Changes of phase of a pure substance

The phase-changes of a pure substance such as sublimation, melting, vaporization etc. are called first order phase transition. These transitions are associated with an abrupt change of first order derivative of free energy. Though G changes continuously but $\left(\frac{\partial G}{\partial P}\right)_T$ and $\left(\frac{\partial G}{\partial T}\right)_P$ will change discontinuously at the point of transition when plotted against T.

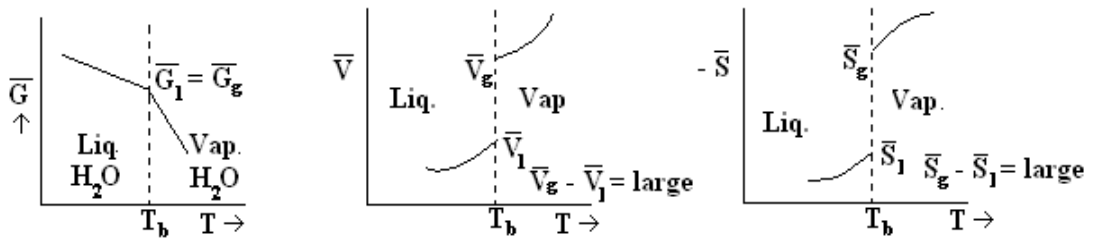**First-order phase transition:**

There are three criteria of the first order phase transitions, phase α → phase β,

(i) $\bar{G}_\alpha = \bar{G}_\beta$ (ii) $\bar{V}_\alpha - \bar{V}_\beta \neq 0$, since $\left(\frac{\partial G}{\partial P}\right)_T = \bar{V}$ as $d\bar{G} = \bar{V}\,dP - \bar{S}\,dT$ (iii) $\bar{S}_\alpha - \bar{S}_\beta \neq 0$.

The difference of $\bar{V}_\alpha$ and $\bar{V}_\beta$ or $\bar{S}_\alpha$ and $\bar{S}_\beta$ are very large.

This can be explained by the following diagram of vaporization of water at its boiling point.

Criteria of 1ˢᵗ order phase transition

On the other hand, there are some cases of transitions where second order derivative of free energy of the substance changes abruptly. For example, change of ferromagnetic material to paramagnetic material at the Curie point, liquid He II to liquid I at the λ-point etc.

Clapeyron Equation (effect of P on the transition temperature):

If two phases of a pure substance are in equilibrium with each other, they have same molar free energy at that T and P. when P is changed at constant T, or T is changed at constant P, one of the phases will disappear. But if T and P are both changed in such a way as to keep the two molar free energies (chemical potentials) equal to each other, the two phases will continue to co-exist and remain equilibrium.

Thus for two phases α and β of the substance at equilibrium, we have $\bar{G}_\alpha = \bar{G}_\beta$. If T and P are changed so that equilibrium is maintained, then, $d\bar{G}_\alpha = d\bar{G}_\beta$.

Derivation of the equation.

But, $d\bar{G} = \bar{V}\,dP - \bar{S}\,dT$ hence, $\bar{V}_\alpha\,dP - \bar{S}_\alpha\,dT = \bar{V}_\beta\,dP - \bar{S}_\beta\,dT$.

Or,
$$\frac{dP}{dT} = \frac{\bar{S}_\beta - \bar{S}_\alpha}{\bar{V}_\beta - \bar{V}_\alpha} = \frac{\Delta\bar{S}}{\bar{V}_\beta - \bar{V}_\alpha}$$

But for the phase-change at constant T and P, $\Delta\bar{S} = \frac{\Delta\bar{H}}{T}$,

where, $\Delta\bar{H}$ = molar latent heat transition or molar enthalpy of transition.

Therefore,
$$\frac{dP}{dT} = \frac{\Delta\bar{H}}{T\left(\bar{V}_\beta - \bar{V}_\alpha\right)}.$$ This is called Clapeyron equation.

However molar properties can be replaced and then Clapeyron equation becomes

$$\frac{dP}{dT} = \left(\frac{\Delta H}{T(V_\beta - V_\alpha)} \right).$$

Alternative derivation from Maxwell relation.

From Maxwell's relation, we get $\left(\frac{\partial P}{\partial T} \right)_V = \left(\frac{\partial S}{\partial V} \right)_T.$

When two phases are in equilibrium (say, liquid and vapor), the vapor pressure is independent of the mass and hence volume. So, $\left(\frac{\partial P}{\partial T} \right)_V = \frac{dP}{dT}$.

Again, if we consider latent heat of transition, L as nearly constant, independent of T, then

$$\left(\frac{\partial S}{\partial V} \right)_T = \frac{dS}{dV} = \frac{L}{T\left(V_\beta - V_\alpha\right)} .$$

Therefore the Clapeyron equation is $\quad \frac{dP}{dT} = \left(\frac{\Delta H}{T(V_\beta - V_\alpha)} \right)$

Sign of $\frac{dP}{dT}$ depends on the sign of L and $(V_\beta - V_\alpha)$

(1) For vaporization of liquid, L = (+)ve and $(V_\beta - V_\alpha) = (V_g - V_l) = (+)$ve,

Vaporization of liquids

hence $\frac{dP}{dT} = (+)$ve. This signifies that the vapor pressure of a liquid increases with temperature. It also states that the boiling point of a liquid increases with increase of pressure.

(2) For melting of paraffin or any solid except ice, L = (+)ve and $(V_l - V_s) = (+)$ve,

Melting of solid

hence $\frac{dP}{dT} = (+)$ve so melting point of paraffin increases with increase of pressure.

(3) For melting of ice, L = (+)ve and $(V_l - V_s) = (-)$ve, since $V_{ice} > V_{water.}$

Melting of ice — a special

This indicates that $\frac{dP}{dT} = (-)$ve, indicating that melting point of ice decreases with increase of pressure

.

Clausius Clapeyron equation:

Clausius simplified the relation for sublimation and vaporization processes by assuming that vapor obeys perfect gas equation and neglecting the molar volume of the liquid or solid in comparison to that of the vapor. For the process of vaporization, the

Equation for vaporization and sublimation

Clapeyron equation is $\quad \frac{dP}{dT} = \left(\frac{\bar{L}_v^o}{T(\bar{V}_g - \bar{V}_l)} \right).$

Since $\overline{V_g} \rangle\rangle \overline{V_l}$, hence $\frac{dP}{dT} = \frac{\bar{L}_v^o}{T\bar{V}_g} = \frac{\bar{L}_v^o \times P}{RT^2}$. Separating the variables and integrating,

we get, $\quad \int \frac{dP}{P} = \frac{\bar{L}_v^o}{R} \int \frac{dT}{T^2}$. $\quad$ Or $\ln P = -\frac{\bar{L}_v^o}{R} \cdot \frac{1}{T} + C$ (IC).

When integrated within limits, we get, $\ln \frac{P_2}{P_1} = \frac{\bar{L}_v^o}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$.

This is Clausius-Clapeyron equation or simply called Clausius equation.

$\bar{L}_v^o$ is assumed to be independent of T.

Using this relation, it is possible to calculate the latent heat of vaporization or latent heat of sublimation from the vapor pressure at two temperatures.

However if $\bar{L}_V$ of the process is known, vapor pressure at a given temperature can also be calculated if that at other temperature is known.

Trouton's rule: From the relation, $\quad \ln P = -\dfrac{\bar{L}_v^o}{R} \cdot \dfrac{1}{T} + C,$

we can put P = 1 atm, when T = T_b (normal boiling point). Thus, $0 = -\dfrac{\bar{L}_v^o}{R} \cdot \dfrac{1}{T_b} + C$

or, $\quad \dfrac{\bar{L}_v^o}{T_b} = RC = \text{constant} \approx 21$ (Approx.) for non-associated simple liquids.

Trouton made an important generalization from experimental observation that the ratio of molar heat of vaporization to the normal boiling point is constant for simple and non-associated liquids and the constant is about 21 cal mol^{-1}K^{-1}.

The rule also states that molar entropy-change of vaporization at normal boiling point is same and is about 21 cal mol^{-1}K^{-1}.

That is, $\quad \left(\Delta \bar{S}\right)_{vap.\,at\,normalBP} \approx 21$ for all simple and non-associated liquids.

This consistency of entropy of vaporization from liquids to vapor is readily understood from Boltzmann hypothesis relating entropy to disorder. The change from liquid to vapor leads to increased disorder. The entropy of vaporization is zero at the critical temperature because liquids behave alike not only at their T_C but also equal fraction of their T_C. Hence different liquids should have same entropy of vaporization at their boiling point provided there is no association or dissociation upon vaporization.

Problem (1)

The vapor pressure of water is 23.75 torr at 25°C and 760 torr at 100°C. What will be the heat of vaporization**?**   **[Civil Service Exam. 2003]**

Solution

Clausius Clapeyron equation is, $\quad \ln \dfrac{P_2}{P_1} = \dfrac{\bar{L}_v^o}{R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)$

or, $\ln \dfrac{760}{23.75} = \dfrac{\bar{L}_v^o}{2}\left(\dfrac{373 - 298}{373 \times 298}\right)$, or $\bar{L}_v^o = \dfrac{2 \times 373 \times 298}{75} \ln \dfrac{760}{23.75} = 10,272.8 \; cal\,mol^{-1}$.

Problem (2)
Solution

Calculate the boiling point of water at a pressure of 75 cm of Hg, given that latent heat of vaporization is 540 cal mol^{-1}.

We know that boiling point of water is 100°C when the pressure is 76 cm of Hg.

Putting the values in the Clausius equation, we have, $\quad \ln \dfrac{76}{75} = \dfrac{18 \times 540}{2}\left(\dfrac{1}{T} - \dfrac{1}{373}\right)$

Solving the equation, we get the BP of water is 372.63 K = 99.63°C at 75 cm of Hg

Problem (3)

If the rate of change of vapor pressure of water with respect to T is 2.7 cm of Hg per degree around 100°C, Calculate the molar volume of liquid water (given specific volume of water vapor = 1674 cc gm^{-1}). Calculate also the boiling point of water at a pressure of 75 cm of Hg.

                    [BU'91, Q 7(b) m = 6+3]

Solution:

Given, $\dfrac{dP}{dT} = 2.7$ cm of Hg per degree around 100°C. Putting the values in the Clapeyron

equation, $\dfrac{dP}{dT} = \dfrac{l_v^o}{T(v_g - v_l)}$ or, $2.7 \times 13.6 \times 980$ dyne cm^{-2} K^{-1} = $\dfrac{536 \times 4.18 \times 10^7\,erg\,gm^{-1}}{373 K^{-1}(1674 cc\,gm^{-1} - v_l)}$.

Calculation gives v_l = 5 cc/gm. So molar volume of liquid water = 5 × 18 = 90 cc/mole.

2nd part: given, $\frac{dP}{dT}$ = 2.7 cm of Hg per degree around 100°C

or, $\frac{P_2 - P_1}{T_2 - T_1}$ = 2.7 cm of Hg/°C, Putting the values, $\frac{76-75}{100-t_1}$ = 2.7   or, t_1 = 99.63°C.

Problem (4) Derive Clapeyron equation and show that it can be represented by the equation,

$P = P^* \exp[(-\Delta H_{vap}/R)\{\frac{1}{T} - \frac{1}{T^*}\}]$. For liquid – vapor boundary assuming ideal gas behavior

and making certain approximation**.**   [Civil service Exam, 2001]

Answer : Derive Clausius equation, $\ln \frac{P^*}{P} = \frac{\Delta H_{vap}}{R} \{\frac{1}{T} - \frac{1}{T^*}\}$ and get the required form.

Problem (5) At the normal melting point of NaCl 801°C, its enthalpy of fusion is 28.8 kJmol^{-1}. the density of solid is 2.165 gm cm^{-3} and that of the liquid is 1.733 gm cm$^{-3.}$ What is the increase of pressure needed to raise the melting point by 1.00 °C.

[IISc, Bangalore, adm. test for Int. Ph. D.]

Solution : The process is melting,   NaCl (s) → NaCl (l).
In the Clapeyron equation, dT = 1.00K,   T = 273+801=1074K, ΔH_m = 28.8 kJ mol^{-1}. dP = ?

$dP = dT \times \frac{\Delta \bar{H}_m}{T(\bar{V}_l - \bar{V}_s)}$ $= 1 \text{ K} \times \frac{28.8 kJ \, mol^{-1} \times 10^{10} \, erg \, kJ^{-1}}{1074K \left(\frac{1}{1.733} - \frac{1}{2.165}\right) \times 58.5 \, cc \, mol^{-1}}$

$= 3.98 \times 10^7$ dyne cm^{-2} $= \frac{3.98 \times 10^7}{76 \times 13.6 \times 981}$ atm.

Problem (6) Average value of enthalpy of vaporization (kJ / mole) of water between 363K and 373K
     is (a) 42.50   (b) 40.80   (c) ─ 40.65   (d) – 40.80.
Given vapor pressure of water at 363K & 373K are 529 Torr & 760 Torr.

Solution : The correct answer is (b). Use Clausius equation to get the answer.

Problem (7) At 373.6 K and 372.6 K, vapor pressure of water is 1.018 and 0.982 atm respectively.
Calculate the molar entropy of vaporization and ΔV, the change of volume per mole when
 liquid water vaporizes at 373 K. Assume that the vapor behaves ideally.

[B U, 1994 & 1996]

Solution : Clausius equation (assuming vapor behaving ideally) is

$\frac{\bar{L}_v^o}{R}\left(\frac{T_2 - T_1}{T_1 T_2}\right) \ln \frac{P_2}{P_1} =$. Putting the values given, $\ln \frac{1.018}{0.982} = \frac{\bar{L}_v}{2}\left(\frac{1}{373.6 \times 372.6}\right)$

or, $\bar{L}_v^o$ = 10,023.7 cal mol^{-1} , $\Delta \bar{S} = \bar{L}_v^o/T = 10{,}023.7/373$ = 26.87 cal K^{-1}mol^{-1}.

Now the Clapeyron equation is $\frac{\Delta P}{\Delta T} = \frac{\Delta \bar{S}}{\Delta \bar{V}}$ or, $\frac{(1.018 - 0.982) \, atm}{1 \, K} = \frac{26.87 \, cal \, K^{-1} mol^{-1}}{\Delta \bar{V}}$

or, $\Delta \bar{V} = \frac{26.87}{0.036} \times \frac{0.082}{1.987} lit \, mol^{-1}$ = 30.8 lit mol^{-1} .

BU' 2008, Q 1(g) "The Clausius-Clapeyron equation is a special case of the van't Hoff
 equation for liquid-vapor equilibrium." ─ Justify or criticize. (2).

Answer: The van't Hoff equation is, $\frac{d \ln K_P}{dT} = \frac{\Delta H}{RT^2}$, where ΔH is the enthalpy of the reaction and K_P

is the equilibrium constant of the reaction.
But for the liquid-vapor equilibrium, the Clausius-Clapeyron equation is given by,

$$\frac{d\ln P}{dT} = \frac{\Delta H}{RT^2}$$, here P is the equilibrium pressure and ΔH is also the enthalpy of vaporization. Thus the statement is correct.

BU' 2008, Q 4(b) With increase of pressure, the melting temperature of paraffin increases but that of ice decreases. ─ Explain. (2). **Answer:** See the Text.

BU' 94 Q 3 **(a)** Deduce thermodynamically the first order phase transition. Give illustrations.

Establish the relation $\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T$. Hence deduce the Clapeyron equation. (4+4+4)

Answer: See the Text, page.

(b) Calculate the freezing temperature of water if the pressure be increased by 1 atm, given L = 80 cal/gm, $\rho_{ice(0^oC)} = 0.9168\, gm/cc\ and\ \rho_{H_2O(0^oC)} = 0.9998\, gm/cc$. (4).

Solution: For the process   water → ice, the Clapeyron equation is $\frac{dP}{dT} = \left(\frac{\Delta H}{T(V_{ice} - V_{water})}\right)$.

$$\frac{1\,atm}{dT} = \left(\frac{-80\,cal\,gm^{-1}}{273\,K(\frac{1}{0.9168} - \frac{1}{0.9996})cc\,gm^{-1}}\right),\ or,\ dT = \frac{1atm \times 273K(1.0907 - 1.0004)cc\,gm^{-1}}{-80\,cal\,gm^{-1}}$$

or, dT $= \frac{1 \times 76 \times 13.6 \times 981\,dyne\,cm^{-2} \times 273K\,(1.09075 - 1.0004)\,cc\,gm^{-1}}{-80 \times 4.18 \times 10^7\,erg\,gm^{-1}} = -\,0.075$ K.

Thus the freezing point of water becomes ─ 0.075°C if pressure is increased by 1atm.

BU' 96 Q 5(a). If in a phase transition the first order partial derivative of G with respect to temperature and pressure change continuously in going from one phase to the other, will it be possible to obtain the Clapeyron equation? Give reasons for your answer. (4).

Answer: It is not possible to obtain Clapeyron equation.

The equation is, $\frac{dP}{dT} = \frac{S_\beta - S_\alpha}{V_\beta - V_\alpha}$. But, $\left(\frac{\partial G}{\partial P}\right)_T = V$ and $\left(\frac{\partial G}{\partial T}\right)_P = -S.$

As $\left(\frac{\partial G}{\partial P}\right)_T$ and $\left(\frac{\partial G}{\partial T}\right)_P$ change continuously in going from one phase to the other,

so V and S will change continuously and at the transition point, $V_\beta = V_\alpha$ and $S_\beta = S_\alpha$.

Putting in the Clapeyron equation, RHS of the equation becomes meaningless.

CHEMICAL POTENTIAL (μ):

For pure substance, it is defined as free energy per mole, called molar free energy or chemical potential (name given by G.N. Lewis) its mathematical expression

is given by, $\mu = \left(\frac{\partial G}{\partial n}\right)_{T,P}$.

Definition of μ

For the substance present in multi-component open system (say ith component), it is called partial molar free energy or also chemical potential and is defined actual free energy change of the system when one mole of that substance is added to it provided the system is large enough so that the composition of the system remains unchanged by such addition.

It is mathematically defined as

$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_{j \neq i}} .$$

Chemical potential is a measure of escaping tendency of the substance from the phase in which it exists. Whenever a substance remains in two phases at equilibrium, the chemical potential of the substance in the two phases is same.

This is an important aspect of the chemical potential.

EFFECT OF TEMPERATURE AND PRESSURE ON CHEMICAL POTENTIAL:

The temperature effect is mathematically given by

$$\left(\frac{\partial \mu_i}{\partial T} \right)_P = -\bar{S}_i , \text{ partial molar entropy of the ith component.}$$

Since $\bar{S}_i$ is always positive, hence $\left(\frac{\partial \mu_i}{\partial T} \right)_P = (-)$ ve.

It means that with rise in temperature at constant pressure, chemical potential always decreases. Again, $\bar{S}_i(g) \rangle \bar{S}_i(l) \rangle \bar{S}_i(s),$ the rate of decrease of μ_i with temperature is greater in gaseous phase, least in solid phase and in between in liquid phase of a component.

The pressure effect is given mathematically as

$$\left(\frac{\partial \mu_i}{\partial P} \right)_T = \bar{V}_i , \text{ partially molar volume of the ith component.}$$

Since, $\bar{V}_i = (+)$ve always, so, $\left(\frac{\partial \mu_i}{\partial P} \right)_T = (+)$ve always.

It means that μ_i always increases with increase of P at constant T. The rate of increase of μ_i with P decreases from gas to solid of the component.

EXPRESSION OF CHEMICAL POTENTIAL IN TERMS OF PRESSURE AT CONSTANT TEMPERATURE

For pure substance, chemical potential is expressed as

$$\left(\frac{\partial \mu}{\partial P} \right)_T = \bar{V} .$$

If the substance is in gaseous state and obeying ideal gas equation, $P\bar{V} = RT$,

then, replacing $\bar{V}$ in the above equation and integrating with proper limits, we have

$$\mu(T, P) = \mu^o(T) + RT \ln P$$

where, $\mu^o(T)$ is the standard chemical potential of the substance which is the chemical potential of the substance at one atmosphere pressure (standard state) and at temperature T.

$\mu(T, P)$ is the chemical potential of the substance at pressure P and temperature T.

Since a gas flows from higher pressure to lower pressure until there occurs equalization of pressure, hence it can be alternatively said that a substance escapes spontaneously from higher chemical potential to lower chemical potential until it becomes equal.

Thus chemical potential is a measure of escaping tendency of the substance from the state where it exists to the available phase.

For a component in ideal multi-component system, chemical potential is expressed as,

$$\mu_i(T, P) = \mu_i^o(T) + RT \ln p_i$$

where, $\mu_i(T, P)$ is the chemical potential of the ith component at partial pressure p_i and temperature T.

Since $p_i = x_i P$, hence replacing p_i, we get the expression of $\mu_i(T, P)$ as,

$$\mu_i(T, P) = [\mu_i^o(T) + RT \ln P] + RT \ln x_i$$

or,
$$\mu_i(T, P) = \mu_i^o(T, P) + RT \ln x_i$$

$\mu(T, P)$ is related with x_i of ith component in ideal gas mixture.

where, $\mu_i^o(T, P)$ is the chemical potential of the ith component at temperature T and pressure P when it remains in pure state ($x_i = 1$).

For non-ideal system, the expression is $\mu_i(T, P) = \mu_i^o(T, P) + RT \ln a_i$

where, a_i is the activity of the ith component in the non-ideal mixture.

$$a_i = x_i \gamma_i, \text{ where } \gamma_i = \text{activity co-efficient of the ith component.}$$

$= 1$, when the system is ideal and
$\neq 1$, when the system is non-ideal.

Activity coefficient and ideality of the solution.

Thus, γ_i measures the extent of non-ideality of the component in the system.

Greater the departure of the value of γ_i from unity, greater is the non-ideality of the component in the mixture.

Unit and dimension of μ_i:

It is an intensive property and its unit is energy per mole.

Thus, in CGS system, its unit is cal mol^{-1} or erg mol^{-1}, but in SI system, it is Joule mol^{-1}.

The dimension of μ_i is $ML^2T^{-2}mol^{-1}$.

DILUTE SOLUTIONS

Solution is a homogeneous two-component mixture. The component which is dissolved is called solute and that dissolves is called solvent. The solvent is present in large amount in comparison to the solute in the solution.

Relative amount of solute and solvent is expressed by concentration of the solution. Different modes of expressing the concentration of a solution are given below.

1. Percentage (%) :

$$\text{(i) mass percent (\% m/m)} = \frac{m_2}{m_1 + m_2} \times 100,$$

where m_1 and m_2 are the masses of solvent and solute respectively in the solution in gms.

1 subscript is given for solvent and 2 subscript is for solute. This conc. is used generally when solute and solvent both are solids, such as alloys.

It is temperature- independent.

$$\text{(ii) volume percent (\% v/v)} = \frac{v_2}{v_1 + v_2} \times 100.$$

This conc. is used when solute and solvent both are liquids, such as alcohol solution in water.

It is temperature- dependent.

$$\text{(iii) mass-volume percent (\% m/v)} = \frac{m_2}{v_1 + v_2} \times 100.$$

This conc. is used when solid solute is dissolved in liquid solvent, such as urea solution in water.

It is also temperature-dependent.

2. Molarity (M) :

This is most common conc. unit used. It is expressed as number of moles of solute dissolved per litre of the solution.

$$\text{Molarity (M)} = \frac{n_2}{V}, \text{ where V is the volume of the solution in litre that}$$

contains n_2 moles of the solute. This conc. solution is very easily prepared in the laboratory and this is why it is commonly used.

It is temperature-dependent and as the temperature is increased, conc. is decreased.

3. Molality (m) :

This conc. is defined as the number of moles of solute dissolved per 1000 gms (1 Kg) of the solvent. Thus it is

$$\text{Molality (m)} = \frac{n_2}{m_1}, \text{ where } m_1 \text{ is the mass of the solvent in Kg that}$$

dissolves n_2 moles of solute.

This conc. is temperature-independent and is used for more accurate purpose.

4. Mole-fraction:

$$\text{Mole-fraction of the solute, } x_2 = \frac{n_1}{n_1 + n_2} \text{ and that of solvent, } x_1 = \frac{n_1}{n_1 + n_2}.$$

Thus, $x_1 + x_2 = 1$. The range of x_1 is from 1 (pure solvent) to 0 (pure solute).

For solution, where two components are present, $0 \langle x_1 \langle 1$.

This conc. unit is also temperature-independent.

Problems :

(1) How are conc. expressed in mole-fraction and molality related? Show that for dilute solution they are proportional. [BU'91].

Conc. is used to express the relative amount of two components in the solution.

These are ordinary mode of conc. of solution.

Most commonly used mode of conc. of solution but it is T-dependent

This mode is used for more accurate work and it is T - independent.

Theoretically more used mode of conc. and it is also T– independent.

Problem showing relation between mole-fraction and molality of a solution.

