Comment
1	Normal	Normal	$K = \frac{C_1}{C_2}$	<i>Ideal distribution</i>
2	Normal	Dissociated	$K = \frac{C_1}{C_2(1-\alpha_2)}$	
3	Normal	Associated (nS) ₁ → (S _n) ₂	$K = \frac{C_1}{\sqrt[n]{C_2}}$	
4	Dissociated	Dissociated	$K = \frac{C_1(1-\alpha_1)}{C_2(1-\alpha_2)}$	
5	Normal	Combines with Solvent (Solvation)	$K' = \frac{C_1}{C_2}$	<i>Looks like Ideal distribution. But with different distribution coefficient</i>

Formation of complex ions.

- i) $I_2 + KI \rightarrow KI_3$ [Let the distribution be between water & an organic solvent]

Normal distribution coefficient, $K = \frac{C_{org}}{C_{aq}}$ (without KI)

Add KI of concentration and determine the concentration of I_2 in organic & aqueous layers

Free I_2 in aq layer = $\frac{C_{org}}{K} = x$

$[KI_3] =$ Combined I_2 in aq layer = $C_{aq} - x = y$

$[KI]$ in aq layer = C-KI that has got complexed = C- y = z

Hence, the equilibrium constant, K for the reaction $I_2 + KI \rightarrow KI_3$ in aq layer can be determined.

- ii) Similar treatment can be given to the equilibrium, $NH_3 + Cu^{2+} \rightarrow [Cu(NH_3)_4]^{2+}$

16 EXTRACTION WITH SOLVENTS

- Let V ml of a solvent-1 contain W g of the substance.
- Let v ml of a second solvent (solvent-2) is used for extraction each time.

➤ Let the distribution coefficient $K = \frac{C_1}{C_2}$

➤ Let w_1 g be the amount left un extracted at the end of first extraction

$$K = \frac{w_1/V}{(W - w_1)/v}$$

$$w_1 = \left\{ \frac{KV}{KV + v} \right\} W$$

➤ Let w_2 g be the amount of the substance left un extracted at the end of second extraction

$$K = \frac{w_2/V}{(w_1 - w_2)/v}$$

$$\text{Hence, } w_2 = \left\{ \frac{KV}{KV + v} \right\} w_1$$

➤ Substituting for w_1 we get

$$w_2 = \left\{ \frac{KV}{KV + v} \right\}^2 W$$

Let w_n g be the amount of the substance left un extracted at the end of n^{th} extraction.

$$w_n = \left\{ \frac{KV}{KV + v} \right\}^n W$$

EFFICIENCY OF EXTRACTION

- ❖ For greater efficiency of extraction, the amount of the substance left un extracted at the end of n^{th} extraction, w_n must be less.
- ❖ The substance should have greater solubility in the extracting solvent.
- ❖ The extracting volume, v must be less with more number of extractions.