Solution : Let the mole-fraction of solute is x_2 and molality of the solution is m.

$$\text{So, } x_2 = \frac{m}{\left(1000\big/M_1\right) + m}.$$

But for dilute solution, $\left(1000\big/M_1\right) \gg m$

$$\text{so,} \quad x_2 \approx \left(\frac{M_1}{1000}\right)m. \text{ That is for a given solute, } x_2 \propto m \text{ in dilute solution.}$$

<div style="margin-left:0;">

Problem showing conversion of molarity to mole fraction and molality of a solution.

</div>

(2) Express conc. of urea in mole-fraction and molality for a 0.1 molar aqueous solution of the substance; assuming density of the solution as 1.0542 gms/cc.

Solution : Mass of 1000cc (1 litre) solution = 1000 × 1.0542 = 1054.2 gms.

Mass of the solute = c M_2 = 0.1 × 60 = 6 gms,

Mass of water = 1054.2 – 6 = 1048.2 gm.

$$\text{So, } x_2 = \frac{0.1}{\left(1048.2\big/18\right) + 0.1} = 0.0017 \text{ molality, } (m) = \left(\frac{0.1}{1048.2} \times 1000\right) = 0.095$$

IDEAL SOLUTIONS:

Ideal solutions are those in which there is complete uniformity of cohesive forces between the molecules present in the solutions. In an ideal solution of A and B, the interaction of A-A molecules and B-B molecules is same as A-B molecules.

Thus the escaping tendency from the liquid to the gaseous state of any of them is not influenced by the presence of the other.

This molecular aspect of the ideal solutions is shown by the following thermodynamic criteria.

(a) $\Delta V_{mixing} = 0$, i.e. there is no volume-change due to mixing and thus molar volume

$(\bar{V}_i^0)$ is equal to the partial molar volume ($\bar{V}_i$) of both the components.

Thermodynamic criteria of ideal solutions.

(b) $\Delta H_{mixing} = 0$, there is no heat-change due to mixing of solute and solvent during the preparation of the solution.

(c) $\mu_i(T,P) = \mu_i^0(T,P) + RT\ln x_i$, where $\mu_i^0(T,P)$ is the chemical potential of the ith component in pure state ($x_i = 1$) at the given T and P and $\mu_i(T,P)$ is the chemical potential of the same component of mole-fraction x_i in a mixture under the same T and P.

Ideal solution follows additivity rule.

Ideal solutions follow the additivity rule. It means that value of any extensive property of an ideal solution is the sum of the values of that property of the individual components.

Thus, $V = n_1\bar{V}_1^o + n_2\bar{V}_2^o$

Similar liquids such as n-heptane – n-hexane, ethylene bromide – ethylene chloride benzene – toluene, etc. form ideal solutions.

GATE, 2001

Problem: For an ideal solution, which one of the following statements is correct? (γ and x are activity coefficient and mole fraction respectively).

(A) γ (solvent)→0 as x (solvent) →1   (B) γ (solute) →1 as x (solute) →1   (C) γ (solvent)→1 as x (solvent) →1   (D) γ (solvent)→0 as x (solvent) →1 [Ans. (C)]

RAOULT'S LAW :

Let us take a closed system that contains a solution of two volatile components in equilibrium with their vapors. Thus it is a two-component two phase system. Raoult's law finds a relation between the vapour pressures of any of the components with its concentration in the solution.

The law states that 'at a given temperature, the vapour pressure of any volatile component (p_i) of a solution is equal to the product of vapour pressure of the component in the pure state (p_i^o) and the mole-fraction (x_i) of that component in solution'.

Mathematically it is expressed as $p_i = p_i^o \ x_i$ at constant T.

This is due to the fact that escaping tendency of each component is not influenced by the other component present in the solution. Thus for the solution of two volatile components, Raoult's law is, $p_1 = p_1^o \ x_1$ for the solvent and $p_2 = p_2^o \ x_2$ for the solute.

The total pressure over the solution, $P = p_1 + p_2 = p_1^o \ x_1 + p_2^o \ x_2$.

Raoult's law is valid for ideal solutions only.

In fact the solution is said to be ideal if it obeys Raoult's law over the entire range of composition at all temperatures.

The vapour pressures can be expressed in terms of mole-fraction of one component (say, x_1) of the solution. These relations are given as,

$$p_1 = p_1^o \ x_1 \quad -------- (1) , \qquad p_2 = p_2^o \ x_2 \text{, but } x_2 = 1 - x_1, \quad \text{so,} \quad p_2 = p_2^o \left(1 - x_1\right),$$

or $\qquad p_2 = p_2^o - p_2^o \ x_1$ -----(2) and the total vapour pressure,

$$P = p_1 + p_2 = p_1^o \ x_1 + p_2^o - p_2^o \ x_1,$$

$$P = p_2^o + \left(p_1^o - p_2^o\right) x_1 \quad ------(3).$$

Let us take 1st component is more volatile than 2nd component so that $p_1^o \rangle p_2^o$.

The vapour pressures of the components can be plotted against x_1 and the plots are given as :

p_1 vs. x_1 plot will be straight line passing through the origin and terminate at p_1^o.

p_2 vs. x_1 plot will start from p_2^o and terminate at zero.
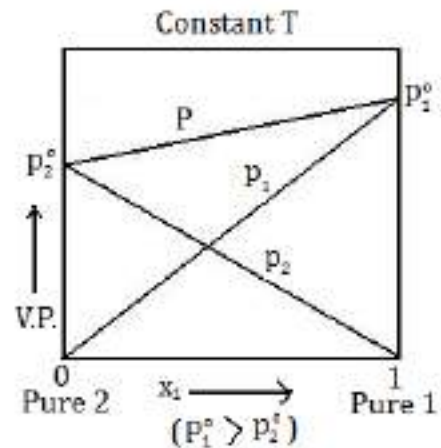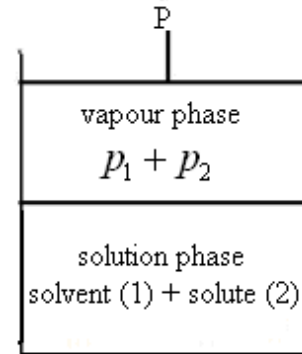
The total pressure, P vs. x_1 will start from p_2^o (when $x_1 = 0$) and terminate at p_1^o (when $x_1 = 1$).

Thermodynamical derivation of the law:

Both the components of the solution remain in equilibrium between the liquid phase and vapour phase at constant T and total pressure P, since the components are volatile (see the above sketch of the system).

Let ith component of the solution remains equilibrium in the liquid and vapour phase, hence the chemical potential of the component in the two phases becomes equal, i.e.,

$$\mu_i(liq) = \mu_i(vap)$$

Margin notes (left column):

Two-component two-phase system with solution phase and vapour phase.

Statement of the Raoult's law.

Expression of p_1, p_2 and P in terms of x_1 and their graphical plots obeying Raoult's law.

The plots of vapour pressure vs. mole fraction of the solvent (x_1)

Condition of a component to remain equil^m. in two phases.

But, $\mu_i(liq) = \mu_i^o(liq) + RT \ln x_i$ (1)

and $\mu_i(vap) = \mu_i^o(vap) + RT \ln p_i$ (2)

where x_i is the mole-fraction of the ith component in the liquid phase and p_i is the partial vapour pressure of the same component in the vapour phase.

From above equations (1) and (2), we get

$$\mu_i^o(liq) + RT \ln x_i = \mu_i^o(vap) + RT \ln p_i.$$

The relation between $\mu_i^o(liq)$ and $\mu_i^o(vap)$ can be obtained by putting $x_i = 1$ (pure state) and

then, $p_i = p_i^o$ (vapour pressure of the pure state), we have

$$\mu_i^o(liq) = \mu_i^o(vap) + RT \ln p_i^o$$

Inserting, $\mu_i^o(liq)$ in the equation, we get

$$\mu_i^o(vap) + RT \ln p_i^o + RT \ln x_i = \mu_i^o(vap) + RT \ln p_i.$$

or, $RT \ln (x_i \, p_i^o) = RT \ln p_i$

or, $p_i = x_i \, p_i^0.$

This is the **Raoult's law** relating the vapour pressure (p_i) in gas phase with the mole-fraction (x_i) of the component in the liquid phase when it remains in both the phases at equilibrium.

Non-ideal solutions:

      In these solutions, cohesive forces are not uniform, that is molecular interactions between A-A and B-B are not same as A-B.

      The escaping tendency of one component is influenced by the presence of other component in the solution.

The thermodynamic criteria for these solutions are given below:

    (a) $\Delta V_{mixing} \neq 0$ (b) $\Delta H_{mixing} \neq 0$ and (c) $\mu_i(T,P) = \mu_i^0(T,P) + RT \ln a_i$,

where a_i is the activity of the ith component in the solution.

But $a_i = x_i \gamma_i$, where γ_i is the activity coefficient of the ith component.

Putting this value of a_i, we get

$$\mu_i(T,P) = [\mu_i^0(T,P) + RT \ln x_i] + RT \ln \gamma_i,$$

and so, $\mu_i(T,P) = \mu_i(T,P)_{ideal} + RT \ln \gamma_i.$

      Non-ideal solutions may be of two types:

(i) Non-ideal solutions with positive deviation:

      In this type, cohesive forces between A-B are less than that of A-A and B-B.

As a result, the following thermodynamic criteria develop.

(a) $\Delta V_{mixing} = (+)ve$, volume is increased due to mixing,

      i.e. $V_{mixture} \rangle (V_A + V_B)$ and $\bar{V}_i \rangle \bar{V}_i^0$

(b) $\Delta H_{mixing} = (+)ve$, heat is absorbed due to mixing,

(c) The activity coefficient $\gamma_i \rangle 1$, $\ln \gamma_i = (+)ve$ and
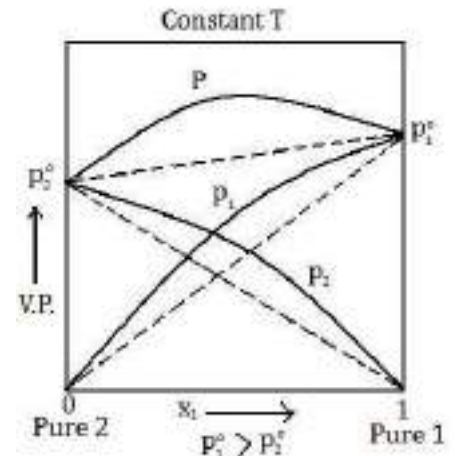
$$\mu_i(T,P) \rangle \mu_i(T,P)_{ideal}.$$

It means that the escaping tendency of the ith component is greater than that in the ideal solution.

The vapour pressure of each component and also the total

Margin notes (left column):

Expression of Raoult's law,

$p_i = x_i \, p_i^o$

Thermodynamic condition for non-ideal solution.

Thermodynamic condition for non-ideal solution with (+)ve deviation.

Vapour pressure vs. x_1 plot for this type of non-ideal solution is shown here.

Figure (right): Constant T — plot showing P, P_2^o, p_1, p_2, p_1^o vs x_1; V.P. axis; from 0 Pure 2 to 1 Pure 1; $P_1^o \rangle P_2^o$.

vapour pressure over the solution are greater than that obtained from Raoult's law.
Solid line is for the vapour pressure over the non-ideal solution with (+)ve deviation

and dotted line is for vapour pressure from Raoult's law (ideal solution). 1st component is assumed as more volatile than the 2nd component i.e. $p_1^o \rangle p_2^o$

Example of these type of solutions are the mixture of ethanol and water, ether and acetone etc.

(ii) Non-ideal solutions with negative deviation:

In this type, cohesive forces between A-B are greater than that of A-A and B-B molecules. As a result, the following thermodynamic criteria develop.

Thermodynamic conditions for non-ideal solutions with (−)ve deviation.

(a) $\Delta V_{mixing} = (-)ve$, volume is decreased due to mixing and $\bar{V}_i \langle \bar{V}_i^0$

(b) $\Delta H_{mixing} = (-)ve$, heat is evolved due to mixing, and

(c) The activity coefficient $\gamma_i \langle 1$, $\ln \gamma_i = (-)ve$ and $\mu_i(T,P) \langle \mu_i(T,P)_{ideal}$.

It means that the escaping tendency of the ith component is less than that in the ideal so that the vapour pressure of each component and also the total vapour pressure over the

Vapour pressure vs. x_1 plot for this type of non-ideal solutions.

non-ideal solution with (−)ve deviation are less than that obtained from Raoult's law.
Solid line is for the vapour pressure over the non-ideal solution with (−)ve deviation and dotted line is for vapour pressure from Raoult's law (ideal solution).
Examples of these type solutions are the mixture of halogen acid (such as HCl) and water, pyridine and acetic acid etc.
However non-ideal solutions behave ideal (i.e. they obey Raoult's law)
when $x_1 \rightarrow 1$ and $\gamma_1 \rightarrow 1$,
i.e., when the solutions are dilute.

General expression of the relation between p_i and x_i of a solution.
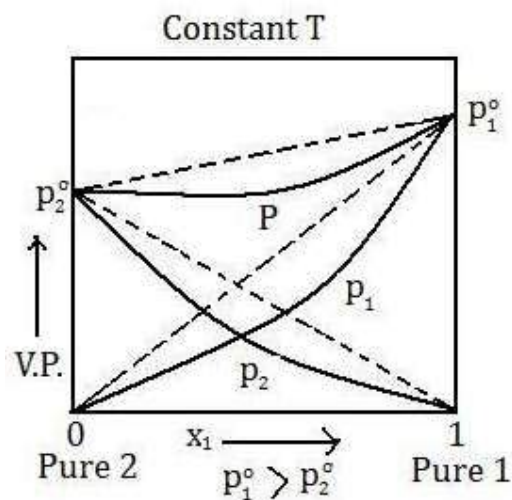
In non-ideal solutions, molecules of A will affect the escaping tendency of B and vice-versa. This molecular interaction reflects in the expression of vapour pressure of the components.

$$p_1 = x_1 \, p_1^o \, e^{\alpha x_2^2} \qquad \text{and} \qquad p_2 = x_2 \, p_2^o \, e^{\alpha x_1^2}$$

α is constant and same value for both components.
For ideal solutions, $\alpha = 0$, for non-ideal solutions with (+)ve deviation, $\alpha > 0$
and for non-ideal solutions with (−)ve deviation, $\alpha < 0$.

Statement of Duhem-Margules equation.

This is supported by the Duhem-Margules equation which states that if one component behaves ideal then other component also behaves ideal.
If one component behaves non-ideal with (+)ve deviation, the other component should also follow the same. This comment is also valid for solutions with (−)ve deviation. Large (+)ve deviation leads the system from complete miscibility to partial miscibility.
Large (−)ve deviation does the reverse effect.

Expression of p_i over non-ideal solutions :

The component of the non-ideal solution remains in equilibrium between the liquid phase and vapour phase. So the thermodynamic condition is

$$\mu_i(liquid) = \mu_i(vapor)$$

or, $\qquad \mu_i^o(liquid) + RT \ln a_i = \mu_i^o(vapor) + RT \ln p_i$

But, $\quad a_i = x_i \gamma_i$. $\qquad$ Putting, we have

$$\mu_i^o(liquid) + RT \ln(x_i \gamma_i) = \mu_i^o(vapor) + RT \ln p_i$$

Now, when $x_i = 1$, the solution is ideal as the ith component is in pure state and $\quad p_i = p_i^o$,

$$\mu_i^o(liquid) = \mu_i^o(vapor) + RT \ln p_i^o,$$

putting $\mu_i^o(liquid)$ in the equation,

$$\mu_i^o(vapor) + RT \ln p_i^o + RT \ln a_i = \mu_i^o(vapor) + RT \ln p_i$$

The relation between p_i and x_i of a non-ideal solution.

Or, $\qquad RT \ln a_i p_i^o = RT \ln p_i \quad$ or, $\ p_i = a_i p_i^o \quad$ and $\ \dfrac{p_i}{p_i^o} = a_i$.

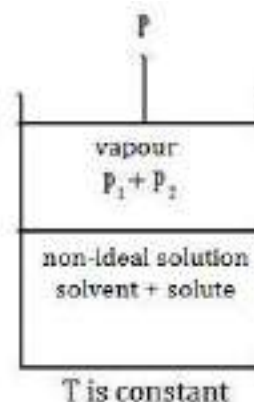Therefore, we can write, $\qquad p_i = a_i p_i^0 \qquad$ or, $\qquad p_i = (x_i p_i^o) \gamma_i$.

For ideal solution, $\gamma_i = 1$, so $\ p_i = x_i p_i^o$, the solution obeys Raoult's law.

For non-ideal with (+)ve deviation, $\gamma_i > 1 \quad$ and so $\quad p_i \rangle x_i p_i^o$.

The vapour pressure of the ith component is greater than that obtained from Raoult's law.

For non-ideal with (−)ve deviation, $\gamma_i < 1$ and so $p_i \langle x_i p_i^o$.

The vapour pressure of the ith component is less than that obtained from Raoult's law.

Problems :

(1) For an ideal solution, which one of the following statements is correct?
(γ and x are activity coefficient and mole fraction respectively).
(A) γ (solvent)$\to 0$ as x (solvent) $\to 1$ (B) γ (solute) $\to 1$ as x (solute) $\to 1$ (C) γ (solvent)$\to 1$ as x (solvent) $\to 1$ (D) γ (solvent)$\to 0$ as x (solvent) $\to 1$ **[GATE, 2001]**
[Ans. (C)]

(2) The vapour pressure of pure component P and Q are 700 torr and 500 torr r*espe*ctively. two phases are in equilibrium at 1.0 atm, the mole-fraction of P in liquid phase is 0.6 and in the vapour phase 0.4. The activity coefficient of component P in the solution on the basis of Raoult's law is (a) 0.60 (b) 0.72 (c) 0.92 (d) 1.0.
[GATE, 2004]

Solution : Given, $p_P^0 = 700\,torr$, $p_Q^0 = 500\,torr$ and P $= 1.0$ atm $= 760$ torr.

$$p_P = x_P(vap) \times 760 = 304\,torr. \qquad a_P(liq) = \dfrac{p_P}{p_P^0} = \dfrac{304\,torr}{700\,torr} = 0.434.$$

$$\gamma_P = \dfrac{a_P}{x_P} = \dfrac{0.434}{0.6} = 0.72.$$

(b) is correct.

(3) An aqueous solution of NaCl ($x_{NaCl} = 0.015$) at 298K is in equilibrium with a water vapour pressure (torr) of   (a) 23.64   (b) 748.60   (c) 24.36   (d) negligible. [Given VP of water at 298K = 24 torr].   **[GATE, 2005]**

Solution: $p_{water} = x_{water} \; p^0_{water} = (1 - x_{NaCl}) p^0_{water} = (1 - 0.015) \times 24 = 23.64 \, torr.$
[Ans. (a)].

HENRY'S LAW: [Solubility of gases in liquids]

Solubility of a gas in a liquid may be defined as the amount of the gas in gms per litre of the solvent forming a saturated solution at a given temperature.
Solubility of a gas in a liquid depends on the following factors.
(a) The nature of the gas and the liquid. Usual proverb is that "like dissolves like"
(b) Temperature of the solution:

Factors affecting the solubility of a gas in a liquid.	General effect is that with rise in temperature, solubility of the gas is decreased and the effect is quantitatively given by Van't Hoff equation.

$$\ln \frac{m_2}{m_1} = \frac{\Delta \bar{H}_{solution}}{R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

where, m_1 and m_2 are the solubilities of the gas at temperatures T_1 and T_2 respectively.

$\Delta \bar{H}_{solution}$ is the heat of the solution at constant pressure and it i

(c) Pressure of the gas over the solution $\rightarrow$ Henry's law.

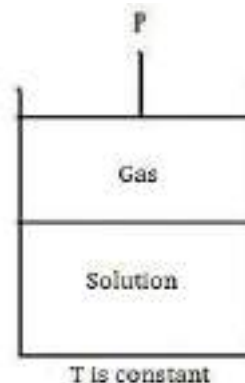|	
Henry's law – effect of pressure on the solubility of a gas in a liquid at given T.	According to Le Chatelier's principle, solubility of a gas is increased with increase of pressure of the gas over the solution. Henry's law states that "the mass of the gas (m) dissolved in unit volume of a solvent at constant temperature is directly proportional to the pressure of the gas with which it is in equilibrium". That is,

        $m \propto P$,   when T is constant.
or,   m = K P,   where K is called Henry's constant.
It remains constant for a gas in a solvent at a given T.

Validity of the law	This law is valid when the gas and the solution behave ideally.

Thus for real gases, the law holds good when the pressure is low and temperature is not very low. Further the dissolved gas neither reacts with the solvent nor dissociates or associates in the solution.

Nernst distribution law can be deduced from Henry's law.

Nernst distribution law from Henry's law.	The mass of the gas dissolved per litre of the solvent (may be read solution is very dilute to behave ideally) is directly proportional to the molar concentration (c_2)

      i.e. m = c_2 M_2, where M_2 is the molar mass of the gas (solute).

Again, the gas over the solution is ideal so, P = c_1 RT, where, c_1 is molar conc. of the gas.

Putting in Henry's law, c_2 M_2 = K c_1 RT or, $\dfrac{c_2}{c_1} = \dfrac{K \, RT}{M_2}$,   or $\dfrac{c_2}{c_1} = K_d$.

This states that conc. of the substance in liquid phase bears a constant ratio with that in the gas phase at constant temperature.
This is Nernst distribution law and K_d is Nernst distribution coefficient of the substance between liquid phase and the gas phase.

Problem :

(1) At 20°C, the V P of benzene is 74.7 torr and toluene is 22.3 torr. A certain solution of benzene and toluene at the same T has a V P of 46.0 torr. Find the benzene mole-fraction in the solution and in the vapour above the solution.(Ph. Ch. – Levine).

Hints: Used eqn. $\rightarrow P = p_t^o + (p_b^o - p_t^o)x_b((sol)$, $p_b = p_b^o x_b(sol)$ and $p_b = x_b(vap) P$.

[**Ans.** $x_b(sol.) = 0.45$ and $x_b(vap.) = 0.73$].

(2) A solution of chloroform and ethanol at their mole-fractions of 0.01 and 0.99 respectively has a vapour pressure of 177.95 torr at 45°C, while pure ethanol has a vapour pressure of 172.76 torr. The solution is essentially ideally dilute. Find
  (i) the partial pressure of the component gases in equilibrium with their solution at 45°C.
  (ii) vapour pressure of pure chloroform at 45°C.
  Comment on the ideality/non-ideality of a 2 % solution of chloroform in ethanol at 45°C. Given that the experimental vapour pressure of the solution is 183.38 torr.

[IIT,KGP, Adm. to M Sc, 96]

Ans. (i) $p_c = p_c^o x_c = 692 \times 0.01 = 6.92 \, torr$ and $p_e = p_e^o x_e = 172.76 \times 0.99 = 171.03 \, torr$.

  2nd part $\rightarrow$ $P = p_c^o x_c + p_e^o x_e = 692 \times 0.02 + 172.76 \times 0.98 = 183.14 \, torr$.

  (ii) $P = p_c + p_e = p_c^o x_c + p_e^o x_e$ $or, 177.95 = p_c^o \times 0.01 + 172.76 \times 0.99$.

  or, $p_c^o = 692$ torr.

  The experimental value of total vapour pressure is also 183.38 torr.
  So, 2 mole percent solution of chloroform in ethanol is ideal.

(3) Show that two liquids (l_1 and l_2) are mixed in the weight ratio $w_1 : w_2$, then vapour pressure (P) of the mixture is

$P = \dfrac{w_1 M_2 p_1^o + w_2 M_1 p_2^o}{w_2 M_1 + w_1 M_2}$, where p^o is the vapour pressure of the pure liquid

M = molecular weight. **[IIT,KGP, Adm. to M Sc, 97]**

Ans. No. of moles of the two liquids in the mixture are $\dfrac{w_1}{M_1}$ and $\dfrac{w_2}{M_2}$ ratio.

$P = p_1^o x_1 + p_2^o x_2 = p_1^o \times \dfrac{n_1}{n_1 + n_2} + p_2^o \times \dfrac{n_2}{n_1 + n_2} = \dfrac{1}{n_1 + n_2}\left[p_1^o n_1 + p_2^o n_2 \right]$

$= \dfrac{1}{\dfrac{w_1}{M_1} + \dfrac{w_2}{M_2}}\left[\dfrac{w_1}{M_1} p_1^o + \dfrac{w_2}{M_2} p_2^o \right] = \dfrac{\left(w_1 M_2 p_1^o + w_2 M_1 p_2^o \right)}{\left(w_1 M_2 + w_2 M_1 \right)}$ proved.

(4) 5.0 gm of a mixture of two non-volatile non-electrolyte solutes of MW 128 and 178 is dissolved in 250 gm of benzene. The solution started freezing at 4.8°C. If the normal freezing point of benzene is 5.5°C and its molal freezing point depression constant is 5.1°C Kg/mol, find the composition of the mixture by weight.

[IIT,KGP, Adm. to M Sc, 98]

Ans. Let x g of the 1st solute of MW 128 and (5-x) g of the 2nd solute is present in the solution. The molality of the solution, m $= \left(\dfrac{x}{128} + \dfrac{5-x}{178} \right) \times \dfrac{1000}{250} = \dfrac{4x}{128} + \dfrac{20-4x}{178}$.

Use $\Delta T_f = K_f m$ and find x = 2.8 g and 2nd solute = 2.2 g.

# NERNST'S DISTRIBUTION LAW:

Statement of the law

The law states that at constant temperature, when different quantities of a solute are allowed to distribute between two immiscible solvents in contact with each other then at equilibrium, the ratio of conc. of the solute in two layers is constant.

If I_2 solute remains in equilibrium between two immiscible solvents, benzene and water then the ratio of conc. of iodine in benzene, $[c_{I_2(b)}]$ and conc. of iodine in

Example of the law with solute I₂ in benzene and water

water, $[c_{I_2(w)}]$ remains constant at a given temperature.

$$\frac{c_{I_2(b)}}{c_{I_2(w)}} = K_d \text{ , called distribution constant of iodine}$$

between benzene and water
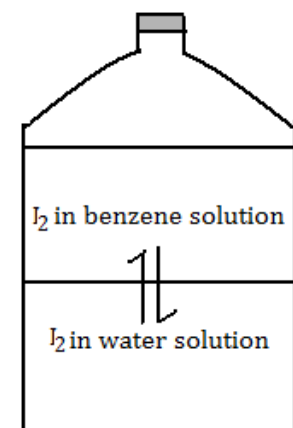
Same form of the solute in two immiscible solvents forming ideal solution.

Condition of validity of the law,

The essential precondition for the law to be valid are:

(1) The same molecular form of the solute should be present in both solvents.
(2) The solution should be ideal and it is to be dilute.
(3) The two solvents should be completely immiscible.

Derivation of the law:

If a solute X is distributed in the two solvents α and β constituting the two different phases, then chemical potential of the solute will be same in both the phases when it is in equilibrium

Thermodynamic condition for the solute to remain in equilᵐ. in the two phases.

That is,

$$\mu_{X(\alpha)} = \mu_{X(\beta)}$$

or,

$$\mu_{X(\alpha)}^0 + RT \ln a_{X(\alpha)} = \mu_{X(\beta)}^0 + RT \ln a_{X(\beta)}$$

or,

$$\ln \frac{a_{X(\alpha)}}{a_{X(\beta)}} = \frac{\mu_{X(\beta)}^0 - \mu_{X(\alpha)}^0}{RT}.$$

or,

$$\frac{a_{X(\alpha)}}{a_{X(\beta)}} = e^{\frac{\mu_{X(\beta)}^0 - \mu_{X(\alpha)}^0}{RT}} = K_d \text{ , called distribution constant}$$

When the solutions are dilute, it behaves ideal and activity is replaced by conc. and the law is written as, $\dfrac{c_{X(\alpha)}}{c_{X(\beta)}} = K_d$. This is Nernst distribution law. It is the distribution of of X between the phases α and β .

K_d is constant but it depends on temperature and the nature of the solute and the solvents.

Limitation of the law: Nernst also pointed out that if the solute undergoes dissociation or association, the form of the law becomes different. We can discuss the several cases considering the dissociation or association of the solute separately.

(a) Distribution of a solute with same molecular form in two phases:

When iodine is distributed between benzene and water, iodine remains in the same form in both the solvents and the law holds good, $K_d = \dfrac{c_1}{c_2}$, where, c_1 and c_2 are the molar conc. of iodine in benzene and water respectively.

This is also confirmed by experiment. Similar cases are found in the distribution of $HgBr_2$ in benzene and water, boric acid in water and amyl alcohol, H_2O_2 in water and ether etc.

(b) Distribution of a solute which dissociates in one of the phases:

This case is illustrated by the distribution of oxalic acid between ether and water. In ether layer, the molecular species remains unchanged and let its conc. is c_1. In aqueous solution, oxalic acid suffers dissociation as,

$$H_2Ox \rightleftharpoons HOx^- + H^+ .$$

Let c_2 is the molar conc. of oxalic acid in aqueous layer and α is the degree of dissociation at the conc., then conc. of molecular form of oxalic acid $= (1-\alpha)c_2$.

In this case c_1/c_2 will not be constant but the ratio of the conc. of undissociated molecules in the two solvents will be constant.

$$\frac{c_1}{(1-\alpha)c_2} = \text{constant } (K_d).$$

K_d is the distribution or partition constant of oxalic acid between ether and water. Degree of dissociation α can be obtained from the dissociation constant of oxalic acid using the relation,

$$K_a \approx \alpha^2 c .$$

(c) Distribution of a solute when it associates in one of the phases:

Let us suppose that there is no change in molecular species of the solute in solvent (1) but it undergoes association in solvent (2), yielding the associated form X_n, according to the equilibrium. $nX \rightleftharpoons X_n$.

Let c_2 is the molar conc. of X in solvent (2) and β is the degree of association, then at equilibrium,

$$[X] = c_2(1-\beta) \text{ and } [X_n] = \beta c_2/n$$

and the equilibrium constant, $K = \dfrac{c_{X_n}}{c_X^n} = \dfrac{\beta c_2/n}{\{c_2(1-\beta)\}^n}$ or, $c_2(1-\beta) = \left(\dfrac{\beta c_2}{nK}\right)^{1/n}$

The distribution constant, $K_d = \dfrac{c_1}{c_2(1-\beta)} = \dfrac{c_1}{\left(\dfrac{\beta c_2}{nK}\right)^{1/n}}$ or, $\dfrac{c_1}{\sqrt[n]{c_2}} = K_d\left(\dfrac{\beta}{nK}\right)^{1/n}$

If we assume that there is complete association ($\beta = 1$),

(c) Distribution of a solute when it associates in one of the phases:

Let us suppose that there is no change in molecular species of the solute in solvent (1) but it undergoes association in solvent (2), yielding the associated form X_n, according to the equilibrium. $nX \rightleftharpoons X_n$

Let c_2 is the molar conc. of X in solvent (2) and β is the degree of association, then at equilibrium,

$$[X] = c_2(1 - \beta) \quad \text{and} \quad [X_n] = \beta c_2/n$$

and the equilibrium constant, $\quad K = \dfrac{c_{X_n}}{c_X^n} = \dfrac{\beta c_2 / n}{\{c_2(1-\beta)\}^n} \quad$ or, $\quad c_2(1-\beta) = \left(\dfrac{\beta c_2}{nK}\right)^{1/n}$

The distribution constant, $\quad K_d = \dfrac{c_1}{c_2(1-\beta)} = \dfrac{c_1}{\left(\dfrac{\beta c_2}{nK}\right)^{1/n}} \quad$ or, $\quad \dfrac{c_1}{\sqrt[n]{c_2}} = K_d\left(\dfrac{\beta}{nK}\right)^{1/n}$

If we assume that there is complete association ($\beta = 1$),

then $\qquad \dfrac{c_1}{\sqrt[n]{c_2}} = K_d{}'$, a constant.

Taking log in both sides, it is possible to find the value of n by suitable plotting.

$$\log c_1 = \frac{1}{n}\log c_2 + \log K'_d$$
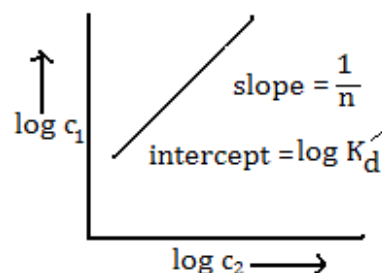
Example: Benzoic acid remains as dimmer in benzene and as monomer in water. The law is then

$$K'_d = \frac{c_1}{\sqrt{c_2}}$$

Applications of the distribution law:

(1) Solvent extraction:

The most important application of the law is the extraction of a solute from a solution by another immiscible solvent. This method is widely used both in laboratory and in industry. A solute is generally extracted from an aqueous solution with the help of suitable organic solvents such as benzene, ether, chloroform etc. These are called extracting solvents.

The extracting solvent should meet the following requirements.

(a) It should be completely immiscible with the aqueous solution.

(b) The solute should be more soluble in the extracting solvent.

(c) The extracting solvent should be volatile so that the solute can be recovered from it by warming the solution on a water bath.

On shaking the solution containing solute with the extracting solvent, there forms two layers. The layers are separated and non-aqueous solution is distilled to obtain the solute.

The extraction can be done in two ways:

(I) by using the entire volume of the extracting solvent in one lot, and

(II) by using the extracting solvent in fractional quantities and repeating the process of extraction several times .

It can be shown that stepwise extraction is more advantageous than the single step extraction. A general formula can be built up for the amount of solute remaining unextracted after a given number of operations.

Let V cc of a solution containing gms of substance be extracted with L cc of a solvent.

Let x_1 gms of the substance remains unextracted in aqueous layer.

Then, conc. of the substance in the solvent $= (x_0 - x_1)/L$ and in water $= x_1/V$. Then,

$$K_d = \frac{(x_0 - x_1)/L}{x_1/V} = \frac{(x_0 - x_1)V}{x_1 L} \quad x_1 K_d L = x_0 V - x_1 V \quad or, \quad x_1 = x_0\left(\frac{V}{V + K_d L}\right) = x_0\left[\frac{1}{1 + K_d\left(\frac{L}{V}\right)}\right]$$

$$x_1 = x_0\left[1 + K_d\left(\frac{L}{V}\right)\right]^{-1}$$

For extraction again with L cc solvent, the quantity unextracted (x_2)

$$x_2 = x_1\left[1 + K_d\left(\frac{L}{V}\right)\right]^{-1}$$

Now, inserting x_1 *from the above,* $\quad x_2 = x_o\left[1 + K_d\left(\frac{L}{V}\right)\right]^{-2}$

Similarly, after nth extraction, the quantity left behind would be

$$x_n = x_o\left[1 + K_d\left(\frac{L}{V}\right)\right]^{-n} \quad \textit{Fraction unextracted}, f_n = \frac{x_n}{x_o} = \left(1 + \frac{L}{K_d V}\right)^{-n}$$

If the entire quantity of the extracting solvent be used in one lot, the unextracted amount of the substance is,

$$x = x_o\left[1 + K_d\left(\frac{nL}{V}\right)\right]^{-1}, \quad \textit{Fraction unextracted in } \sin gle \textit{ lot extraction.} f_n = \frac{x_n}{x_o} = \left(1 + \frac{L}{K_d V}\right)^{-n}$$

Since the quantity within bracket is less than unity, x_n is smaller than x To get the extraction most efficient x_n should have the smallest possible value. This happens only if the term within the bracket is as high as possible. This is possible when n has largest possible value.

So it follows that multi step extraction is more economical than the single step extraction. However complete extraction is impossible.

This could be shown by expanding the polynomial $\frac{x_o}{x_n} = \left[1 + K_d\left(\frac{L}{V}\right)\right]^n$ and comparing with $\frac{x_o}{x}$.

One application is the desilverisation of lead. Ag is more soluble in Zn than Pb in molten state. Thus when Zn is added to argentiferous lead, a large quantity of Ag goes to molten Zn, leaving little Ag in the molten lead. K_d of Ag between Zn and Pb is 300 at 880°C.

Problem: The solubility of methylamine at 298 K in water is 8.49 times higher than in $CHCl_3$. Calculate the % of the base that remains unextracted in 1000 ml of $CHCl_3$ if it is extracted
(i) four times, always with 200 ml of water, (ii) two times, with 400 ml of water and (iii) once with 800 ml of water. Draw a conclusion from these results.

[B. U. (Old Reg), 2007].

Solution: Fraction of unextracted solute remaining after nth lot extraction is given by

$$f_n = \frac{x_n}{x_o} = \left(\frac{K_d V}{K_d V + L}\right)^n = \left(\frac{K_d V + L}{K_d V}\right)^{-n} = \left(1 + \frac{L}{K_d V}\right)^{-n},$$

where K_d is distribution of the solute between solution and extracting solvent, then $1/K_d$ is the distribution of the solute between extracting solvent and the solution. If this one is taken as K_d then the relation becomes

Extraction is more economical if small amount of solvent is used in several lots – the necessary formulation.

Application in desilverisation of lead

$$f_n = \left[1 + K_d\left(\frac{L}{V}\right)\right]^{-n}.$$

Now the fraction (and %) of unextracted solute remaining in $CHCl_3$ in the processes is

(i) $f_4 = \left[1 + 8.49\left(\frac{200}{1000}\right)\right]^{-4} = 0.0189 = 1.89\%$ · (ii) $f_2 = \left[1 + 8.49\left(\frac{400}{1000}\right)\right]^{-2} = 0.0517 = 5.17\%$

(iii) $f_1 = \left[1 + 8.49\left(\frac{800}{1000}\right)\right]^{-1} = 0.1283 = 12.83\%$

It is concluded from the results that using extracting solvent in fractional amount and repeating the process gives more extraction of the solute than taking whole amount of the solvent in one lot.

(2) Equilibrium constant from distribution law:

The equilibrium constant (K_c) of a reaction can be determined if one of the reacting component is soluble in two immiscible solvents. The following reaction can be taken as example. $KI + I_2 \rightleftharpoons KI_3$,

and the equilibrium constant, $K_C = \dfrac{[KI_3]}{[KI][I_2]}$

A solution of KI of known conc. (c) is taken in a stoppered bottle to which some iodine is added, and a portion of I_2 combines with KI to form KI_3. To this is then added some benzene, and the mixture is shaken for several hours at constant temperature until equilibrium is reached.
On standing, the mixture separates into two layers of benzene and water.
Only I_2 is distributed between benzene and water layers and KI_3 and KI are ionic compounds so they are not dissolved in benzene.
The conc. of iodine is determined in both the layers by titration with standard thiosulphate solution.

Let c_1 = conc. of iodine in benzene layer and c_2 = conc. of iodine in aqueous layer in mole /litre.
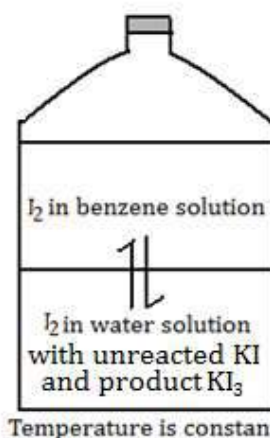
Thus, the distribution constant, $K_d = \dfrac{c_1}{[I_2]}$.   so, $[I_2] = \dfrac{c_1}{K_d}$.

Then, $[KI_3] = c_2 - \dfrac{c_1}{K_d}$ and if c is the molar conc. of KI taken

initially, then at equilibrium, $[KI] = c - \left(c_2 - \dfrac{c_1}{K_d}\right)$

Thus, the equilibrium constant $K_c = \dfrac{\left(c_2 - \dfrac{c_1}{K_d}\right)}{\left\{c - \left(c_2 - \dfrac{c_1}{K_d}\right)\right\} \times \dfrac{c_1}{K_d}}$

K_d of iodine between benzene and water is determined in a separate experiment.

I_2 in benzene solution

I_2 in water solution with unreacted KI and product KI_3

Temperature is constant

Only one of the reacting components should be soluble in two immiscible solvents.

(3) Determination of hydrolysis constant and degree of hydrolysis of a salt:

If one of the reacting components of hydrolysis of a salt is soluble in an immiscible solvent like benzene while others are not, this method can be utilized to evaluate the hydrolysis constant of a salt like aniline hydrochloride, ammonium chloride etc.

$$C_6H_5NH_2.HCl + H_2O \rightleftharpoons C_6H_5NH_2 + (H_3O^+Cl^-)$$

If an aqueous solution of the salt is shaken with benzene, aniline gets distributed between water and benzene whereas the salt and HCl are insoluble in benzene and remains in water solution.

The hydrolysis constant, $K_h = \dfrac{[C_6H_5NH_2][HCl]}{[C_6H_5NH_2.HCl]}$

Let, the distribution coefficient, $K_d = \dfrac{c_{a(b)}}{c_{a(w)}}$. So, $c_{a(w)} = \dfrac{c_{a(b)}}{K_d} = \dfrac{c_1}{K_d}$

where, $c_1 =$ conc. of aniline in benzene layer.

Thus $[C_6H_5NH_2] = c_1/K_d$, $[HCl] = c_1 + c_1/K_d$ and $[C_6H_5NH_2.HCl] = c - (c_1 + c_1/K_d)$,

where, c = initial conc. of the alt taken

Thus, the hydrolysis constant of the salt, $K_h = \dfrac{\left(\dfrac{c_1}{K_d}\right)\left(c_1 + \dfrac{c_1}{K_d}\right)}{\left\{c - \left(c_1 + \dfrac{c_1}{K_d}\right)\right\}}$.

The degree of hydrolysis, x is obtained from the relation, $K_h \approx x^2 c$

(4) Determination of the co-ordination number of the complex salt :

The co-ordination number of the complex salt can also be ascertained and this is illustrated by an example worked out as below :

Worked – out example:

Two bottles, each containing about 30 ml of $CHCl_3$, were marked I and II. Then some quantity of aqueous ammonia solution was added to bottle I. To bottle II, 30 ml aqueous ammonia solution and 5 ml of 0.3(M) $CuSO_4$ solution were added. Two bottles were then vigorously shaken until partition equilibrium was established in each of the bottles.

The ammonia in each layer in the bottles was then titrated with standard H_2SO_4 solution and the following results were obtained (for exact neutralization).

[BU ' 2001, Q6(a), m = 10].

Bottle I

     5 ml of aqueous layer required 10.15 ml of 0.908 (N/2) H_2SO_4

     5 ml of $CHCl_3$ layer required 5.10 ml of 0.908 (N/20) H_2SO_4

Bottle II

     5 ml of aqueous layer required 9.15 ml of 0.908 (N/2) H_2SO_4

     5 ml of $CHCl_3$ layer required 3.65 ml of 0.908 (N/20) H_2SO_4

Find the co-ordination number of Cu^{+2} ion in the blue complexed formed in the aqueous layer of bottle II

Bottle I: $\quad c_{NH_3(w)} = \dfrac{10.15 \times 0.908(N/2)}{5}$ and $c_{NH_3(c)} = \dfrac{5.10 \times 0.908(N/20)}{5}$.

Solution:

The distribution coefficient , $K_d = \dfrac{c_{NH_3(w)}}{c_{NH_3(c)}} = \dfrac{10.15 \times 0.908(N/2)/5}{5.10 \times 0.908(N/20)/5} = 20$

Bottle II $c_{NH_3(w)} = \dfrac{9.15 \times 0.908(N/2)}{5} = 0.831(N) = 0.831$ (M) since for NH_3, normality and

molarity are same. Thus, $c_{NH_3(w)}[free] + c_{NH_3(w)}[complexed] = 0.831(M)$.

$$c_{NH_3(c)} = \dfrac{3.65 \times 0.908(N/20)}{5} = 0.033(M) ,$$

So, $c_{NH_3(w)}[free] = K_d \times c_{NH_3(c)} = 20 \times 0.033 = 0.66(M)$

The conc. of complexed NH_3 in the aqueous layer $= 0.831 - 0.66 = 0.171(M)$.

Again in the aqueous layer, $c_{Cu^{+2}} = \dfrac{5 \times 0.30}{(30+5)} = 0.043(M)$.

Thus in the aqueous layer. $\quad c_{Cu^{+2}} : c_{NH_3(w)}[complexed] = 0.043 : 0.171 = 1 : 4$.

So the co-ordination number of Cu^{+2} ion $= 4$.

Problem: The distribution ratio of NH_3 between water and chloroform at 291K is 25.8. When a 0.0225 mol dm^{-3} CuSo$_4$ was equilibriated with NH_3 and chloroform the aqueous and CHCl$_3$ layer contained 0.385 mol dm^{-3} and 0.0112 mol dm^{-3} of NH_3 respectively. Determine how much of NH_3 is complexed with Cu^{+2} ion and the value of x in the formula $[Cu(NH_3)_x]^{+2}$.

Solution: $c_{NH_3(w)}(complexed) = 0.389 - 0.289 = 0.096 \ mol \ dm^{-3}$

as, $c_{NH_3(w)}(free) = 25.8 \times 0.0112 = 0.289 \ mol \ dm^{-3}$. The value of $x = 0.096 \Big/ 0.0225 = 4$.

COLLIGATIVE PROPERTIES OF DILUTE SOLUTIONS :

Definition of the Colligative properties.

When a non-volatile solute is dissolved in volatile solvent, some properties of the solvent are changed. Vapour pressure of the solvent is lowered, boiling point is elevated, freezing point is depressed and there develops an osmotic pressure if the solvent is separated from its solution by semi permeable membrane. These properties viz. relative lowering of vapour pressure, elevation of boiling point, depression of freezing point and osmotic pressure of the solution are called Colligative properties. These properties do not depend on the nature of the solute but depend only on the number of solute molecules (or particles) relative to the total number of molecules (i.e. depend on the relative collection of particles in the solution – hence the name Colligative prosperity).

Chemical potential of the solvent in solution is lower than that of the pure solvent.

All these properties are originating from one common cause and that is the lowering of chemical potential of the solvent in solution. This can be understood

$$\mu_1(T,P) = \mu_1^o(T,P) + RT \ln x_1$$

$\mu_1(T,P)$ is the chemical potential of the solvent in solution with mole-fraction, x_1 at temperature T and pressure P.

$\mu_1^o(T,P)$ is the chemical potential of the pure solvent ($x_1 = 1$) at the same temperature and same pressure.

$$\text{Since } x_1 \langle 1, so, \mu_1(T,P) \langle \mu_1^o(T,P)$$

This means that chemical potential of the solvent in solution is lower than that of the pure solvent We shall study the above properties in details provided the following conditions are being maintained.

(1) The solution behaves ideal and this may happen when the solution is kept dilute. Condition of dilute solution is necessary as vapour pressure curves of non-ideal solutions coincide with Raoult's law curves only when the solution is dilute.

(2) The solute is non-volatile so that the vapour over the solution is only due to solvent alone. The solute is also taken non-electrolyte in the present discussion.

Lowering of chemical potential is an entropy effect.

Lowering of chemical potential of the solvent in solution is the entropy effect.
When the solute is added to the solvent, the randomness of the solvent increases.
This results an increase of entropy of the solvent. Since enthalpy remains same for ideal solution, the chemical potential of the solvent is lowered.

This lowering of chemical potential decreases the escaping tendency of the solvent to the vapour state and vapour pressure of the solvent is lowered.

$$\mu_1 = \overline{H_1} - T\overline{S_1}$$

$\overline{S_1}$ is increased so μ_1 is decreased as $\overline{H_1}$ remains cons$\tan t$.

The lowering of chemical potential of the solvent in solution gives rise to elevation of BP and depression of FP of the solution.

Chemical potential of the solvent vs. T plots show that BP is elevated and FP is depressed in solution.

This is nicely shown in the adjoining figure, chemical potential vs. temperature for the solvent in solid, liquid and vapour in pure state and in solution.
This figure clearly shows that BP is elevated, FP is depressed and

$$\Delta T_f \, \rangle \, \Delta T_b.$$

FP depressed   BP elevated
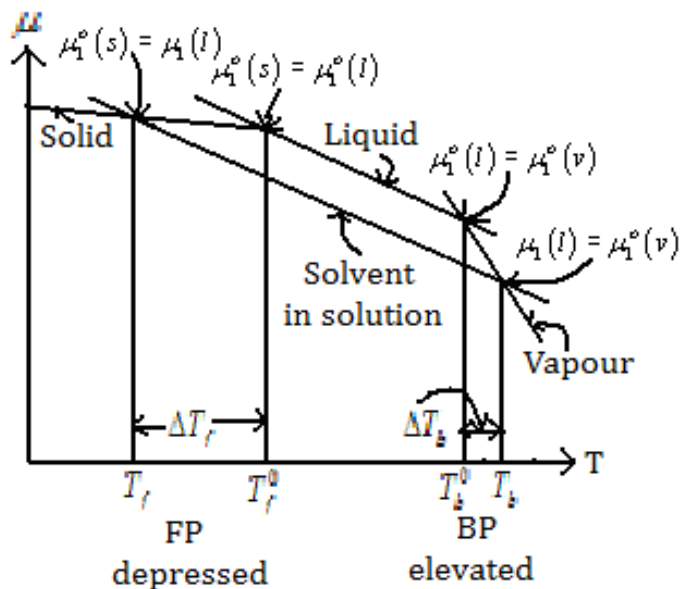
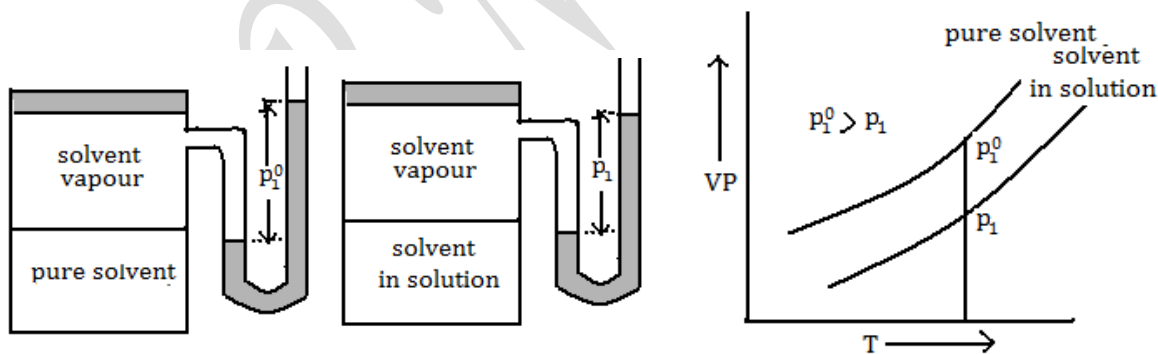## RELATIVE LOWERING OF VAPOUR PRESSURE (R L V P) :

When a non-volatile solute is dissolved in volatile solvent, the vapour pressure of the solvent is lowered. If p_1 and p_1^o the vapour pressures of the solvent over the solution and pure solvent, then $p_1^o \, \rangle \, p_1.$

What is meant by the property?

Vapour pressure of a liquid increases with increase of temperature according to the

C-C eqn. relates the variation of p with T

Clausius-Clapeyron equation, $p = A \, e^{-\bar{L}_{vap}/RT}$. The slope varies with T as $\dfrac{d \ln p}{dT} = \dfrac{\bar{L}_{vap}}{RT^2}$

Slope of p vs.T plot decreases with T according to the above relation.

$p_1^o - p_1 =$ lowering of vapour pressure of the solvent and $\dfrac{p_1^o - p_1}{p_1^o}$ is the relative lowering of vapour pressure of the solvent in solution.

This is a Colligative property and it depends on the number of solute molecules relative to the total number of molecules in the solution. It does not depend on the nature of the solute particles. This lowering of vapour pressure originates from the lowering of chemical potential of the solvent due to addition of solute.

Raoult's law of relative lowering of vapour Pressure.

Relating experimental law :

Raoult's law states that relative lowering of vapour pressure is equal to the mole-fraction of the solute (x_2) in the solution provided that the solution is ideal and solute is non-volatile and non-electrolyte. That is, $\dfrac{p_1^o - p_1}{p_1^o} = x_2$

This relation shows that RLVP is independent of temperature as x_2 is independent of temp..

It can be shown that this RLVP is Colligative property. Since, $x_2 = \dfrac{n_2}{n_1 + n_2}$.

But the solution is dilute, hence $n_1 \rangle\rangle n_2$ so, the Raoult's law is, $\dfrac{p_1^o - p_1}{p_1^o} \approx \dfrac{n_2}{n_1}$.

This means that equimolar of different solutes (n_2) dissolved in the same quantity (n_1) of a given solvent will have the same amount of relative lowering of vapour pressure. Hence it is a Colligative property since it does not depend on the nature of the solute particles.

Application of the law: Molar mass of the solute (M_2) can be determined by determining the RLVP of solution of known composition using the Raoult's law.

Determination of molecular weight of solute.

$$\frac{p_1^o - p_1}{p_1^o} \approx \frac{n_2}{n_1} \approx \frac{w_2/M_2}{w_1/M_1} = \frac{w_2 \times M_1}{w_1 \times M_2} \quad \text{or,} \quad M_2 = \frac{w_2 \times M_1}{M_1 \times \left(\dfrac{\Delta p_1}{p_1^o}\right)} .$$

Experimental determination of RLVP of a solution :

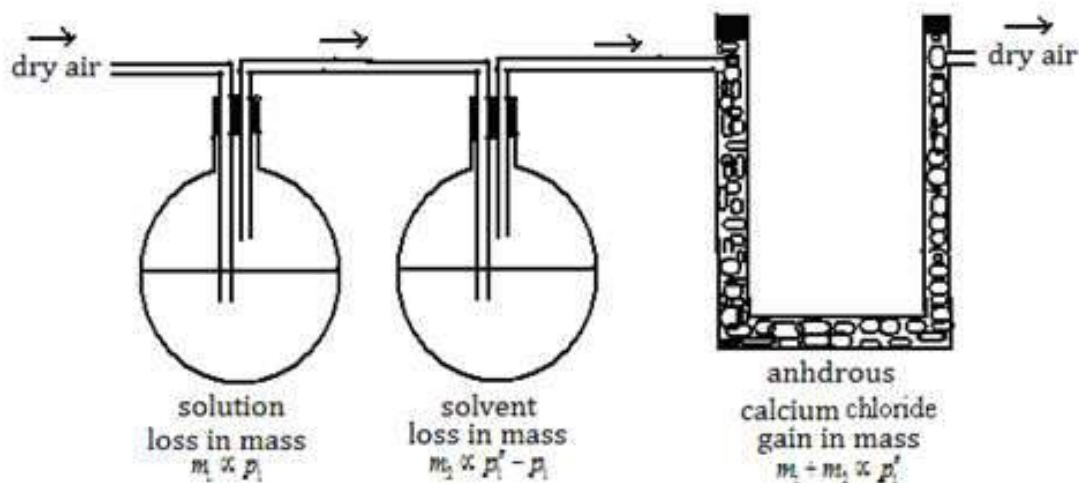Several methods are there, out of which one method is discussed.

Ostwald and Walker method:

Ostwald and Walker method for determination of RLVP of a solution.

Dry air is passed through the solution then it is saturated with solvent vapour (water is taken as solvent) up to the vapour pressure p_1. The loss of mass of the solution is m_1.

Then it is passed through the pure solvent (water) and it is further saturated up to the vapour pressure, p_1^o and the loss of mass of the solvent is m_2.

When it is passed through anhydrous $CaCl_2$ tube, the gain in mass of the tube = ($m_1 + m_2$).

dry air

solution
loss in mass
$m_1 \propto p_1$

solvent
loss in mass
$m_2 \propto p_1^o - p_1$

anhdrous
calcium chloride
gain in mass
$m_1 + m_2 \propto p_1^o$

dry air

$$RLVP = \frac{p_1^o - p_1}{p_1^o} = \frac{m_2}{m_1 + m_2} .$$ Thus getting the value of m_1 and m_2, RLVP

of the solution can be determined.

RLVP is temperature independent :

This is shown by the use of Clausius Clapeyron equation.

For pure solvent, the equation is, $\ln p_1^o = -\dfrac{\bar{L}_{vap}^o}{R}\left(\dfrac{1}{T}\right) + Const.$ or, $\dfrac{d \ln p_1^o}{dT} = \dfrac{\bar{L}_{vap}^o}{RT^2}$ ----(1)

Clausius – Clapeyron equation is used to prove the comment.

and for solvent in solution, the equation is, $\dfrac{d \ln p_1}{dT} = \dfrac{\bar{L}_{vap}}{RT^2}$ ------ (2)

where, $\bar{L}_{vap}^o$ and $\bar{L}_{vap}$ are the molar latent heat of vaporization of the pure solvent and solvent in solution.

Subtracting (2) from (1), we get, $\dfrac{d \ln p_1}{dT} - \dfrac{d \ln p_1^o}{dT} = \dfrac{\bar{L}_{vap} - \bar{L}_{vap}^o}{RT^2}$

or, $\dfrac{d \ln\left(p_1 \big/ p_1^o\right)}{dT} = -\dfrac{\bar{L}_{vap}^o - \bar{L}_{vap}}{RT^2}$ or, $\dfrac{d \ln\left(1 - \dfrac{p_1^o - p_1}{p_1^o}\right)}{dT} = -\left(\dfrac{\bar{L}_{vap}^o - \bar{L}_{vap}}{RT^2}\right)$

$\bar{L}_{vap}^0 = \bar{L}_{vap}$

for ideal solutions.

But, $\dfrac{p_1^o - p_1}{p_1^o} \langle\langle 1$ so, $-\dfrac{d\left(\dfrac{p_1^o - p_1}{p_1^o}\right)}{dT} = -\left(\dfrac{\bar{L}_{vap}^0 - \bar{L}_{vap}}{RT^2}\right) = 0.$

As, $\Delta H_{mixing} = 0$ for ideal solution so molar latent heat of vaporization of the solvent is equal to that of the solvent in solution. This shows that RLVP is independent of temperature.

Derivation of the law :

The law can be derived from the Raoult's law of vapour pressure as outlined earlier. This law is $p_1 = x_1 p_1^o$ or, $\dfrac{p_1}{p_1^o} = x_1$ or, $1 - \dfrac{p_1}{p_1^o} = 1 - x_1$ or, $\dfrac{p_1^o - p_1}{p_1^o} = x_2$

Thus the Raoult's law of RLVP is formulated from Raoult's law of vapour pressure.

Problems :

NET 2000

(1) The pressure of benzene is 400 torr at 60°C. The vapour pressure of a 0.1(M) solution of non-volatile compound in benzene at 60°C would be
(1) 404 torr   (2) 400 torr   (3) 396 torr   (4) 4 torr.   **[Ans. (3)]**

GATE 2005

(2) Change in chemical potential (in kJ mol^{-1}) for the equilibrium'
H_2O (liquid) $\rightarrow$ H_2O (gas) at 298 K is [VP of water at 298°C = 24 torr]
(a) 8.6   (b) -3.8   (c) 7.87   (d) 3.72.   **[Ans. (a)]**

GATE 2002

(4) The vapour pressure of ethanol at 20°C is 44.5 mm. When a 15 g of a non-volatile compound A is dissolved in 500 g of ethanol, the vapour pressure decreases to 43.5 mm. Calculate the molecular weight of A. (mark = 2).   **[Ans. 61.4]**

ELEVATION OF BOILING POINT OF A DILUTE SOLUTION (ΔT_b):

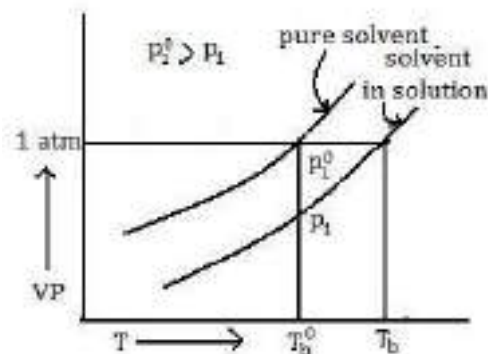|	
What is meant by the property?	Let T_b^0 is the boiling point of the pure solvent and T_b is that of the solution then, $T_b \rangle T_b^0$ and $T_b - T_b^0 = \Delta T_b$, called elevation of boiling point of the solution. It is a Colligative property of the solution.
	Elevation of boiling point of the solution can be understood by the following arguments. The liquid boils at a temperature when the vapour pressure of the liquid becomes equal to the super-incumbent pressure (1 atm usually). But due to addition of solute, the vapour pressure of
Occurrence of the property is explained by argument.	the solvent is lowered and since the solute is non-volatile, the vapour pressure over the solution is thus less than 1 atm at the boiling point of the solvent, (T_b^0). Thus temperature must be raised so that the vapour pressure over the solution becomes equal to 1 atm. The BP point of the solution becomes higher than that of the solvent.
	Alternatively, the elevation of BP can be explained by the VP vs. T diagram. For the diagram, following two facts are considered.
The property is explained by VP vs. T curve.	(1) VP of the solvent and solution increases with T according to the Clausius-Clapeyron equation. (2) VP of the solution is lower than that of pure solvent at any temperature. **Relating experimental law :**

Relating experimental law :

|	
Statement of Raoult's law of elevation of BP.	Raoult's law states that elevation of BP of a solution is directly proportional to the molal conc. of the solution (m). $\Delta T_b \propto m$ or, $\Delta T_b = K_b \, m$.
	Where, K_b is constant and called ebullioscopic constant.
Significance of K_b	It depends solely on the nature of the solvent. It can be defined as,
	$$K_b = \left(\frac{\Delta T_b}{m} \right)_{m \to 0} \qquad K_b = \text{i.e. } K_b \text{ is the elevation of BP of the solution at 1 molal conc.}$$
Validity of the law	This is why, it is called molal elevation constant of the solvent. This law is valid only when the solution is dilute so to behave ideally, and the solute is used non-volatile and non-electrolyte.
Alternative expression of the law	f w_2 gm of solute of molecular weight M_2 is dissolved in w_1 gm of the solvent, then he Raoult's law of elevation of BP becomes
	$$m = \frac{w_2 \times 1000}{w_1 \times M_2} \quad or, \quad \Delta T_b = K_b \times \frac{w_2 \times 1000}{w_1 \times M_2}.$$
The property is a Colligative in nature.	The equation $\Delta T_b = K_b \times m$, shows that equimolar of different solutes dissolved in a given quantity of a solvent elevates the boiling point to the same extent. This elevation of boiling point does not depend on the nature of the solute used in the solution. Hence it is a Colligative property of the solution. The cause of the property is due to lowering of chemical potential of the solvent by the added solute.
Application for determination of molecular weight of solute.	This property can be used to determine the molecular weight of the solute with the help of the relation, $$M_2 = K_b \times \frac{w_2 \times 1000}{w_1 \times \Delta T_b}.$$
	Knowing the composition of the solution and determining ΔT_b, the molecular weight of the solute can be determined.

Determination of ΔT_b of a solution:

Description of
Beckmann's
thermometer
and necessary
precautions to
be taken.

ΔT_b of dilute solution is very small of the order of 0.05^oC when water is used as solvent. So it cannot be recorded by ordinary thermometers.

Beckmann constructed a special kind of thermometer, called Beckmann thermometer.

It consists of two reservoirs of mercury. The lower reservoir is called bulb that connects with long narrow capillary tube. It consists of only six degrees; each is again divided by 100 small divisions so that one can read 0.01^o very accurately. Upper reservoir serves to keep excess mercury.

The thermometer is immersed in the boiling solvent and mercury is adjusted between the two reservoirs such that the mercury thread should stand in the middle of the scale.

Beckmann's
experimental
set-up for
determination of
elevation of BP.
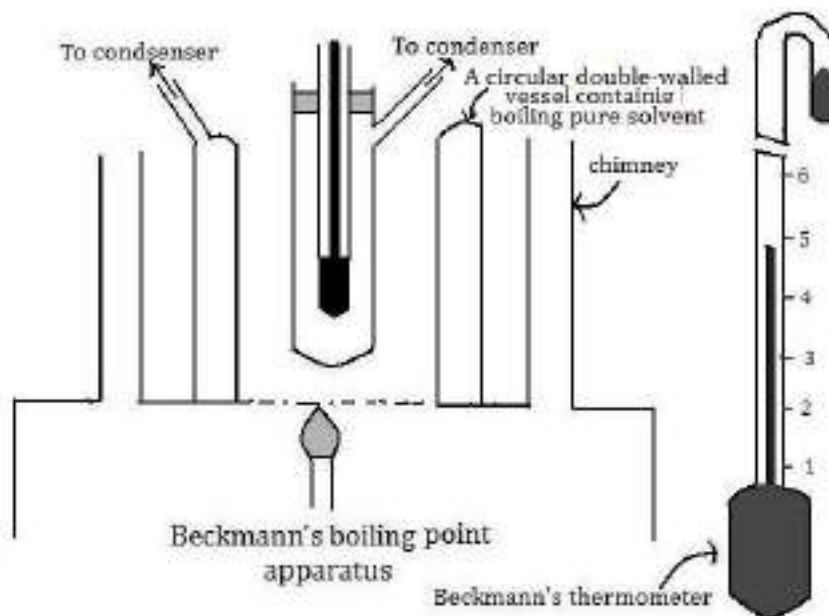
This is called 'setting of Beckmann thermometer'. Now some weighed amount of solute (w_2) is added to the solvent, stirred and the thermometer reading is recorded while it is boiling. The difference between the two readings is ΔT_b.

This thermometer cannot record the boiling point of the solvent or solution, it can only record the difference of temperature and so it is called differential thermometer.

Since the thermometer is dipped into the liquid to record the boiling point, necessary precautions are taken to prevent the superheating.

Derivation of the law:

(A) Using Clausius-Clapeyron equation:

Let us consider a solution of non-volatile non-electrolyte solute in volatile solvent. The chemical potential of the solvent in solution (μ_1) is related with that of pure solvent (μ_1^o) at constant temperature and pressure as,

$$\mu_1(T,P) = \mu_1^o(T,P) + RT \ln x_1.$$

Since $x_1 \langle 1$, hence the chemical potential of the solvent in solution is less than that of the pure solvent. The chemical potential is a measure of escaping tendency of the substance from the phase it exists, so vapor pressure over the solvent in solution (p_1) is lower than that of the pure solvent (p_1^o).

Again, when the vapor remains in equilibrium with the liquid solvent, vapor pressure increases with the increase of temperature. This can be explained by the Clapeyron equation as given below.

$$\ln p = -\frac{\bar{L}_v^o}{R}\left(\frac{1}{T}\right) + IC.$$

Thus, p increases with increase of T. With these two facts keeping in mind, it is possible to draw curve p vs. T as shown here. It is seen that the boiling point of solution is elevated

and the elevation of boiling point, $\Delta T_b = T_b - T_b^o$

Clausius- Clapeyron equation can be used to derive Raoult's law of elevation of boiling point of a solution,

$$\Delta T_b = K_b \times m$$

Where, K_b is molal elevation constant or called ebullioscopic constant of the solvent and m is concentration of the solution in molality.

Let us apply Clausius-Clapeyron equation for the equilibrium,

Solvent in solution $\square$ solvent vapour.

For the curve, DEF at the point E, the vapor pressure is p_1 at temperature T_b^0 and at the point F, the vapor pressure is p_1^o at the temperature, T_b.
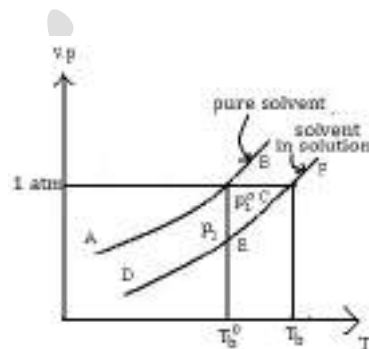
Thus the C-C equation is, $\quad \ln\dfrac{p_1}{p_1^o} = \dfrac{\bar{L}_v^o}{R}\left(\dfrac{T_b^o - T_b}{T_b T_b^o}\right).$

But, $T_b - T_b^o = \Delta T_b$, $\dfrac{p_1}{p_1^o} = x_1$ and since T_b and T_b^0 are close to each other, so $T_b \, T_b^0 = \left(T_b^o\right)^2$,

Putting in these, $\ln x_1 = -\dfrac{\bar{L}_v^o}{R} \times \dfrac{\Delta T_b}{\left(T_b^o\right)^2}$. But, $-\dfrac{\bar{L}_v^o}{R} \times \dfrac{\Delta T_b}{\left(T_b^o\right)^2}$ $\ln x_1 = \ln\left(1 - x_2\right) - x_2$, as, $x_2 \langle\langle 1$.

Thus, $\qquad x_2 = \dfrac{\bar{L}_v^o}{R} \times \dfrac{\Delta T_b}{\left(T_b^o\right)^2}$ $\qquad$ or, $\qquad \Delta T_b = \dfrac{R\left(T_b^o\right)^2}{\bar{L}_v^o} \times x_2$.

This is the relation between elevation of BP and mole-fraction of the solution. This relation is useful to interconnect different Colligative properties of a dilute solution.

Again, $\qquad x_2 = \dfrac{n_2}{n_1 + n_2} \approx \dfrac{n_2}{n_1} \approx \dfrac{w_2/M_2}{w_1/M_1} \approx \dfrac{w_2 \times M_1}{w_1 \times M_2}$

or, $\qquad \Delta T_b = \dfrac{R\left(T_b^o\right)^2}{\bar{L}_v^o} \times \dfrac{w_2 \times M_1}{w_1 \times M_2}$

or, $\qquad \Delta T_b = \dfrac{R\left(T_b^o\right)^2}{1000\left(\bar{L}_v^o/M_1\right)} \times \dfrac{w_2 \times 1000}{w_1 \times M_2}$

or, $\qquad \Delta T_b = \dfrac{R\left(T_b^o\right)^2}{1000 l_v^o} \times \dfrac{w_2 \times 1000}{w_1 \times M_2} \qquad$ or, $\Delta T_b = K_b \times m$

Where, $K_b = \dfrac{R\left(T_b^o\right)^2}{1000\, l_v^o}$, molal elevation constant and is the property of the solvent only.

l_v is the latent heat of vaporization of the solvent per gm and $m = \dfrac{w_2 \times 1000}{w_1 \times M_2}$, molality

of the solution. Thus Raoult's law of elevation of dilute solution is derived.

Several assumptions and approximations are used for the derivation of the law.

Assumptions:

Assumptions and approximations used in the derivation.

(1) The solution is assumed ideal so it is valid only for very dilute solution.
(2) The solute is non-volatile and so the vapour contains solvent in pure state.
(3) The solute is also taken non-electrolyte.

Approximations:

(1) $\ln(1 - x_2) \approx x_2$ *and* $x_2 \approx \dfrac{n_2}{n_1}$, since the solution is very dilute.

(2) $\bar{L}_v^o$ is taken independent of temperature over the temperature range.

(3) $T_b^0 T_b \approx \left(T_b^0\right)^2$ as temperatures are very close to each other.

(B) Using the concept of chemical potential:

Thermodynamic condition for solvent to remain in equil^m. between two phases.

Let us consider a cylinder, covered by a piston and it contains a solution of non-volatile solute in equilibrium with the vapour of the solvent. Since the solvent is in equilibrium in the two phases viz. vapour and liquid,

so $$\mu_1^o(v) = \mu_1(l),$$

where, $\mu_1^o(v)$ = chemical potential of the solvent in vapour phase

and $\mu_1(l)$ = that of solvent in the solution of mole fraction, x_1 .

vapour of the sovent

$\mu_1^o(v)$

$\mu_1(l)$

solution of non-volatile solute
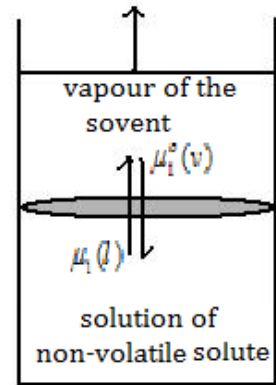
Writing the expression of $\mu_1(l)$, we have, $\mu_1^o(v) = \mu_1^o(l) + RT \ln x_1$.

Rearranging the equation and dividing by T,

$\dfrac{\mu_1^o(v)}{T} - \dfrac{\mu_1^o(l)}{T} = R \ln x_1$. Now, differentiating with respect to T at constant P,

$$\left[\frac{\partial}{\partial T}\left\{\frac{\mu_1^o(v)}{T}\right\}\right]_P - \left[\frac{\partial}{\partial T}\left\{\frac{\mu_1^o(l)}{T}\right\}\right]_P = R\left[\frac{\partial}{\partial T}\{\ln x_1\}\right]_P$$

Using Gibbs-Helmholtz equation,

Gibbs-Helmholtz equation is used for the formulation.

$$\left[-\frac{\bar{H}_1^0(v)}{T^2}\right]_P - \left[-\frac{\bar{H}_1^0(l)}{T^2}\right]_P = R\left[\frac{\partial}{\partial T}\{\ln x_1\}\right]_P$$

or,
$$-\left[\frac{\bar{H}_1^0(v) - \bar{H}_1^0(l)}{T^2}\right] = R\left[\frac{\partial}{\partial T}\{\ln x_1\}\right]_P .$$

But $\bar{H}_1^0(v) - \bar{H}_1^0(l) = \Delta\bar{H}_1^0(vap)$, molar enthalpy of vaporization or called molar latent heat

of vaporization of the solvent, $\bar{L}_v$

Thus, $-\dfrac{\bar{L}_v^o}{RT^2} = \dfrac{d \ln x_1}{dT}$. Integrating within limits, $-\dfrac{\bar{L}_v^o}{R}\displaystyle\int_{T_b^o}^{T_b} \dfrac{dT}{T^2} = \displaystyle\int_1^{x_1} d \ln x_1$.

$\bar{L}_{vap}$ is assumed to be independent of T between small range of T_b and T_b^o

Or, $-\dfrac{\overline{L}_v^o}{R}\left[-\dfrac{1}{T}\right]_{T_b^0}^{T_b} = \ln x_1 - 0$ or, $-\dfrac{\overline{L}_v^o}{R}\left[\dfrac{1}{T_b^o}-\dfrac{1}{T_b}\right]=\ln(1-x_2)$. But for dilute solution, $x_2 \langle\langle 1$

so, $-\dfrac{\overline{L}_v^o}{R}\left[\dfrac{T_b - T_b^o}{T_b T_b^o}\right]=-x_2$, again T_b and T_b^o are close to each other so $\dfrac{\overline{L}_v^o}{R}\dfrac{\Delta T_b}{\left(T_b^o\right)^2}=x_2$.

This can be used to get Raoult's law of elevation of boiling point, $\Delta T_b = K_b \times m$.

<table>
<tr><td>Calculation
of
K_b of water.</td><td>

Problem: Calculate the value of K_b of water.

We have the relation, $\quad K_b = \dfrac{R\left(T_b^o\right)^2}{1000\, l_v^o} = \dfrac{2\ cal\ mol^{-1}K^{-1}\times(373K)^2}{1000\ gm\ Kg^{-1}\times 540\ cal\ mol^{-1}} = 0.51\ K\ Kg\ mol^{-1}$.

</td></tr>
</table>

What happens when the solute is volatile?

The vapour in this case contains both the solvent and solute.
Let the mole fraction of the solvent in the solution and in the vapour are x_1 and x_1' respectively.
Since the solvent vapour remains in equilibrium with that in solution, hence

$$\mu_1(v) = \mu_1(l)$$

or, $\qquad\qquad \mu_1^0(v) + RT\ln x_1' = \mu_1^0(l) + RT\ln x_1$

or, $\qquad\qquad \dfrac{\mu_1^0(v)-\mu_1^0(l)}{T} = R\ln x_1 - R\ln x_1'$.

Differentiating with respect to T at constant pressure and using Gibbs Helmholtz equation,

$$\Delta T_b = \dfrac{R\left(T_b^0\right)^2}{\overline{L}_v}x_2\left(1-\dfrac{x_2'}{x_2}\right) \quad\text{or, } \Delta T_b = K_b\,m(1-k)\text{, where, } k=\dfrac{x_2'}{x_2} .$$

With this equation we may consider three cases.
(1) When $x_2' = 0$, it means that the solute is non-volatile, k = 0 and $\Delta T_b = K_b \times m$.
     Raoult's law is obeyed.

<table>
<tr><td>BP of the solution
may be depressed
if the solute is
more volatile than
the solvent.</td><td>

(2) $x_2' \langle x_2$, $\ k < 1\ $ and $\ \Delta T_b \langle K_b \times m$, that is elevation of BP is less than that expected
                                    from Raoult's law when the solute is non-volatile.
(3) $x_2' \rangle x_2$, that is solute is more volatile than the solvent, k > 1 and $\Delta T_b = (-)ve$
   But $\Delta T_b = T_b - T_b^0$, it means $T_b \langle T_b^0$. The BP of the solution is depressed when the
   solute is more volatile than the solvent.

</td></tr>
</table>

<table>
<tr><td>**BU' 94**</td><td>

To show that for a solution of a solute in a non polar solvent in a particular conc., $\dfrac{\Delta T_b}{T_b^0}$ is

independent of the nature of the solvent. State also the assumptions involved.

</td></tr>
<tr><td>**Solution:**</td><td>

We have Raoult's law of elevation of BP, $\Delta T_b = K_b \times m$.

Where, $\qquad K_b = \dfrac{R\left(T_b^o\right)^2}{1000\, l_v}$ and $m = \dfrac{w_2 \times 1000}{w_1 \times M_2}$.

Putting these expressions in the Raoult's law,

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</table>

Trouton's rule is utilized.

$$\Delta T_b = \frac{R\left(T_b^o\right)^2}{1000\, l_v^o} \times \frac{w_2 \times 1000}{w_1 \times M_2} \quad \text{or,} \quad \Delta T_b = \frac{R\left(T_b^o\right)^2}{\overline{L}_v^o} \times \frac{w_2 \times M_1}{w_1 \times M_2} \quad \text{or}$$

$$\Delta T_b = \frac{RT_b^o}{\left(\overline{L}_v^o \Big/ T_b^0\right)} \times \frac{n_2}{n_{1\,1}} - 0 . \text{But,} \quad \overline{L}_v^o \Big/ T_b^0 \text{ is constant for non-polar solvent according to the}$$

Trouton's rule. Therefore, $\dfrac{\Delta T_b}{T_b^o} = \dfrac{R}{21} \times x_2$. Since the solution is dilute so $\dfrac{n_2}{n_1} = \dfrac{n_2}{n_1 + n_2} = x_2$.

$\dfrac{\Delta T_b}{T_b^o}$ is constant for particular conc. (x_2) of the solution and independent of the nature of the

solvent. The assumption involved is that $\overline{L}_v \Big/ T_b^0 = \Delta \overline{S}_{1(at\,boiling\,point)} \approx 21$ for non-polar solvents.

DEPRESSION OF FREEZING POINT OF A DILUTE SOLUTION (ΔT_f) :

Freezing point of the solution is depressed.
$T_f^0 \rangle T_f$

If T_f^0 is the freezing point of a pure solvent and T_f is that of a solution of a non-volatile solute and only solid solvent separates from the solution at the freezing point, then

$$T_f^0 \rangle T_f .$$

It means there is a depression of freezing point of the solution. And $T_f^0 - T_f = \Delta T_f$, called depression of freezing point of the solution. The depression of freezing point of a solution can be explained on the basis of VP vs. T curve considering the following points given below:

VP vs. T curve explains the depression of freezing point of the solution.

(1) VP increases with temperature.
(2) VP of solution is lower than that of pure solvent
(3) At 1 atm pressure, freezing point is given
    by the intersections of solid and dashed
    lines with the horizontal line at 1 atm pressure.
    The curve shows that $T_f^0 \rangle T_f$.
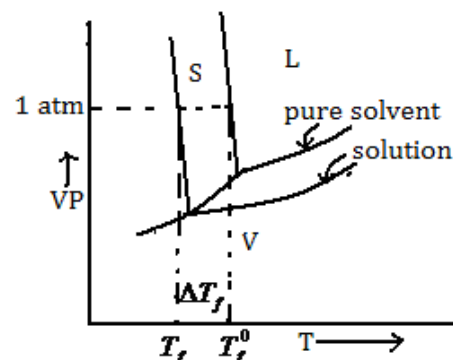
The curve shows that
$$T_f^0 \rangle T_f$$

Relating experimental law :

Raoult's law of depression of freezing point of a solution.

Raoult stated the law as, $\Delta T_f \propto m$ or, $\Delta T_f = K_f\, m$.

Where, K_f is called cryoscopic constant or molal depression constant of the solvent, and m = molality of the solution, if w_2 gm of the solute of molar mass M_2 is dissolved in w_1 gm of the solvent then, $m = \dfrac{w_2 \times 1000}{w_1 \times M_2}$. Then the law is $\Delta T_f = K_f \times \dfrac{w_2 \times 1000}{w_1 \times M_2}$.

It is a Colligative

ΔT_f is a Colligative property as equimolar quantity of different solutes dissolved in a given amount of a solvent depresses the freezing point to the same extent.

Molar mass of the solute can be determined.

Molar mass of the solute (M_2) can be obtained using the law by measuring the depression of freezing point of its solution of known composition.

$$M_2 = K_f \times \frac{w_2 \times 1000}{w_1 \times \Delta T_f}, \text{ where } K_f \text{ is the molal depression constant of the solvent.}$$

Determination of ΔT_f of a dilute solution :

(a) Beckmann's method:

Beckmann's thermometer is used to record the freezing point of a solution when K_f of the solvent is small. The thermometer is dipped directly in solvent in a tube and cooled by freezing mixture. The setting of the thermometer is such that Hg thread should stand in the middle of the scale when the pure solvent freezes.

The tube is warmed in hand, known amount of solute is added and then again allowed to freeze by freezing mixture. The difference of freezing point is recorded and it is ΔT_f.

(b) Rast's method:

For the solvent of K_f is high, ordinary thermometer can be used.

For example, in camphor solvent (K_f = 40 K Kg mol^{-1}) even in dilute solution, ΔT_f is high. Usually FP of pure camphor is first determined and then known amount of a known molar mass solute is added to a definite amount of camphor and melted.

The mixture is then cooled, powdered and subsequently FP is determined.

Value of K_f is thus determined. This is repeated with unknown molar mass solute.
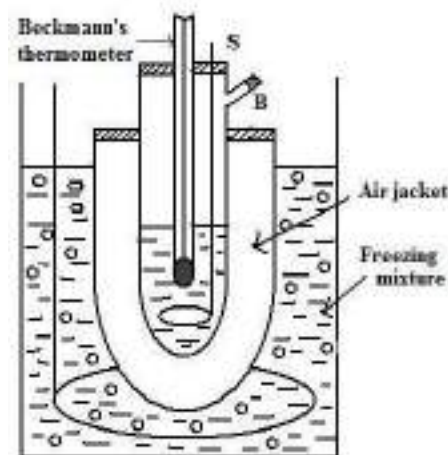
Derivation of Raoult's law of depression of FP of a dilute solution ($\Delta T_f = K_f \times m$) :

(A) Using the Clausius – Clapeyron equation:

Raoult's law can be derived by the use of Clausius – Clapeyron equation. Vapour pressure vs. temperature curves for solvent in solution, pure liquid solvent and pure solid solvent in equilibrium are given below. In the sublimation curve ABC, at the points B and C,

$$\ln \frac{p_s}{p_1^o} = -\frac{\bar{L}_s^o}{R}\left(\frac{1}{T_f} - \frac{1}{T_f^o}\right) = -\frac{\bar{L}_s^o}{R}\left(\frac{T_f^o - T_f}{T_f^o T_f}\right).$$

But T_f and T_f^o are close to each other

hence, $\quad \ln \frac{p_s}{p_1^o} = -\frac{\bar{L}_s^o}{R} \times \frac{\Delta T_f}{\left(T_f^o\right)^2}$. ---------- (A)

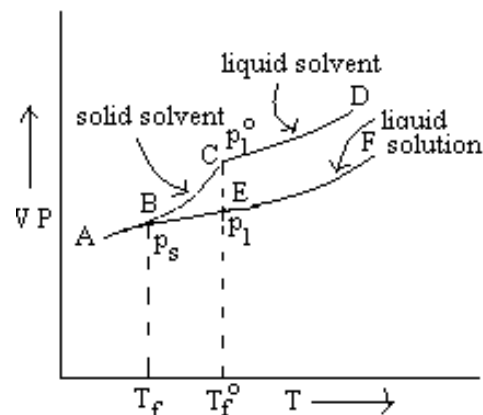Again in the vaporization curves BEF, at the points B and E, the C-C equation is,

$$\ln \frac{p_s}{p_1} = -\frac{\bar{L}_v^o}{R}\left(\frac{1}{T_f} - \frac{1}{T_f^o}\right)$$

or, $\quad \ln \frac{p_s}{p_1} = -\frac{\bar{L}_v^o}{R} \times \frac{\Delta T_f}{\left(T_f^o\right)^2}$. ---------- (B)

Taking difference of (A) and (B), we get $\quad \ln \frac{p_1}{p_1^o} \quad \left(\ R\ \right) \frac{}{\left(T_f^o\right)^z}$

But, $L_s - L_v = L_f$, molar latent heat of fusion of the pure solvent and $p_1 / p_1^o = x_1$,

so $\qquad$ inserting, we have $\ln x_1 = -\dfrac{\bar{L}_f^o}{R} \times \dfrac{\Delta T_f}{\left(T_f^o\right)^2}$.

Since $x_2 \langle\langle\, 1$ for dilute solution, $\ln x_1 = \ln\left(1-x_2\right) = -x_2$.

Therefore, $\qquad\qquad x_2 = \dfrac{\bar{L}_f^o}{R} \times \dfrac{\Delta T_f}{\left(T_f^o\right)^2}$.

This gives the relation between depression of FP and mole fraction of the solution. By the same previous way, we can proceed to arrive at the Raoult's law of depression of FP.

or, $\qquad\qquad \Delta T_f = \dfrac{R\left(T_f^0\right)^2}{1000\, l_f^o} \times \dfrac{w_2 \times 1000}{w_1 \times M_2}$

or, $\qquad \Delta T_f = K_f \times m \qquad$ where, $\qquad K_f = \dfrac{R\left(T_f^0\right)^2}{1000\, l_f^o} \qquad$ and $\quad m = \dfrac{w_2 \times 1000}{w_1 \times M_2}$.

(B) Using the concept of chemical potential:

Let us consider a solution in equilibrium with the solid solvent and solute is insoluble in solid solvent. Hence

$$\mu_1^0(s) = \mu_1(l) .$$

Where, $\mu_1(l) = $ chemical potential of the solvent in solution and

$\mu_1^0(s) = $ that of pure solid solvent.
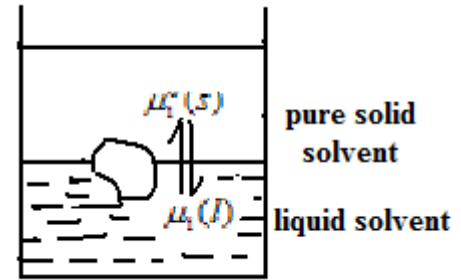
Solute is not soluble in solid solvent.

But, $\qquad \mu_1(l) = \mu_1^0(l) + RT \ln x_1$

so, $\qquad \mu_1^0(s) = \mu_1^0(l) + RT \ln x_1$

or, $\qquad \mu_1^0(s) - \mu_1^0(l) = RT \ln x_1$.

Dividing by T and differentiating with respect to T at constant P,

$$\left[\frac{\partial}{\partial T}\left\{\frac{\mu_1^o(s)}{T}\right\}\right]_P - \left[\frac{\partial}{\partial T}\left\{\frac{\mu_1^o(l)}{T}\right\}\right]_P = R\left[\frac{\partial}{\partial T}\left\{\ln x_1\right\}\right]_P$$

Using Gibbs Helmholtz equation and rearranging,

Gibbs-Helmholtz equation is used.

$$-\left[\frac{\bar{H}_1^0(s) - \bar{H}_1^0(l)}{T^2}\right] = R\frac{d\ln x_1}{dT} \qquad \text{or,} \qquad -\left[\frac{\Delta\bar{H}_1^0(fusion)}{RT^2}\right] = \frac{d\ln x_1}{dT}$$

.

Raoult's law,
$\Delta T_f = K_f \times m$
is derived

But, $\Delta\bar{H}_1^0(fusion) = -\bar{L}_f^o$, molar latent heat of fusion. So, $\dfrac{\bar{L}_f^o}{R}\displaystyle\int_{T_f^0}^{T_f}\dfrac{dT}{T^2} = \int_1^{x_1} d\ln x_1$.

or, $\dfrac{\bar{L}_f^o}{R}\left[-\dfrac{1}{T}\right]_{T_f^0}^{T_f} = \ln x_1 \quad$ or, $\quad -\dfrac{\bar{L}_f^o}{R}\left[\dfrac{T_f^0 - T_f}{T_f^0 T_f}\right] = \ln\left(1 - x_2\right) \quad$ or, $\quad -\dfrac{\bar{L}_f^o}{R}\dfrac{\Delta T_f}{\left(T_f^0\right)^2} = -x_2$

or, $\Delta T_f = \dfrac{R\left(T_f^0\right)^2}{\bar{L}_f^o} \times x_2$ (Used to connect other properties)

This can be used to derive the Raoult's law of depression of FP, $\Delta T_f = K_f \times m$

Problem: Calculate the freezing point depression constant (K_f) for pure water having latent heat of fusion if ice 1.436 Kcal/mole **[BU;98].**   **Ans.** 1.868 K Kg mol⁻¹.

Calculation of K_b of water.

What happens when the solute is soluble in solid solvent?

In this case, let x_1 and x_1' are mole fractions of the solvent in liquid solution and in solid solution respectively. Then, $\mu_1(s) = \mu_1(l)$.

Or $\mu_1^0(s) + RT \ln x_1' = \mu_1^0(l) + RT \ln x_1$

or, $\dfrac{\mu_1^0(s) - \mu_1^0(l)}{T} = R \ln x_1 - R \ln x_1'$

Differentiating with respect to T at constant pressure, P and using Gibbs Helmholtz equation,

$$-\left[\dfrac{\Delta \bar{H}_1^0(fusion)}{RT^2}\right] = \dfrac{d \ln x_1}{dT} - \dfrac{d \ln x_1'}{dT} .$$

But $\Delta \bar{H}_1^0(fusion) = -\bar{L}_f^o$. Integrating within limits,

$$\Delta T_f = \dfrac{R\left(T_f^0\right)^2}{\bar{L}_f^o} x_2 \left(1 - \dfrac{x_2'}{x_2}\right)   \text{or, } \Delta T_f = K_f \times m\,(1-k) .$$

Chances of elevation of FP of a solution.

When the solute is more soluble in solid solvent than in liquid solvent, $x_2' \rangle x_2$ and k > 1

and $\Delta T_f = (\square)ve$, or $T_f^0 - T_f = (-)ve$ or, $T_f \rangle T_f^0$.

In that case the freezing point of the solution is elevated instead of depression.
  Example, Cu – Ni alloy system, Ni is more soluble in solid Cu than in molten Cu.

Problem: Sulphur dissolves in benzene as S_x. A 0.25% solution shows $\Delta T_f = 0.05$ K.

Given that K_f for benzene is 5.0 K Kg mol⁻¹, find x. **[BU' 2002].**

Solution: Raoult's law is $\Delta T_f = K_f \times m$ where, $m = \dfrac{w_2 \times 1000}{w_1 \times M_2} = \dfrac{0.25g \times 1000g\, Kg^{-1}}{99.75g \times M_{S_x}}$.

But from the law, $m = \dfrac{\Delta T}{K_f} = \dfrac{0.05\,K}{5.0\,K\,Kgmol^{-1}} = 0.01\,mol\,Kg^{-1}$.

Thus, $\dfrac{0.25g \times 1000g\,Kg^{-1}}{99.75g \times M_{S_x}} = 0.01\,mol\,Kg^{-1}$ or, $M_{S_x} = 250$ g Kg⁻¹ .

But, $M_{S_x} = 32 \times x$.   So, $32 \times x = 250$ or $x \approx 8$.

THERMODYNAMICS OF TWO-PHASE EQUILIBRIUM − DR N C DEY   35

OSMOSIS AND OSMOTIC PRESSRE OF DILUTE SOLUTIONS

What is meant by the phenomenon, Osmosis

Abbe Nollet in 1746 observed that when a solution is separated from the pure solvent by a semi-permeable membrane (that allows through it only the solvent molecules), there is a spontaneous flow of solvent into the solution. This spontaneous flow of solvent to solution or from dilute solution to more concentrated solution through semi permeable membrane is called OSMOSIS.

Cause of osmosis.

Due to addition of solute to the solvent, chemical potential of the solvent is lowered. Thus the chemical potential of the pure solvent becomes greater than that of solvent in solution. This inequality of chemical potential drives the solvent from pure solvent side to the solution side spontaneously until it becomes equal.

Chemical potential of the pure solvent is greater than that of the solvent in solution.

Let the mole fraction of the solvent in solution is x_1 hence chemical potential of the solvent in solution, $$\mu_1(l) = \mu_1^0(l) + RT \ln x_1$$

Here $\mu_1^0(l)$ = Chemical potential of the pure solvent.

Since $x_1 < 1$, $ln\ x_1 = (-)ve$

so, $\mu_1^0(l) > \mu_1(l)$ at the same T and P.

As the solvent flows to the solution, there develops a hydrostatic pressure ($h\rho g$) on the solution side.

The flow of the solvent stops when the level on the solution side reaches a definite height (h).

This hydrostatic pressure developed to check the osmosis, is called osmotic pressure (π).

When the chem. pot. of the solvent is equal on the both sides, osmosis stops.

At this excess pressure on the solution side, chemical potential of the solvent becomes equal on the both sides.

$$\mu_1^0(T, P) = \mu_1(T, P + \pi).$$

Definition of osmotic pressure can be given in another way. When the solvent is separated from solution by semi permeable membrane (SPM) and both are under the P_0, there occurs osmosis. This flow of solvent due to osmosis can be checked by applying pressure from $P_0 \rightarrow P$ on the piston of the solution side.

Alternative definition of osmotic pressure.

Three cases we may consider.

(1) When $P - P_0 \langle \pi$, osmosis will still occur.

(2) When $P - P_0 = \pi$, osmosis stops.

(3) When $P - P_0 \rangle \pi$, back osmosis will develop,

Back osmosis and its practical applications.

i.e. solvent will flow from solution side to the solvent side. Taking advantage of back osmosis, common salt is extracted from sea water, drinking water is also collected from sea water etc.

If solvent is replaced by lower concentrated solution, same effect is observed. Two solutions having same osmotic pressures are called isotonic solutions. Red blood corpuscles do not change in appearance when placed in 0.85% NaCl solution. They have same osmotic pressures and are called isotonic solutions. Blood corpuscles swell and burst when placed in hypotonic solution and shrink in hypertonic solutions.

Isotonic solutions have same osmotic. pressure.

Another example is: a dry currant swells up in water but shrinks in concentrated NaCl solution.
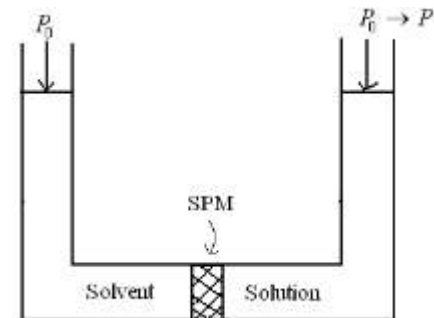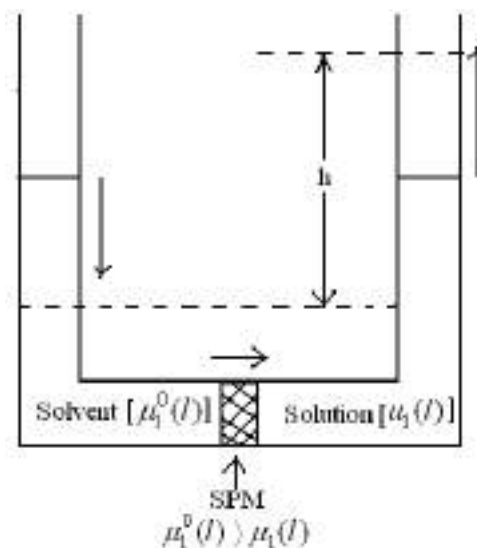
Semi permeable membrane:
Natural semi permeable membranes are egg-cell linings, fish bladder, parchment paper, plant cells etc. But these membranes can not withstand high pressure and so these are of not much practical use.

Artificial semi permeable membrane is prepared by the deposition of $Cu_2[Fe(CN)_6]$ on the pore channels of porous wall.
The process is accelerated by electrodeposition as shown in the adjoining
When electric field is applied, Cu^{+2} ions move towards the cathode and $[Fe(CN)_4]^{-4}$ ions moves owards the anode through the pore channels.
When the ions meet within the pores, they f precipitates and deposit on the pore channel
Electric bell rings so long the ions move through the wall.
When the pores are totally blocked by the precipitate $Cu_2[Fe(CN)_6]$, the ions fail to move through, the current stops and the bell also stops ringing. The preparation of the semi permeable membrane becomes complete. This type of membrane can withstand high pressure.

Related law (van't Hoff equation):

Studying osmotic pressure of different solutions of non-volatile and non-electrolyte solutes, van't Hoff established the following empirical laws.

(i) At constant temperature, osmotic pressure of dilute solution is directly proportional to its molar conc. (c).
$$\pi \propto c \text{ , when T is constant.}$$

(ii) At constant conc. of a solution, osmotic pressure is directly proportional to temperature,
$$\pi \propto T \text{ , when c is constant.}$$

When both the factors vary, we have $\pi = k\,c\,T$, where k is constant.
Evaluation of k is identical with unit and dimension of universal gas constant, R.
Thus, the van't Hoff equation of osmotic pressure is $\pi = c\,RT$,

c is molar conc. so $c = n/V$, hence the van't Hoff equation becomes $\pi V = n\,RT$

Again, $n = w_2/M_2$, so van't Hoff equation is $\pi V = \left(w_2/M_2\right)RT$.

This van't Hoff equation has got striking similarity with the ideal gas equation,
$$PV = nRT.$$

Where, n is the number of moles of the gas occupying V volume at temperature T and exerting the pressure P on the wall of the gas container. This amazing formal analogy makes van't Hoff to remark as,

"The osmotic pressure of a substance in solution is equal to the pressure it would exert if it were a gas occupying the same volume as that occupied by the same solution at the same temperature."

The solute molecules dispersed in the solvent are analogous to the gas molecules dispersed in empty space.

Let us consider an experiment in which the membrane is attached to a movable piston.
As the solvent diffuses through the membrane, the piston is pushed to the right; this continues until the piston is flushed against the right-hand wall. The observed effect is same as if the solution exerted a pressure against the membrane to push it to the right.
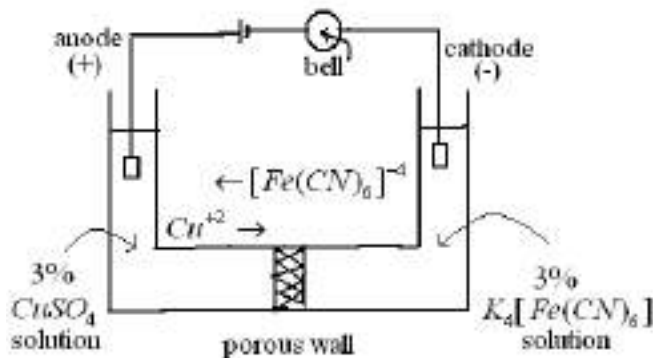
semi permeable membrane

solution (gas) | pure solvent (vacuum)

The situation is comparable to the free expansion of a gas into vacuum.
If the volume of the solution doubles in the experiment, the dilution will reduce the final pressure by half, just as the pressure of the gas is halved by doubling its volume.
In spite of the similarity, it is wrong to consider the osmotic pressure is a sort of pressure that is somehow exerted by the solute.

The analogy is deceptive.

Osmosis is the passage of solvent through the membrane and is due to the inequality of the chemical potential on the two sides of the membrane. The kind of membrane does not matter, it is necessary only that the solvent contains dissolved foreign matter which is not passed by the membrane.

It is a Colligative property – explanation.

The above equation $\pi = c\,RT$ shows that osmotic pressure of a solution depends on the conc. of the solution (relative number of solute particles to the total number of particles) and does not depend on the nature of the solute particles. Hence, it is a Colligative property of the solution.

Application of van't Hoff 's equation to determine molar mass of solute.

The above equation can be utilized to determine molar mass of the solute in the solution. The molar mass of the solute, $M_2 = \dfrac{w_2\,RT}{\pi V}$.

Measurement of osmotic pressure of the solution of unknown molar mass but known composition at a given temperature gives value of M_2.

Determination of osmotic pressure (π) of a solution:
Berkeley and Hartley's method:-

External pressure is applied on the solution side just to prevent the osmosis. This external pressure is osmotic pressure (π) of the solution.

The inner porcelain tube has electrically deposited copper ferrocyanide in the pores of its wall an membrane. At one end of the tube is fitted a capillary tube A and at other end, there is a tube leading to a funnel through a stop cock. A much wider gun metal tube B surrounds the inner tube and is tightly cemented to it. B is provided with a piston to which a pressure gauge (M) is attached.

Description of the experiment for determination of OP.

The annular space between the tubes is filled with solution, while inside the inner tube is introduced pure solvent up to a definite mark A in the capillary tube.

π, pressure gauze, A, solvent, solution, B

A pressure is applied on the piston so that the solvent level in the capillary remains constant. This pressure is recorded from the gauze is the osmotic pressure (π) of the solution.
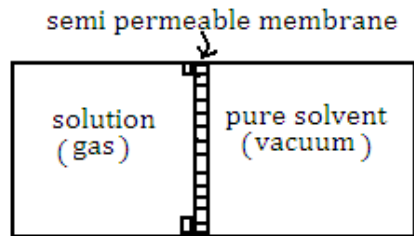
Thermodynamical derivation of van't Hoff's equation, $\pi = c\,RT$.

Osmosis is checked when the excess pressure, equal to osmotic pressure (π) is applied on the solution side. Under this condition, solvent on both sides remains in equilibrium.

Thermodynamic condition for the solvent in both sides to remain in equil^m.

$$\mu_1^0(T, P_0) = \mu_1(T, P_0 + \pi) .$$

Since, pure solvent under T and P_0 $\rightleftharpoons$ solvent in solution under T and $P_0 + \pi$.
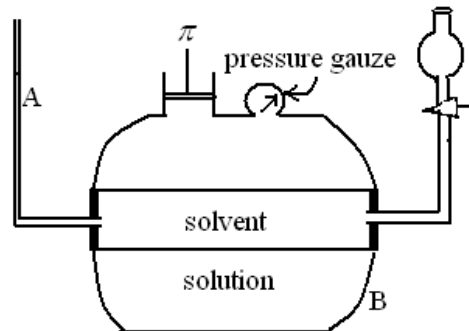But, $\mu_1(T, P_0 + \pi) = \mu_1^0(T, P_0 + \pi) + RT \ln x_1$.

Putting this expression in the above equilibrium equation and
$$-RT \ln x_1 = \mu_1^0(T, P_0 + \pi) - \mu_1^0(T, P_0).$$

Again, $\left(\dfrac{\partial \mu_1^0}{\partial P}\right)_T = \bar{V}_1^0$ or, $\displaystyle\int_{\mu_1^0(T, P_0)}^{\mu_1^0(T, P_0 + \pi)} d\mu_1^0 = \bar{V}_1^0 \int_{P_0}^{P_0 + \pi} dP$

$\mu_1^0(T, P_0) = \mu_1(T, P_0 + \pi)$

or, $\mu_1^0(T, P_0 + \pi) - \mu_1^0(T, P_0) = \bar{V}_1^0 \left(P_0 + \pi - P_0\right)$
$$= \bar{V}_1^0 \times \pi.$$

or, $-RT \ln x_1 = \bar{V}_1^0 \times \pi$, where $\bar{V}_1^0$ = molar volume of pure solvent.

Or, $\qquad -RT \ln(1 - x_2) = \pi \times \bar{V}_1^0 \qquad$ or, $RT\, x_2 = \pi \times \bar{V}_1^0$

or, $\pi \times \bar{V}_1^0 = RT\left(\dfrac{n_2}{n_1}\right)$, since the solution is dilute, so $n_1 \rangle\rangle\, n_2$ and thus $x_2 = \dfrac{n_2}{n_1 + n_2} \approx \dfrac{n_2}{n_1}$.

$\pi\left(\bar{V}_1^0 \times n_1\right) = n_2 RT$, again for dilute solution, $\bar{V}_1^0 \times n_1 = V^0$, volume of the solvent
$$\approx V,\ \text{volume of the solution.}$$

Thus, $\pi V = n_2 RT$ or, $\pi = \left(\dfrac{n_2}{V}\right) RT$ or, $\pi = c\, RT$.

Van't Hoff's equation of osmotic pressure is derived thermodynamically.
The following assumptions and approximations are used while the equation is derived.

Assumption: (1) Solution is assumed ideal and so $\mu_1 = \mu_1^0 + RT \ln x_1$ is used.

(2) Solvent is incompressible and so $\bar{V}_1^0$ is taken independent of pressure.

Approximation: (1) Solution is taken very dilute and so $\ln(1 - x_2) \approx -x_2$ and $x_2 \approx \dfrac{n_2}{n_1}$.

(2) The volume of the solvent is taken as the volume of the solution.

Inter-relation of different Colligative properties of a solution:

The mole fraction of solute (x_2) can be used as bridge to inter connect different Colligative properties of the solution.

$$x_2 = \frac{\Delta p_1}{p_1^0} = \frac{\bar{L}_{vap}}{R} \cdot \frac{\Delta T_b}{\left(T_b^0\right)^2} = \frac{\bar{L}_{fusion}}{R} \cdot \frac{\Delta T_f}{\left(T_f^0\right)^2} = \frac{\pi \bar{V}_1^0}{RT}.$$

ABNORMAL VALUES OF COLLIGATIVE PREOPERTIES:

The laws of Colligative properties are strictly valid for ideal solutions of non-volatile and non-electrolyte solutes. When these conditions are not obeyed, observed Colligative properties are found to deviate from the value obtained by calculation using the related laws. Van't Hoff 'i' factor is used to measure the extent of deviation and it is defined as,

$$i = \frac{observed\ colligative\ properties}{calculated\ colligative\ properties}$$

Side notes (left margin):

Chemical potential of the solvent (μ_1^0) is increased with increase of pressure at constant T.
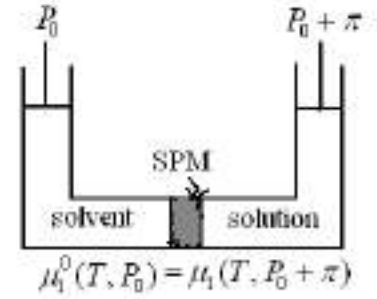
Assumptions and approximations used in the

Van't Hoff factor, i is used to measure the extent of deviation.

$$i = \frac{\left(\Delta p_1 / p_1^0\right)_{observed}}{\left(\Delta p_1 / p_1^0\right)_{calculated}} = \frac{\left(\Delta T_b\right)_{observed}}{\left(\Delta T_b\right)_{calculated}} = \frac{\left(\Delta T_f\right)_{observed}}{\left(\Delta T_f\right)_{calculated}} = \frac{\pi_{observed}}{\pi_{calculated}} = \frac{\left(M_2\right)_{calculated}}{\left(M_2\right)_{observed}}.$$

Where, $(M_2)_{observed}$ = observed molar mass of the solute from actual experiment of Colligative properties.

and $(M_2)_{calculated}$ = calculated value of molar mass of the solute from the formula weight.

When i = 1, there is no deviation and departure of the value from unity measures the extent of deviation (i.e. the extent of abnormality of the property).

Abnormality of the property originates from the following three causes.

(A) Non-ideality of the solution:

Non-ideality of a solution arises due to non-uniformity of cohesive forces among the molecules in solution. However, when the solution is dilute ($x_2 \to 0$), non-ideal solutions approach to the ideality and it obeys Raoult's law.
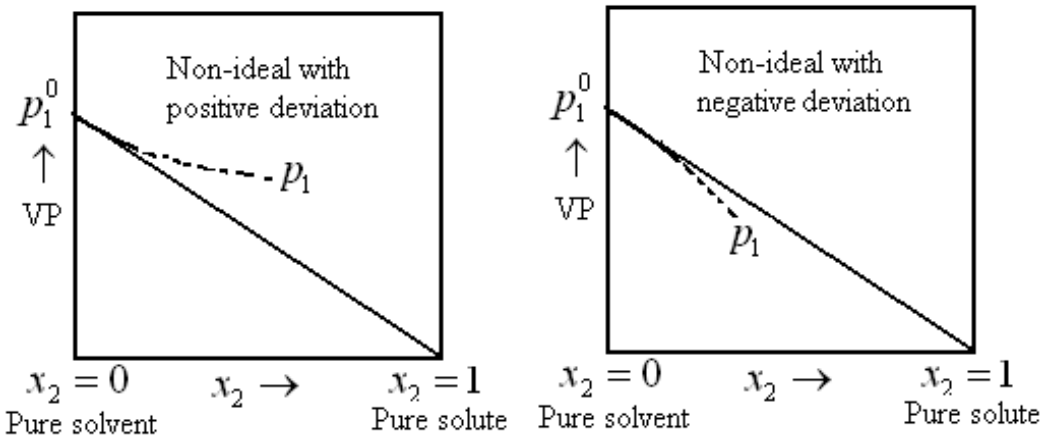
But non-ideal solution curves coincide with ideal solution curve when $x_2 \to 0$.

(1) For non-ideal solution with (+)ve deviation, $p_1(actual) \rangle p_1(ideal)$.

So, RLVP, $\left(\dfrac{p_1^0 - p_1}{p_1^0}\right)_{actual} \langle \left(\dfrac{p_1^0 - p_1}{p_1^0}\right)_{ideal}$. That is, $\left(\dfrac{\Delta p_1}{p_1^0}\right)_{obs.} \langle \left(\dfrac{\Delta p_1}{p_1^0}\right)_{cal}$

Therefore, $i \langle 1$, when the solution is not very dilute.

(2) For non-ideal solution with (−)ve deviation, it is possible to show $i \rangle 1$.

(B) Dissociation of the solute molecules:

For the electrolyte solutions, it is found that observed Colligative property is always greater than the calculated value, so $i \rangle 1$ always.

For NaCl solution, $i = 2$, for CaCl$_2$, $i = 3$ etc. when the solution is dilute.

The cause of this deviation is due to dissociation of the electrolyte in solution. The numbers of particles (here, ions) are increased due to dissociation and thus the value of the Colligative properties is also increased.

It is possible to relate the degree of dissociation (α) with the van't Hoff 'i' factor.

Left margin notes:

When, $i = 1$, no deviation and when $i \neq 1$, there is deviation

VP vs. x_2 plot for ideal solution Van't Hoff factor, ' i ' $\langle 1$ for non-ideal solutions (+)ve deviation and $i \rangle 1$ for non-ideal solutions with (-)ve deviation.

Van't Hoff factor is always greater than one for electrolyte solutions.

	Let us consider a molecule A dissociating into n ions or particles of B in the solution.

Van't Hoff factor is used to calculate the degree of dissociation of

Let c is the molar conc. of A and

$$A \rightleftharpoons nB$$

α is the degree of dissociation then the equil^m. conc. are $\quad c(1-\alpha) \quad n\alpha c$.

The total equilibrium conc. $= c(1-\alpha) + n\alpha c = c[1+(n-1)\alpha]$.

Thus the observed Colligative property, let it be osmotic pressure,

$$\pi_{obs} = c[1+(n-1)\alpha]\,RT.$$

The calculated value using van't Hoff's equation, $\pi_{cal} = cRT$.

Values of 'i' for different electrolyte solutions.

Thus van't Hoff factor, $\quad i = \dfrac{\pi_{obs}}{\pi_{cal}} = \dfrac{c[1+(n-1)\alpha]\,RT}{c\,RT}$ or $i = 1+(n-1)\alpha$ or, $\alpha = \dfrac{i-1}{n-1}$.

For uni-univalent strong electrolytes, such as NaCl, $\alpha = 1$, $n = 2$ so, $i = 2$.
For bi-univalent strong electrolytes such as CaCl$_2$, $\alpha = 1$, $n = 3$ so, $i = 3$.
The dissociation of the electrolyte is assumed to be complete in the dilute solution.

Problem:

Calculate osmotic pressure of human blood which is isotonic with 0.85 % saline water at 27 °C. Assume that NaCl in the saline water is completely dissociated.

Solution:

The osmotic pressure of 0.85 % NaCl solution at 27 °C, $\pi = icRT$, but $i = 1 + (n-1)\alpha$,

here $\alpha = 1$ and n = 2, so i = 2. Thus $\pi = 2cRT = 2 \times \dfrac{w_2 RT}{V \times M}$

$$= \dfrac{2 \times 0.85\ gm \times 82\ cc\ atm\ mol^{-1}K^{-1}}{100\ cc \times 58.5\ gm\ mol^{-1}} = 7.15\ atm.$$

Since human blood is isotonic with this solution so its osmotic pressure is **7.15 atm.**

(C) Association of the solute molecules:

Van't Hoff factor 'i' < 1 when association of the solute occurs in solution.

Some solutes are associated in solution. Such as, benzoic acid in benzene are dimerised. Acetic acid is also dimerised in aqueous solution. The number of molecules are decreased due to association and this results in the decrease of Colligative properties. The van't Hoff factor, $i \langle 1$ always.

$$n A \rightleftharpoons B$$

The degree of association (β) can also be related with van't Hoff 'i' factor.

Let c is the molar conc. of the solute, A and β is the degree of association, then the equil^m. conc.,

$c(1-\beta)$, $\quad \dfrac{\beta c}{n}$

Van't Hoff factor 'i' is used to calculate the degree of association (β) of the solute in solution.

Total conc. of particles $= c\left[1+\left(\dfrac{1}{n}-1\right)\beta\right]$. So, $\quad \pi_{obs} = c\left[1+\left(\dfrac{1}{n}-1\right)\beta\right]RT$

and $\pi_{cal} = c\,RT$. The van't Hoff factor, $i = \dfrac{\pi_{obs}}{\pi_{cal}}$ so, $i = 1+\left(\dfrac{1}{n}-1\right)\beta$ or, $\beta = \dfrac{i-1}{\dfrac{1}{n}-1}$.

So for complete dimerisation, $\beta = 1$, n = 2 and $i = \dfrac{1}{2}$. For complete trimerisation, $i = \dfrac{1}{3}$.

Problem: A solution containing 122 gm of benzoic acid in 1000 gm of benzene boils at 81.5 °C. If the boiling point of benzene be 80 °C, find the percentage of dimmer and the apparent molecular weight of benzoic acid.
[Molar entropy change of vaporization of benzene = 20.8 cal mol⁻¹ K⁻¹].

[B.U. 1984]

Solution : $\left(\Delta T_b\right)_{observed} = 81.5 - 80 = 1.5\,^oC = 1.5$ K. The elevation of BP is calculated as

$$\left(\Delta T_b\right)_{calculated} = \frac{R\left(T_b^o\right)^2}{\bar{L}_{vap}}x_2 = \frac{RT_b^o}{\bar{L}_{vap}/T_b^o} \times \frac{n_2}{n_1+n_2} = \frac{RT_b^o}{\Delta\bar{S}} \times \frac{n_2}{n_1+n_2}.$$

Putting the values, we have

$$\left(\Delta T_b\right)_{calculated} = \frac{2\,cal\,mol^{-1}\,K^{-1} \times (273+80)\,K}{20.8\,cal\,mol^{-1}\,K^{-1}} \times \frac{(122/122)}{(1000/18)+(122/122)} = 2.65\,K.$$

The van't Hoff factor, $i = \dfrac{\left(\Delta T_b\right)_{observed}}{\left(\Delta T_b\right)_{calculated}} = \dfrac{1.5}{2.65} = 0.57.$

% of dimmer $= \left(\dfrac{i-1}{\frac{1}{n}-1}\right) \times 100 = \left(\dfrac{0.57-1}{\frac{1}{2}-1}\right) \times 100 = 86.7$ and $i = \dfrac{\left(M_2\right)_{calculated}}{\left(M_2\right)_{apparent}},$

so, $\left(M_2\right)_{apparent} = \dfrac{122}{0.57} = 215.$

Problem:

A solution of KI is isotonic with a 0.01M solution of I_2 at 27°C. When equal volume of the two solutions were mixed together, the osmotic pressure dropped by 18.5% of that of the individual solutions. Calculate the % of conversion of I^- to I_3^-. Assume the solutions behaving ideally and the salts are completely dissociated. **[IIT-KGP Adm. Test to MSc, 1991]**

Solution:

$\pi_{obs} = 0.01\,mol\,L^{-1} \times 0.082\,L\,atm\,mol^{-1}K^{-1} \times 300\,K = 0.246$ atm. Let x mol of I^- is converted into I_3^-, so the decrease of total conc. is also x. This decrease of conc. produces a decrease of osmotic pressure

$$= 0.246 \times \left(\frac{18.5}{100}\right) = 0.0455 \text{ atm.}$$

Thus, $0.0455\,atm = xRT = x \times 0.083$ L atm mol⁻¹ K⁻¹ × 300K or, $x = 0.00187$ M.

Since KI and I_2 solutions are isotonic so 0.246 atm $= i\,c_{KI}RT$, but $i = 2$.

So, $$c_{KI} = \frac{0.246\,atm}{2 \times 0.082\,L\,atm\,K^{-1}mol^{-1} \times 300\,K} = 0.005\,mol\,L^{-1}.$$

When equal volume of two solutions are mixed up, each solution is double diluted and

the initial conc. of $I^- = \dfrac{c_{KI}}{2} = \dfrac{0.05M}{2} = 0.0025M.$

Thus the extent of conversion from I^- to I_3^- = mol of I^- converted to I_3^- (x) / initial conc. of I^-
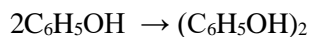$= 0.00187/0.0025 = 0.74 = 74\%.$

Problem:

7.52 g of phenol is dissolved in 100 g of a solvent of $K_f = 14$. If the depression of freezing point is 7 K, then find the percent of phenol that dimerises. **[Sample Question for IIT-JAM]**

Solution:

The conc. of phenol in the solvent $= \dfrac{(7.52/94)}{100} \times 1000 = 0.8\,molal.$

If β is the degree of dimerisation of phenol, then according to reaction,

$$2C_6H_5OH \rightarrow (C_6H_5OH)_2$$

we have, the respective conc. $m(1 - \beta)$ $m\beta/2$ and the total conc. $= m(1 - \beta/2)$

The van't Hoff equation for depression of freezing point is, $\Delta T_f = K_f \times m(1 - \beta/2)$.

Putting the values, we get, $7\,K = 14\,K\,\text{molal}^{-1} \times 0.8\,(1 - \beta/2)$ molal.

Solving we have $\beta = 0.75$ and so % of dimerisation of phenol $= 75$.

Problem:

Addition of 1.0 g of a compound to 10 g of water increases the BP by 0.3 °C. The amount of compound needed to prepare a 500 ml of 0.1 M solution is (given: assume negligible dissociation or association of the compound, BP constant K_b of water $= 0.513$ K kg mol^{-1})

(A) 0.855 g   (B) 17.1 g   (C) 8.55 g   (D) 85.5 g   **[IIT-JAM, 2010]**

[**Answer is (B)**]

Problem:

Acetic acid associates in benzene to form dimmer. 1.65 gm acetic acid when dissolved in 100 gm benzene raised the boiling point of the solvent by 0.36 °C. Calculate the degree of association of acetic acid in benzene. [Given, $K_b = 2.6$]

(A) 70 %   (B) 90 %   (C) 50 %   (D) 100%   [**Hyderabad Central Univ. Adm. to MSc, 2014**]

Answer: (D).

BU, 2000

1(b) Does the boiling point of water change with pressure? How? (1)
   Ans. Yes . Boiling point of water increases with increase of pressure.
 (e) Why is partial molar temperature of a component in a mixture irrelevant? (1)
   Ans. Temperature is an intensive property so it does not depend on the amount of material present in the system.
 (g) How does the chemical potential of the solvent change on addition of a solute? (1)
   Ans. The chemical potential of the solvent is decreased on the addition of a solute.
 (l) What is the dimension of relative lowering of vapor pressure? (1)
   Ans. It is dimensionless.
 (p) When does the solubility of a salt decrease with rise in temperature? (1)
   Ans. When the process of dissolution of the salt is exothermic.

2(b) What is the advantage of mole fraction over molarity as a concentration unit? (2)
   Ans. The mole fraction of solute in solution, $x_2 = \dfrac{n_2}{n_1 + n_2}$ and it is temperature independent while molar

   conc. of the solution, $c_2 = \dfrac{n_2}{V}$ is temperature dependent. With increase of T, V is increased and c_2

   is decreased. So, mole fraction has greater advantage over molar conc.
 (e) Calculate the value of K_b for water. (2)

   Ans. The molal elevation constant of water, $K_b = \dfrac{RT_b^2}{10^3 l_v} = \dfrac{2\,cal\,mol^{-1}K^{-1} \times (373K)^2}{10^3\,gm\,Kg^{-1} \times 540\,cal\,gm^{-1}} = 0.51\,K\,molal^{-1}$.

3(d) What do you mean by vapor pressure of a liquid? Why must it decrease on addition of a non-volatile solute?
   Ans. When a liquid is kept in an evacuated vessel at a given temperature, a portion of the liquid is vaporized and this vapor gives pressure which is called vapor pressure of the liquid and it is fixed at the given temperature. Manometer is used to measure the vapor pressure.
                When a non-volatile solute is added to the solvent, its mole fraction of the liquid is decreased from 1 to lower value. But according to Le Chatelier's principle, the system will try to adjust by increasing the mole fraction of the liquid and it can do so if some vapor condenses to liquid. The net result is thus lowering the vapor pressure over the liquid.
   However this also can be explained by the use of chemical potential of the liquid. The chemical potential of the liquid is lowered when a solute is added to the liquid.
 $$\mu_{liq}(T,P) = \mu_{liq}^0(T,P) + RT \ln x_{liq}, \text{ since } x_{liq} \langle 1 \text{ so, } \mu_{liq}(T,P) \langle \mu_{liq}^0(T,P).$$
   As chemical potential of the liquid is a measure of its escaping tendency to vapor so its vapor pressure is also decreased.

4(a)(i) What thermodynamic function is responsible for osmosis
       and how? (5)
   Ans. Chemical potential of the solvent is the thermodynamic function responsible for osmosis.
       Since, $\mu_1^0(T,P) \rangle \mu_1(T,P)$ and chemical potential (μ_1) signifies the escaping tendency of the solvent, so solvent will flow from solvent side to the solution side through semi permeable membrane spontaneously until it becomes equal on both sides. When the pressure on the solution side is increased to have chemical potential equal on both sides osmosis stops.
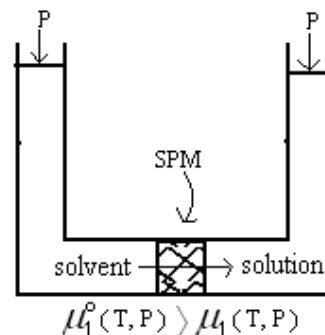
(ii) x g of NaCl, y g of sucrose and z g of urea are mixed and dissolved in 0.5 dm^3 of water. Suppose that no chemical reaction sets in. What would be osmotic pressure of the solution? Give reasons. (5)

Ans. Conc. of NaCl in the solution, $c_{NaCl} = \dfrac{x \times 2}{58.5}(M), c_{sucrose} = \dfrac{y \times 2}{342}(M)$ and $c_{urea} = \dfrac{z \times 2}{60}(M)$.

So, osmotic pressure of the solution, $\pi = \left(2 \times \dfrac{x \times 2}{58.5} + \dfrac{y \times 2}{342} + \dfrac{z \times 2}{60}\right) \times 0.082 \times T$ atm.

NaCl molecules in solution are fully dissociated and give double particles so 2 is multiplied for the conc. of NaCl in the calculation of osmotic pressure.

4(b) Draw the necessary diagram (vapor pressure vs. temperature plot) for showing elevation of boiling point of a solvent by a non-volatile solute, and give a brief explanation for the said phenomena.
Show how Clausius-Clapeyron equation, together with Raoult's law of lowering of vapor pressure can be utilized to obtain the expression for ΔT_b in terms of molality of the solution. (10)
Ans. See the note "Elevation of boiling point of a dilute solution" (page 19) for the 1st part.
and for the 2nd part, see "Application of Clausius-Clapeyron equation" (page 6).

(d)(i) Benzene freezes at 5.6ºC. Its value of K_f = 5.1. Find ΔH_f.

Ans. $K_f = \dfrac{M_1 R (T_f^0)^2}{10^3 \Delta H_f} = \dfrac{78 \times 2 \times (273 + 5.6)^2}{10^3 \Delta H_f} = \dfrac{121048}{\Delta H_f}$ or, $\Delta H_f = \dfrac{12108.4}{5.1} = 2374.2$ cal mol^{-1} .

(ii) An aqueous 20% (by weight) solution of sucrose has density 1.08 g/cc at 25ºC. Express the conc. of solute in molar, molal and mole fraction units. (4.5)
Ans. 20% sucrose solution contains 20 g sucrose in 80 g water. Volume of the solution is

$\dfrac{100 g}{1.08\ g\ cm^{-3}} = 92.6\ cm^3$. So the molar conc. of the solution $= \dfrac{20/242}{92.6} \times 10^3 = 0.63(M)$.

Molal conc. $= \dfrac{20/242}{80} \times 10^3 = 0.73(m)$ and mole fraction of solute, $x_2 = \dfrac{(20/242)}{(80/18)+(20/242)} = 0.013$.

(iii) If 1 Pa = 1 J m^{-3}, convert 1 atm pressure to Pa. (2.5)
Ans. 1 atm = 76 × 13.6 × 980 dyne/cm^2 = 1.013 × 10^6 erg cm^{-3} = 1.013 × 10^6 (10^{-7} J) (10^{-2} m)$^{-3}$
= 1.013 × 10^5 J m^{-3}. So 1 atm = 1.013 × 10^5 Pa..

5(c) Arrive at Clapeyron equation and explain how the melting point of ice depends on pressure. (5)

Ans. Using Maxwell relation, $\left(\dfrac{\partial P}{\partial T}\right)_V = \left(\dfrac{\partial S}{\partial V}\right)_T$, the Clapeyron equation, $\dfrac{dP}{dT} = \dfrac{\Delta H_t}{T(V_\beta - V_\alpha)}$ can be

derived for the phase transition, $\alpha \to \beta$ (See the text "Formulation of Clapeyron equation").

2nd Part : $\dfrac{dP}{dT} = \dfrac{\bar{L}_f}{T(\bar{V}_w - \bar{V}_{ice})}$. But $\bar{V}_{ice} \rangle \bar{V}_w$ and $\bar{L}_f = (+)$ve, so $\dfrac{dP}{dT} = (-)ve$.

It means that higher pressure lowers the melting point of ice.

6(b)(i) Derive Nernst distribution law and remark on its validity when solute is associated in one phase. (3+2).

Ans. Using the concept of chemical potential, derive Nernst equation, $K_d = c_1/c_2$ and for the rest part,

see the text.

BU, 2001

1(a) In cryoscopic study of solutions, which conc. unit is preferable – molarity or molality? why? (1)
Ans. Molality. It is T – independent due to its weight basis. This conc. does not change due to temperature fluctuation in the study.

(j) Arrange the following in order of increasing freezing point.

0.1(M) HCl, 0.1(M) CH₃COOH, 0.1(M) sucrose. (1).

Ans. $\left(\Delta T_f\right)_{HCl} \rangle \left(\Delta T_f\right)_{CH_3COOH} \rangle \left(\Delta T_f\right)_{sucrose}$. So FP increasing is, $\left(T_f\right)_{HCl} \langle \left(T_f\right)_{CH_3COOH} \langle \left(T_f\right)_{sucrose}$.

(m) Evaporation of solvent from the surface of a saturated KCl solution at room temperature does not change the conc. of the solution. Why? (1)

Ans. Conc. of a saturated solution (solubility) at a given temperature is constant. When the solvent evaporates from the surface of a saturated KCl solution, it becomes super saturated and excess KCl solute removes by precipitation maintaining conc. same at the temperature.

(t) Benzoic acid is monomeric in aqueous solution and dimeric in benzene. Write down the expression for its distribution coefficient between benzene and water. (1)

Ans. We have the relation as, $K_d = \dfrac{c_{benzoic\,acid\,in\,water}}{\sqrt{c_{benzoic\,acid\,in\,benzene}}}$,

where, K_d = distribution co-efficient of benzoic acid between benzene and water.

(u) Brisk effervescence is observed when a soda water bottle is opened. State the physical law to which this observation is related. (1)

Ans. It is Henry's law. The law states that "The mass of the gas (m) dissolved in unit volume of a solvent at constant temperature is directly proportional to the pressure of the gas with which it is in equilᵐ." i.e. m ∝ P or, m = K P, where K is Henry's constant.

(y) Write down the Maxwell's relation which is used to derive Clapeyron equation. (1)

Ans. $\left(\dfrac{\partial S}{\partial V}\right)_T = \left(\dfrac{\partial P}{\partial T}\right)_V$.

2(g) Define chemical potential. What is its dimension? (2)

Ans. It is the change of free energy per mole of the component added at constant T and P keeping the composition of the multi component system unchanged. Mathematically, $\mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$.

Its unit is energy per mole, $M\,L^2\,T^{-2}\,mol^{-1}$.

3(c) The vapor pressure of a liquid increases with rise in temperature. Explain it quantitatively considering the liquid-vapor equilibrium. (5)

Ans. The equilibrium is given as, liquid ⇌ vapor of a pure substance. Now starting with Maxwell's relation build up Clapeyron equation,

$$\frac{dP}{dT} = \frac{\bar{L}_{vap}}{T(\bar{V}_g - \bar{V}_l)}$$. Since, $\bar{V}_g \rangle \bar{V}_l$, and $\bar{L}_{vap}$ = (+)ve, so $\dfrac{dP}{dT}$ = (+)ve.

It explains that as T is increased, the vapor pressure (P) is also increased.

6(a) Two bottles, each containing about 30 ml of CHCl₃, were marked as I and II. Then some quantity of aqueous ammonia solution was added to bottle I. To bottle II, 30 ml of aqueous ammonia solution and 5 ml of 0.3(M) CuSO₄ solution were added. Two bottles were then vigorously shaken until partition equilᵐ. was established in each of the bottles. The ammonia in each layer in the bottles then titrated with standard H₂SO₄ solution and the following results were obtained (for exact neutralization).

Bottle I:

5 ml aqueous layer required 10.15 ml of 0.908 (N/2) H₂SO₄

5 ml of CHCl₃ layer required 5.10 ml of 0.908 (N/20) H₂SO₄

Bottle II:

5 ml aqueous layer required 9.15 ml of 0.908 (N/2) H₂SO₄

5 ml of CHCl$_3$ layer required 3.65 ml of 0.908 (N/20) H$_2$SO$_4$.

Find the coordination number of Cu^{+2} ion in the blue complex formed in the aqueous layer of the bottle II.

Ans. See the text, "Thermodynamics of two-phase equilibrium". Coordination of Cu^{+2} ion is 4.

BU, 2002

1(q) What is the driving force in osmosis? (1)

Ans. Difference of chemical potential ($\Delta\mu_1$) between the pure solvent and solvent in solution is the driving force in osmosis. Higher chemical potential of the pure solvent drives it to flow to the solution side.

5(d) Some I$_2$ is dissolved in 100 cc water. If 90 % of that iodine is to be extracted in one step by CCl$_4$, find the volume of CCl$_4$ required, given that the partition coefficient of I$_2$ between CCl$_4$ and water is 85.

Ans. Let x gm I$_2$ remains dissolved in 100 cc water before extraction. Thus the partition coefficient,

$$K_d = \frac{\left(0.9x / V\right)}{\left(0.1x / 100\right)} = 85$$, let V cc CCl$_4$ is required to extract 90 % iodine. Solving, V = 10.6 cc.

(e) Sulphur dissolves in benzene as S_x. A 0.25 % solution shows $\Delta T_f \approx 0.05 K$ .Given that K$_f$ for benzene is 5.0 Kg/molal. Find x.

Ans. Let the molecular weight of S_x is M. So Raoult's law, $\Delta T_f = K_f \times \dfrac{w_2 \times 1000}{w_1 \times M}$ or, $M = K_f \times \dfrac{w_2 \times 1000}{w_1 \times \Delta T_f}$.

Putting data, we have $M = 5.0 \times \dfrac{0.25 \times 1000}{99.75 \times 0.05} = 250$. But M = 32 $\times$ x or, $x = \dfrac{250}{32} \approx 8$.

6(a)(i) Melting of ice at 1 atm and 0°C involves 1500 cal of heat and dP/dT is about $-1 \times 10^8 \, dyne / cm^2 / \deg$. Find the change in volume. (5)

Ans. The Clapeyron equation is $\dfrac{dP}{dT} = \dfrac{\overline{L}_{vap}}{T \Delta V}$, where $\overline{L}_{vap}$ = 1500 cal mol^{-1}. ΔV , change in volume

$$= \frac{\overline{L}_{vap}}{T \left(dP / dT\right)} = \frac{1500 \, cal \, mol^{-1}}{273 \, K \times (-1 \times 10^8 \, dyne \, cm^{-2} K^{-1})} = -\frac{1500 \, cal \, mol^{-1} \times 4.2 \times 10^7 \, erg \, cal^{-1}}{273 \, K \times (-1 \times 10^8 \, dyne \, cm^{-2} K^{-1})} = -2.1 \text{cc mol}^{-1}.$$

So the change in volume due to melting of 1 mole of ice is $-$ 2.1 cc mol^{-1}.

(ii) Assuming Raoult's law, explain why boiling point should increase when some solute is added to the solvent. (5)

Ans. See the text, "Thermodynamics of two-phase equilibrium".

(d)(i) Show that it is more economical to use a smaller volume of solvent in stages then the whole volume of solvent at a time in solvent extraction process. (7)

Ans. See the text, "Thermodynamics of two-phase equilibrium".

(ii) Discuss how the partition coefficient takes care of dissociation of a solute in one of the two-immiscible layers. (3)

Ans. The Nernst distribution law takes care of the law by taking the conc. of the solute in both the immiscible solvents as same molecular form, The law is modified to $K_d = \dfrac{c_1(1-\alpha)}{c_2}$,

$c_1(1-\alpha)$ is the conc. of the undissociated solute in the solvent where it is dissociated.

BU, 2003

2(f) Define chemical potential. What is its dimension? (2). **Ans.** See **BU'2001, Q2 (g).**

6(d)(i) For a certain solvent, the BP is 127°C and the latent heat of vaporization is 120 cal /g.

Find the molal elevation constant. (4)

Ans. $$K_b = \frac{R\left(T_b^0\right)^2}{10^3 \, l_{vap}} = \frac{2 \, cal \, mol^{-1} K^{-1} \left(273+127\right)^2 K^2}{10^3 \, g \, Kg^{-1} \times 120 \, cal \, g^{-1}} = 2.66 K (mol / Kg)^{-1}.$$

(ii) On addition of a solute, the vapor pressure of a liquid reduces to (9/10)th of its original value. If 2 g of the solute (molar mass = 100) is added to 100 g of the liquid to achieve the reduction, find the molar mass of the solvent, assuming ideality. (6)

Ans. $p_1 = \left(\frac{9}{10}\right) p_1^0$. Thus, $\frac{p_1}{p_1^0} = x_1 = \frac{n_1}{n_1 + n_2}$ or, $\frac{9}{10} = \dfrac{100/M_1}{\dfrac{100}{M_1} + \dfrac{2}{100}}$. Solving, $M_1 = 555.55$ g mol^{-1}.

BU, 2004

1(m) On what factors does K_f depend? (1)

Ans. $K_f = \frac{R\left(T_f^0\right)^2}{10^3 \, l_f}$ K_f depends on the magnitude of freezing point and latent heat of fusion of the solvent. That is, it depends on the nature of the solvent only.

(w) Identify X and Y in Henry's law: $X \propto Y$. (1)

Ans. X = m, solubility of the gas in a liquid and Y = P, pressure of the gas in equil^m. with the solution.

2(d) Define an ideal solution. (2)

Ans. When solute-solute, solute-solvent and solvent-solvent interactions are uniform, the solution becomes ideal. For ideal solution, (i) Raoult's law $p_i = x_i \, p_i^0$ is obeyed. (ii) $\Delta H_{mixing} = 0$, (iii) $\Delta V_{mixing} = 0$ and (iv) $\mu_i = \mu_i^0 + RT \ln x_i$ relation is applicable.

(g) Explain whether the partition coefficient is independent of temperature. (2)

Ans. It is the ratio of conc. of the solute in two immiscible solvents. The conc. of the solute in the two solvents may not be same with temperature variation, so K_d in general depends on temperature.

Further, thermodynamic expression of K_d is given by, $K_d = e^{\frac{\mu_X^0 (B) - \mu_X^0 (A)}{RT}}$ in which the solute X is distributed between the solvents A and B. This shows K_d depends on T.

5(e) Given the vapor pressure $p^0(H_2O) = 0.02308$ atm and $p(H_2O) = 0.02239$ atm in a solution where 0.12 Kg of a non-volatile solute (M = 240 g mol^{-1}) is dissolved in 0.918 Kg of water, calculate the activity coefficient of water in the solution. (5)

Ans. The activity of water in the solution (a_{H_2O}) $= \frac{p(H_2O)}{p^0(H_2O)} = \frac{0.02239 \, atm}{0.02308 \, atm} = 0.9701$.

And $x(H_2O) = \frac{0.918/(18 \times 10^{-3})}{0.918/(18 \times 10^{-3}) + 0.12/(240 \times 10^{-3})} = 0.993$. So, $\gamma(H_2O) = \frac{a(H_2O)}{x(H_2O)} = \frac{0.9701}{0.993} = 0.98$.

6(c)(i) At one atm pressure, the boiling point of a liquid is 350 K. If the heat of vaporization is 30 kJ mol^{-1}, find its boiling temperature at 0.5 atm pressure. (5)

Ans. The Clausius-Clapeyron equation is, $\ln \frac{p_2}{p_1} = \frac{\bar{L}_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$ or, $\frac{1}{T_1} = \frac{R}{\bar{L}_{vap}} \ln \frac{p_2}{p_1} + \frac{1}{T_2}$.

Now putting the values, $\frac{1}{T_1} = \frac{8.31 \times 10^{-3} kJ \, mol^{-1} K^{-1}}{30 kJ \, mol^{-1}} \ln \frac{1 \, atm}{0.5 \, atm} + \frac{1}{350 \, K} = 3.05 \times 10^{-3}$ K^{-1}.

Or, $T_1 = 327$ K. The BP of the liquid at 0.5 atm is 327 K.

(ii) The vapor pressure of liquids is often written as $\ln P = A - B/T - c \ln T$ to account for the change with temperature. Explain the significance of this equation with respect to the enthalpy of vaporization. (3+2)

Ans. The Clausius equation is, $\dfrac{d \ln P}{dT} = \dfrac{\Delta \bar{H}_{vap}}{RT^2}$. The given equation can be differentiated w. r. t. T as

$$\frac{d \ln P}{dT} = \frac{B}{T^2} - \frac{C}{T} = \frac{B - CT}{T^2} \text{ . Comparing, we get } \Delta \bar{H}_{vap} = BR - CRT \text{ .}$$

This equation signifies that enthalpy of vaporization ($\Delta \bar{H}_{vap}$) varies linearly with T and it decreases with T

6(d) In the equation $\bar{V}_A \pi = RT \ln \left(p_A^0 / p_A \right)$, where π is osmotic pressure of a solution, What do $\bar{V}_A$, p_A^0 and

p_A actually signify? Arrive at this equation from the definition of chemical potential. Arrive also at the simpler form $\pi = cRT$ from the above equation pointing out the various approximations involved at the subsequent steps. (10)

Ans. $\bar{V}_A$ = partial molar volume of the solvent, A in solution, p_A^0 = vapor pressure of the pure solvent, A

and p_A = that of solvent A in solution.

Solvent and solution are separated by semi permeable membrane and solvent under pressure P is in equil^m. with solution under pressure P + π . So the chemical potential of the solvent in the both sides are equal. i.e.

$$\mu_A^0(T,P) = \mu_A(T, P+\pi) = \mu_A^0(T, P+\pi) + RT \ln x_A$$

or, $-RT \ln x_A = \mu_A^0(T, P+\pi) - \mu_A^0(T,P)$, but $\left[\dfrac{\partial \mu_A^0}{\partial P} \right]_T = \bar{V}_A$

or, $\displaystyle\int_{\mu_A^0(T,P)}^{\mu_A^0(T,P+\pi)} d\mu_A^0 = \bar{V}_A \int_P^{P+\pi} dP$ or, $\mu_A^0(T, P+\pi) - \mu_A^0(T,P) = \bar{V}_A \times \pi$.
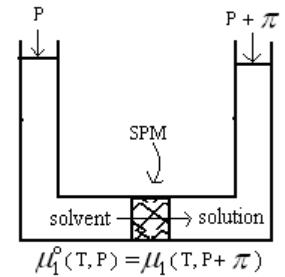
Equating with above equation and putting $x_A = p_A / p_A^0$, we get $-RT \ln \left(p_A / p_A^0 \right) = \bar{V}_A \times \pi$

or, $\bar{V}_A \times \pi = RT \ln \left(p_A^0 / p_A \right)$. The relation is thus deduced from the concept of chemical potential.

Again, $\bar{V}_A \times \pi = -RT \ln x_A = -RT \ln(1-x_B)$ where, x_B is the mole fraction of the solute, B

Since the solution is dilute so $x_B \langle\langle\, 1$ and hence, $\ln(1-x_B) \approx -x_B$. Thus, $\bar{V}_A \times \pi = x_B RT$.

But $x_B = \dfrac{n_B}{n_A + n_B} \approx \dfrac{n_B}{n_A}$. Putting, we get $\bar{V}_A \times \pi = RT \dfrac{n_B}{n_A}$ or, $\left(\bar{V}_A \times n_A \right) \times \pi = n_B RT$,

again, $\bar{V}_A \times n_A = V_A$, volume of the solvent in the solution $\approx$ V, volume of the solution.

Therefore, $\pi = \left(n_B / V \right) RT$ or, $\pi = c\,RT$, where, c is the molar conc. of the solution.

Approximation: (1) V_A is assumed to be V. (2) $x_A = p_A / p_A^0$ i.e. ideal solution is assumed.

(3) $\ln(1-x_B) \approx -x_B$ as $x_B \langle\langle\, 1$ in dilute solution .and also (4) $\dfrac{n_B}{n_A + n_B} \approx \dfrac{n_B}{n_A}$.

BU, 2005

1(n) What is the expression for cryoscopic constant of a substance in terms of its freezing point? (1)

Ans. The expression of cryoscopic constant, $K_f = \dfrac{R(T_f^0)^2}{10^3\, l_f}$, the terms have their usual meanings.

5(e) Justify physically that the chemical potential of a solvent in solution will be less than that of the pure solvent. Explain, on its basis, the lowering of vapor pressure. (5)

Ans. From the definition, chemical potential of the solvent is $\mu_1 = \bar{H}_1 - T\bar{S}_1$.

When the solute is added to a solvent, the degree of randomness is increased, resulting an increase of $\bar{S}_1$ but for formation of ideal solution, $\bar{H}_1$ remains constant. This lowers the chemical potential of the solvent in solution., μ_1.

The solvent in solution remains in equil^m. with its vapor and also chemical potential of a substance is a measure of escaping tendency of that substance from the phase it exists. Thus, lower chemical potential of the solvent in solution have lower tendency to escape into the vapor phase than that have in pure solvent. This explains the lowering of vapor pressure of the solvent in solution physically.

6(b)(i) State and derive the Clausius-Clapeyron. Explain, on its basis, whether the boiling point of a liquid can ever decrease with rise of pressure. (5)

Ans. The equation states the dependency of vapor pressure of a liquid with temperature, and with rise in temperature, the vapor pressure of a liquid is always increased.

For derivation of Clausius-Clapeyron equation, see the text "Principles of Thermodynamics".

The equation, $\ln\dfrac{P_2}{P_1} = \dfrac{\bar{L}_{vap}}{R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)$, where T_1 and T_2 are the BP of the liquid at pressure P_1 and P_2 respectively. When the pressure is raised, $P_2 \rangle P_1$, so, LHS $= \ln\dfrac{P_2}{P_1} = (+)$ve. So to keep RHS of the equation also $(+)$ve, $T_2 \rangle T_1$ as $\bar{L}_{vap}$, molar latent heat of vaporization is always $(+)$ve.

It follows that BP of a liquid can never decrease with rise of pressure.

6(c)(i) Deduce an expression for the variation chemical potential of a component i with pressure, and hence express μ_i in terms of p_i in a mixture of ideal gases. (6)

Ans. The chemical potential of the *i*th component, $\mu_i = \left(\dfrac{\partial G}{\partial n_i}\right)_{T,P,n_{j\neq i}}$, so $\left(\dfrac{\partial \mu_i}{\partial P}\right)_T = \dfrac{\partial^2 G}{\partial P \partial n_i}$.

Again, the free energy change in a multi-component system, $dG = -SdT + VdP + \Sigma\mu_j dn_j$.

Or, $\left(\dfrac{\partial G}{\partial P}\right)_{T,n_j} = V$, or $\dfrac{\partial^2 G}{\partial n_i \partial P} = \left(\dfrac{\partial V}{\partial n_i}\right)_{T,P,n_{j\neq i}} = \bar{V}_i$, partial molar volume of the *i*th component.

Since, G is a state function, it obeys Euler's theorem and $\dfrac{\partial^2 G}{\partial n_i \partial P} = \dfrac{\partial^2 G}{\partial P \partial n_i}$. So, $\left(\dfrac{\partial \mu_i}{\partial P}\right)_T = \bar{V}_i$.

It shows that μ_i increases with increase of P as $\bar{V}_i$ is always $(+)$ve.

This is the expression for variation of chemical potential of a component *i* with pressure.

If the gas is considered ideal, then $\bar{V}_i = \dfrac{RT}{P}$. So, $\left(\dfrac{\partial \mu_i}{\partial P}\right)_T = \dfrac{RT}{P}$.

Integrating within limits, $\displaystyle\int_{\mu_i^0}^{\mu_i} d\mu_i = RT\int_{1atm}^{P} dP$ or, $\mu_i = \mu_i^0 + RT\ln P$,

where, μ_i^0 is standard chemical potential of the component i. Thus, $\mu_i(T) = \mu_i^0(T) + RT\ln P$.

Let the pure component i is separated from the mixture of the other component gases by a membrane permeable to this component i only.

Since component i is in equil^m. in both the compartments, so
$$\mu_i(mixture) = \mu_i(pure).$$

As the component *i* remains in equilibrium, so the pressure of pure component is equal to the partial pressure of the component i in the mixture. Thus,

membrane permeable to component i only

| pure component i μ_i(pure) | component i in a mixture of ideal gases μ_i(mixture) |

$$\mu_i(mixture) = \mu_i(pure) = \mu_i^0 + RT \ln P = \mu_i^0 + RT \ln p_i \text{ or, } \mu_i(mixture) = \mu_i^- + RT \ln p_i.$$

So more precisely we can write, $\mu_i = \mu_i^0(T) + RT \ln p_i$.
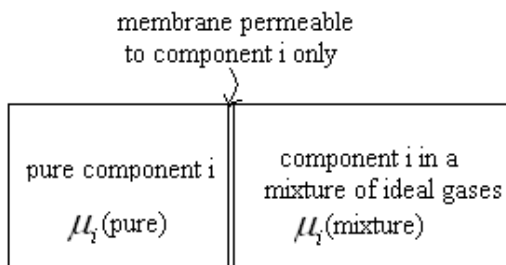
(ii) Sulphur dissolves in an organic solvent ($K_f = 5.0$ K Kg/mol) as S_x. A 0.25 % solution shows $\Delta T_f = 0.05$ K. Find x . (4). **Ans. 8. See BU'2002, Q5(e).**

6(d)(i) Show that, in a solvent extraction process, it is more economical to use a smaller volume of solvent in stages than the total amount of solvent at a time. (5)
Ans. See BU'2002, Q6(d)(i)

(ii) Some I_2 is dissolved in 100 ml water. If 90 % of that iodine is to be extracted in one step by CCl_4, find the volume of CCl_4 required, given that the partition coefficient of I_2 between CCl_4 and water is 85. (5)
Ans. See BU'2002, Q5(d).

BU, 2006

1(g) Latent heat of vaporization (ΔH_{vap}) at one temperature is known, what other parameters are needed to estimate ΔH_{vap} at some other temperature? (1)

Ans. Kirchhoff equation can be used to estimate ΔH_{vap} . The equation is, $\Delta H'_{vap} = \Delta H_{vap} + \Delta C_P(T' - T)$.

Besides temperature, $\Delta C_P = C_{P,vap} - C_{P,liq}$, molar heat capacity of vapor and liquid are needed.

(q) Which thermodynamic law governs the dissolution of CO_2 in water in the preparation of cold drinks? (1)
Ans. It is Henry's law which states that solubility of a gas is proportional to the pressure of the gas in equil^m. with the solution at constant pressure.

(t) Which one is greater, chemical potential of a solvent in a solution or the molar free energy of the pure solvent , temperature remaining same? (1)
Ans. Molar free energy of a pure solvent is greater than the chemical potential of the solvent in solution.

The required expression is $\mu_1(T,P) = \mu_1^0(T,P) + RT \ln x_1$, where $\mu_1^0(T,P)$ is the molar free energy of the pure solvent and $\mu_1(T,P)$ is the chemical potential of the solvent in solution.

$$\text{As } x_1 \langle 1, \text{ so } \mu_1^0(T,P) \rangle \mu_1(T,P).$$

(u) What is the cause of deviation of concentrated solution of sucrose from Raoult's law of lowering of vapor pressure. (1)
Ans. The concentrated solution of sucrose is non-ideal solution but Raoult's law is valid only for ideal solution. This is the cause of deviation.

(w) What is the basic difference between Clapeyron equation and Clausius-Clapeyron equation? (1)
Ans. Clapeyron equation is applicable to any 1st order phase transition of a pure substance but Clausius-Clapeyron equation is valid for the same phase transition but one of the phases is vapor. So former equation is more general than the latter.

2(f) Justify or criticize: Equimolar aqueous solutions of urea and sodium chloride are isotonic. (2)
Ans. The statement is not correct. NaCl in aqueous solution is completely dissociated and so one molecule produces two particles. Thus osmotic pressure of aqueous NaCl solution is almost double to that of aqueous urea solution.

(h) Experimental data of vapor pressure of a liquid at a number of temperatures are supplied. What graphical plot would you utilize to determine the latent heat of vaporization? Why? (2)

Ans. $\ln p$ can be plotted against T^{-1} in which straight line is obtained and from the slope, $\bar{L}_{vap}$ is determined. The Clausius-Clapeyron equation is used for the purpose, $\ln p = -\dfrac{\bar{L}_{vap}}{R}\left(\dfrac{1}{T}\right) + const$

5(e) Using Clausius-Clapeyron equation, show that the relative lowering of vapor pressure of a dilute solution is independent of temperature. Explain that the relative lowering of vapor pressure is an enthalpy effect. (5)

Ans. The C-C equation for vaporization of pure solvent is $\dfrac{d\ln p_1^0}{dT} = \dfrac{\bar{L}_{vap}^0}{RT^2}$ and for solvent in solution

$\dfrac{d\ln p_1}{dT} = \dfrac{\bar{L}_{vap}}{RT^2}$, where, $\bar{L}_{vap}^0$ and $\bar{L}_{vap}$ are molar latent heat of vaporization of pure solvent and

solvent in solution respectively.

Subtracting the two, $\dfrac{d\ln\left(p_1/p_1^0\right)}{dT} = \dfrac{\bar{L}_{vap} - \bar{L}_{vap}^0}{RT^2}$ or, $\dfrac{d\ln\left[1 - \dfrac{p_1^0 - p_1}{p_1^0}\right]}{dT} = \dfrac{\bar{L}_{vap} - \bar{L}_{vap}^0}{RT^2}$. But, $\dfrac{p_1^0 - p_1}{p_1^0} \langle\langle 1$.

So, $-\dfrac{d\ln\left[\dfrac{p_1^0 - p_1}{p_1^0}\right]}{dT} = \dfrac{\bar{L}_{vap} - \bar{L}_{vap}^0}{RT^2}$ or, $\dfrac{d\ln\left[\dfrac{p_1^0 - p_1}{p_1^0}\right]}{dT} = \dfrac{\bar{L}_{vap}^0 - \bar{L}_{vap}}{RT^2}$, but for ideal solution,

$\Delta H_{mixing} = 0$, i.e. $\bar{L}_{vap}^0 - \bar{L}_{vap} = 0$. So, $\dfrac{d\ln\left[\dfrac{p_1^0 - p_1}{p_1^0}\right]}{dT} = 0$ or, $\dfrac{p_1^0 - p_1}{p_1^0}$ is independent of temperature.

Lowering of vapor pressure of solvent is due to lowering of chemical potential of the solvent when some solute is added to it. The expression for change of chemical potential of solvent is
$$d\mu_1 = d\bar{H}_1 - Td\bar{S}_1$$
$d\bar{H}_1 = 0$ (as the solution is ideal) hence, $d\mu_1 = -Td\bar{S}_1$. Due to addition of solute, randomness of the solution is increased and hence $d\bar{S}_1 \rangle 0$ and thus $d\mu_1 \langle 0$.

This explains the lowering vapor pressure of the solvent in solution is the enthalpy effect.

6(c)(i) Derive thermodynamically an expression for osmotic pressure of an ideal solution. (5)

Ans. See text "Thermodynamics of two-phase equil^m." page, 28.

(ii) The van't Hoff equation for osmotic pressure is identical in form and similar in content with the ideal gas equation. (3)

Ans. The van't Hoff equation is $\pi = cRT$, since c = n/V where n moles of solute is dissolved in V litre, so, the equation can be written as $\pi V = n RT$. Again, the ideal gas equation is PV = nRT.

These two equations are identical in form as all the terms of each equation are same in units also.

Now let us see the internal content of these two equations. In the gas equation n is the number of moles of the gas occupying V volume at temperature T and exerting the pressure P on the wall of the gas container.

In van't Hoff's equation, π is the osmotic pressure developed by the solute present in V volume of solution at the temperature T. The striking analogy is rightly reflected by van't Hoff's remark, "The osmotic pressure of a substance in solution is equal to the pressure it exert if it were a gas occupying the same volume as that occupied by the same solution at same temperature."

See the text, "Thermodynamics of two-phase equil^m." for further details.

(iii) Show that for non-associated solvents, $\Delta T_b / T_b$ is independent of the nature of the solvent. (2)

Ans. The thermodynamic formulation of the expression of elevation of BP of a solution is,

$$\Delta T_b = \frac{RT_b^2}{\bar{L}_{vap}} \times x_2 \ \text{ or, } \ \frac{\Delta T_b}{T_b} = \frac{RT_b}{\bar{L}_{vap}} \times x_2 = \frac{R}{\left(\bar{L}_{vap}/T_b\right)} \times x_2 = \frac{R}{\left(\Delta S_{vap}\right)_{at\,BP}} \times x_2 \, .$$

But $\left(\Delta S_{vap}\right)_{at\,BP}$ = constant ≈ 21 cal mol^{-1} K^{-1} (Trouton's rule) for non-associated solvents.

Thus for a given conc. (x_2) of the solution $\Delta T_b / T_b$ is independent of the nature of solvents used.

BU, 2007

1(k) What is van't Hoff 'i' factor and why it is required? (2)

Ans. The van't Hoff factor, 'i' = $\dfrac{observed\ value\ of\ colligative\ property}{calculated\ value\ of\ the\ property}$ for same molar conc.

It is required to measure the deviation of the property from the ideal value. For ideal solution, 'i' = 1. Greater the departure of the value of 'i' from unity, more the solution is non-ideal.

(*l*) Draw a relationship between van't Hoff 'i' factor and the degree of dissociation (α) of a solute M_xA_y dissociating as $M_xA_y \ \square \ xM^{z+} + yA^{z-}$.

Ans. See the text, "Thermodynamics of two-phase equil^m.", $i = 1 + (n-1)\alpha$, here $n = x + y$.

So the relation is, $i = 1 + (x + y - 1)\alpha$.

3(a) Draw the vapor pressure – temperature plot for the case of lowering of freezing point of a solution. Label the different parts properly. Apply the Clausius-Clapeyron equation and obtain the expression for molal cryoscopic constant. (3 + 3 + 3 = 9)

Ans. See "Thermodynamics of two-phase equil^m." page, 38, and obtain the expression, $K_f = \dfrac{R(T_f^0)^2}{10^3\, l_f}$.

Old Reg. 1(u) Under what condition, is the van't Hoff factor for an aqueous solution of an electrolyte A_mB_n equal to (m + n)? (1)

Ans. The van't Hoff factor for the electrolyte, $i = 1 + (m + n - 1)\alpha$ so, i = m + n only when $\alpha = 1$. i.e. when the electrolyte in aqueous solution is completely dissociated.

(v) Why is camphor suitable as a solvent for determination of molar mass by Rast method? (1)

Ans. Camphor has K_f = 40 K Kg/mol. Thus ΔT_f is large and ordinary thermometer can be used to determine the depression of freezing point of the solution (ΔT_f).

(w) For ice, the graphical plot of melting point (X – axis) against pressure (Y – axis) has (-)ve slope. Why? (1)

Ans. Clapeyron equation is, $\dfrac{dP}{dT} = \dfrac{L_{fusion}}{T\left(V_{water} - V_{ice}\right)}$.

But for a definite mass, $V_{ice} \rangle V_{water}$, and $L_{fusion} = (+)ve$ so, the slope, $\dfrac{dP}{dT} = (-)ve$.

5(c) An organic compound contains 68 % C, 10 % H and the rest oxygen. A solution of 0.032 g of the compound in 0.722 g of cyclohexane had a freezing point of 6.39°C less than that of the solvent. Calculate the molar mass and molecular formula of the compound (K_f for cyclohexane = 20.2). (5)

Ans. Raoult's law of depression of FP is, $\Delta T_f = K_f \times \dfrac{w_2 \times 1000}{w_1 \times M_2}$. Putting data, $6.39 = 20.2 \times \dfrac{0.032 \times 1000}{0.722 \times M_2}$.

Solving the equation, we get, the molecular weight of the organic compound, $M_2 = 140$.

Now,　　C : H : O = 68% : 10% : 22%. $= \dfrac{60}{12} : \dfrac{10}{1} : \dfrac{22}{16} = 4 : 7 : 1$ (atomic ratio).

The empirical formula is C_4H_7O and molecular formula is $(C_4H_7O)_n$. Putting the atomic weights of the elements of the compound, n $(4 \times 12 + 7 \times 1 + 16) = 140$, or, n = 2.
Hence, the molecular formula of the compound is $C_8H_{14}O_2$.

BU, 2008

1(b) What is the advantage of using mole fraction over molarity as a concentration unit? (2)
　　Ans. See Q2(b) of BU'2000, page 1.

(f) Equal weights of ethanol or glycol may be chosen as antifreeze agent in car radiator water for driving snowy region. Which one would you prefer and why? (2)
　　Ans. Both the compounds are used as antifreeze agent, but glycol is preferred over ethanol.
　　Glycol is less volatile, so with equal amount of ethanol and glycol taken in the radiator water, there is less loss of glycol due to evaporation.
　　Further, due to less volatility (BP 197 °C) it prevents to buildup unwanted pressure within the cooling system.

(g) "The Clausius-Clapeyron equation is a special case of the van't Hoff's equation for liquid – vapor equilibrium." – Justify or criticize. (2)
　　Ans. Van't Hoff's equation is, $\ln \dfrac{K_{P_2}}{K_{P_1}} = \dfrac{\Delta \bar{H}_{vap}}{R} \left(\dfrac{1}{T_1} - \dfrac{1}{T_2} \right)$, applicable to any chemical or physical equil^m.

　　The equilibrium constant for the process, liquid ⇌ vapor, $K_a = \dfrac{a_{vap}}{a_{liq}}$, but $a_{liq} = 1$ and $a_{vap} = $ p,

　　vapor pressure of the liquid so, $K_P = $ p. Again, $\Delta \bar{H}_{vap} = \bar{L}_{vap}$.
　　Putting, we get the Clausius-Clapeyron equation,

$$\ln \dfrac{p_2}{p_1} = \dfrac{\bar{L}_{vap}}{R} \left(\dfrac{1}{T_1} - \dfrac{1}{T_2} \right) \text{ and it is applicable to only liquid ⇌ vapor equil}^m .$$

　　This shows that Clausius-Clapeyron equation is a special case of van't Hoff's equation.
　　　　　　See the text, "Principles of thermodynamics".

B(3)(a)(i) State the thermodynamic criteria of an ideal binary liquid mixture.
　　(ii) Which thermodynamic law governs the dissolution of CO_2 in water in the preparation of cold drinks? — State. (4)
　　　　Ans. (i) See BU'2004, Q2 (d), page 5. (ii) Henry's law. See BU'2006, Q1 (q), page 9.

(b) Why is the boiling point of a solution greater than that of a pure solvent? (2)
　　Ans. At 1 atm pressure, pure solvent boils at T_b^0 but solution does not boil since its vapor pressure is lower than 1 atm at T_b^0 .When the temperature is raised to T_b , solution reaches to 1 atm and it boils. Thus, $T_b \rangle T_b^0$.

4(a) Show that in a solvent extraction process, it is more economical to use a smaller volume of solvent in stages than the total amount of the solvent at a time. (4)
　　Ans. See the text "Thermodynamics of two-phase equil^m." page 13.

(b) With increase of pressure, the melting temperature of paraffin increases but that of ice decreases. —Explain. (2)
　　Ans. See the text, "Principles of thermodynamics by N C Dey.

C(7)(a)(i) Deduce Gibbs-Duhem equation. (5)

   Ans. Derive the equation, $0 = \Sigma n_i d\mu_i$. See the text, "Principles of thermodynamics", by N C Dey.

  (ii) Define chemical potential (μ) and state its dimension.

   Explain whether μ is an extensive or intensive property. (5)

   Ans. See BU'2001, Q2 (g).

   Last part: It is Gibb's free energy per mole so it is an intensive property.

 (9)(a)(i) Derive a relation between osmotic pressure of a solution and relative lowering of vapor pressure. (5)

   Ans. See the text "Thermodynamics of two-phase equil^{m}." for derivation of

$$\pi = \frac{RT}{\overline{V}_1^0} \times x_2 \text{ and then insert } x_2 = \frac{\Delta p_1}{p_1^0} \text{ and get the final relation is, } \pi = \frac{RT}{\overline{V}_1^0} \times \frac{\Delta p_1}{p_1^0}.$$

  (ii) At 233K, the osmotic pressure of a solution of urea is 500 mm of Hg. The solution is diluted and temperature is raised to 298K, when the osmotic pressure is found to be 105.3 mm of Hg. Determine the extent of dilution. (5)

   Ans. Let the initial conc. of urea solution is c_1 and final conc. after dilution at the temp. 233K is c_2,

   then osmotic pressure at 233K after dilution is $\pi_{233K} = \pi_{298K} \times \frac{233K}{298K} = 105.3 \times 0.782$ mm of Hg.

   Now the extent of dilution, $\frac{c_1 - c_2}{c_1} = 1 - \frac{c_2}{c_1} = 1 - \frac{\pi_2}{\pi_1} = 1 - \frac{105.3 \times 0.782}{500} = 0.835 = 83.5$ %.

(9)(b) Explain why equimolar solutions of sucrose and sodium chloride in water are not isotonic. (2)

   Ans. See BU'2006, Q2(f), page 8. Write sucrose instead of urea.

BU, 2009

1(f) What thermodynamic function is responsible for osmosis and how? (2)

   Ans. See BU'2000, Q4(a)(i), page 1. There is higher chemical potential of the pure solvent than the solvent in solution when these two are separated by semi permeable membrane. So the solvent flows from the solvent side to the solution side through the semi permeable membrane.

2(b) At one atm pressure, the boiling point of a liquid is 350K. If the heat of vaporization is 30 kJ mol^{-1}, find its boiling point at 0.5 atm. (2)

   Ans. See BU'2004, Q6(c)(i).

3(a) Derive thermodynamically a relation between the elevation of boiling point of a dilute solution and molality of the solute. (4)

   Ans. Derive the relation, $\Delta T_b = K_b \times m$. See the text, "Thermodynamics of two-phase equil^{m}."

 (b) State the assumptions and approximations involved in the above derivation. (2)

   Ans. See the text, "Thermodynamics of two-phase equil^{m}.".

6(b) Can there be any elevation of freezing point of a liquid? — Explain. (2)

   Ans. Yes. When the solute is more soluble in the solid solvent than in the liquid solvent, there occurs elevation of freezing point of the liquid. See "Thermodynamics of two-phase equil^{m}." page 25.

C(7)(ii) Derive Clausius-Clapeyron equation for liquid – vapor equilibrium. (5)

   Ans. See the text, "Principles of thermodynamics" by N C Dey.

 (10)(ii) Show the entropy of mixing of a binary ideal gas mixture is maximum for an isothermal process when $x_1 = x_2 = 0.5$, where x_1 and x_2 are the mole fractions of the components. (5)

Ans. See the text, "Principles of thermodynamics" by N C Dey.

First formulate $\Delta S_{mixing} = -nR\left(x_1 \ln x_1 + x_2 \ln x_2 \right)$, then show that ΔS_{mixing} is maximum when $x_1 = x_2 = 0.5$.

BU, 2010

1(f) What is the difference between 0.1 molar and 0.1 molal $CaCl_2$ solution? (2)

Ans. 0.1 molar $CaCl_2$ solution contains 0.1 mole of the solute in 1 litre solution but 0.1 molal $CaCl_2$ solution contains 1 mole solute in 1 Kg of the solvent. Former is T— dependent while the latter is T— independent.

(g) Raoult's is valid for which type of solution? Write the value of enthalpy change and volume change for such solution. (2)

Ans. Raoult's law is valid for ideal solution in which solute-solute, solute-solvent and solvent-solvent interactions are uniform.

For such solution, $\Delta H_{mixing} = 0$ and $\Delta V_{mixing} = 0$.

4(a) Deduce Clausius-Clapeyron equation from Clapeyron equation mentioning the assumptions therein. (4)

Ans. Clapeyron equation is $\dfrac{dP}{dT} = \dfrac{\Delta \bar{H}}{T\left(\bar{V}_\beta - \bar{V}_\alpha \right)}$ for the phase change $\alpha \to \beta$ of a pure substance.

If the β - phase is vapor and α - phase is either solid or liquid then $\bar{V}_\beta$ is much greater than $\bar{V}_\alpha$.

$\bar{V}_\alpha$ is neglected in comparison to $\bar{V}_\beta$ and deduce Clausius-Clapeyron equation, $\ln \dfrac{P_2}{P_1} = \dfrac{\Delta \bar{H}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2} \right)$.

Assumptions are (1) $\bar{V}_{solid/liquid}$ is neglected. (2) Vapor is assumed to obey ideal gas equation.

(3) $\Delta \bar{H}$ is assumed to be independent of temperature.
See the text, "Principles of thermodynamics" by N C Dey..

(b) When 3.78 g of non-volatile solute is dissolved in 300.0 g of water, the freezing point depression is 0.646°C. Calculate the molar mass of the compound. (2)

Ans. The relating expression is, $\Delta T_f = K_f \times \dfrac{w_2 \times 1000}{w_1 \times M_2}$, putting values, $0.646 = 1.80 \times \dfrac{3.78 \times 1000}{300.0 \times M_2}$.

$K_f = 1.80$ is taken for water. Solving, $M_2 = 35.11$ g/mol is obtained.

5(a) Derive a relation between the total pressure and mole fraction of any one component in an ideal binary liquid mixture. Show the necessary plot. (4)

Ans. See the text, "Thermodynamics of two-phase equil^m." for derivation, $p_i = x_i \, p_i^0$.

Thus, for 1st component, $p_1 = x_1 \, p_1^0$ and for the 2nd component, $p_2 = x_2 \, p_2^0$

so the total pressure, $P = p_1 + p_2 = x_1 \, p_1^0 + x_2 \, p_2^0 = x_1 \, p_1^0 + (1 - x_1) p_2^0$ or, $P = p_2^0 + \left(p_1^0 - p_2^0 \right) x_1$

For the plot, see the same page.

9(a) Prove that same amount of any non-volatile solute dissolved in particular solvent will produce the same lowering of vapor pressure. (3)

Ans. Lowering of vapor pressure of a solvent due to dissolution of non-volatile solute,

$$\frac{\Delta p_1}{p_1^0} = x_2 \ \text{ or, } \ \Delta p_1 = p_1^0 \times x_2 \ \text{ or, } \ \Delta p_1 = p_1^0 \times \frac{n_2}{n_1 + n_2}.$$

For a particular solvent (for which, p_1^0 is fixed at a given temperature), the lowering of vapor

pressure is same for same amount (in number of moles) of any non-volatile solute dissolved in same quantity of the solvent.

(b) What would be the concentration in g/litre of a solution containing a non-electrolyte ($M_w = 180$), isotonic with a decinormal solution of NaCl? The apparent dissociation of solute is 85 %.

Ans. The osmotic pressure of NaCl solution, $\pi = i\,cRT$, but $i = 1 + (n - 1)\alpha = 1 + (2 - 1) \times 0.85 = 1.85$.

Putting values, $\pi = 1.85 \times 0.1 \times RT$, but this solution is isotonic with a non-electrolyte solution. So, $1.85 \times 0.1 \times RT = c\,RT$ or the molar conc. of non-electrolyte solution is, $c = 0.185$.

The conc. of the solution in g/litre is, 0.185 mol litre^{-1} × 180 g mol^{-1} = 33.3 g/litre.

10(c) Write down the expression of 'ebullioscopic constant'. Mention whether it is a property of solute or solvent. (2)

Ans. The expression of ebullioscopic constant, $K_b = \dfrac{R\left(T_b^0\right)^2}{10^3 l_{vap}}$. T_b^0 and l_{vap} are the boiling point and

latent heat of vaporization per gm of the pure solvent, hence it is a property of the solvent only.

BU, 2011

1(d) An ideal solution need not be a dilute solution – comment. (2)

Ans. The statement is not true.

In ideal solution, the molecular interactions of the components are uniform, so the like substances in solution such as benzene-toluene, carbon tetrachloride-chloroform etc. forms ideal solution at all composition. These solutions need not be dilute for being ideal. However all non-ideal solutions behaves ideal when these are dilute and obeys Raoult's law of vapor pressure which is the criteria of the ideal solution.

2(c)(i) Obtain a relation between the relative lowering of vapor pressure and the osmotic pressure, stating clearly the assumptions and approximations. (4)

Ans. See the text for derivation of the relation, $\dfrac{\pi \times \overline{V}_1^o}{RT} = \dfrac{p_1^o - p_1}{p_1^o}$ and the assumptions and approximations.

(ii) 1.0 molal aqueous solution of hydrofluoric acid (HF) has a freezing point of – 1.91°C. Calculate the degree of ionization of HF in solution. What is the ionization constant of the acid? (2)

Ans. $\Delta T_f = T_f^o - T_f = 0 - (-1.91) = 1.91^o C$. The Raoult's law of depression of freezing point of a solution

is given as, $\Delta T_f = i \times K_f \times m$. For aqueous solution, $K_f = 1.86^o C/molal$.

Thus putting the data given in the problem, we have, $1.91^o C = i \times 1.86^o C/molal \times 1.0\,molal$ or, i = 1.027. Again, $i = 1 + (n-1)\alpha$, putting the values we get, the degree of dissociation of the acid, $\alpha = 0.027$.

The dissociation constant of the acid, $K_a = \dfrac{\alpha^2 c}{1-\alpha} = \dfrac{(0.027)^2 \times 1.0}{1 - 0.027} = 7.5 \times 10^{-4}$.

3(c)(i) Benzoic acid is monomeric in aqueous solution and dimeric in benzene. Obtain expressions for its distribution co-efficient between benzene and water. (5)

Ans. See the text for the expression, $K_d = \dfrac{\sqrt{c_{benzene}}}{c_{water}}$.

(ii) At 1 atmospheric pressure, the boiling point of a liquid is 350 K. If the heat of vaporization is 30 kJ mol^{-1}, find its boiling temperature at 0.5 atmospheric pressure. (4)

Ans. The Clausius-Clapeyron equation is, $\ln\left(\dfrac{p_2}{p_1}\right) = \dfrac{\bar{L}^o_{vap}}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$, inserting the data given in the problem,

$$\ln\left(\frac{1\,atm}{0.5\,atm}\right) = \frac{30\,kJ\,mol^{-1}}{8.31\times10^{-3}\,kJ\,mol^{-1}K^{-1}}\left(\frac{1}{T_1} - \frac{1}{350K}\right) \text{ or, } T_1 = 327.96K.$$

Thus the boiling temperature of the liquid at 0.5 atmospheric pressure is 327.96K.

3(d)(iii) Explain the presence of an impurity always lowers the melting point of a pure solid. Can there be a phenomenon like freezing point elevation in any solution?   (2)

Ans. The Raoult's law of depression of freezing point, there occurs a depression of freezing point of a of a liquid when a solute is added to it. This implies that when a minute amount of a substance (impurity) is present there will be lowering of melting point of the solid.

When the solute is more soluble in the solid solvent than in the liquid solvent there can be elevation of freezing point of the solution.

BU, 2012

1(g) In an aqueous solution of sucrose the chemical potential of water is less than the molar free energy of pure water. Explain from the point of spontaneity of mixing.   (2)

Ans. The mixing process at constant T and P is spontaneous so $\Delta G_{mix} \langle 0$. Now taking 1 subscript for water and 2 for sucrose, we can write as

$$\Delta G_{mix} = \left(n_1\mu_1 + n_2\mu_2\right) - \left(n_1\mu_1^o + n_2\mu_2^o\right) = \left(n_1\mu_1 - n_1\mu_1^o\right) + \left(n_2\mu_2 - n_2\mu_2^o\right) \langle 0. \text{ Each term is (–)ve and so}$$

$$\left(n_1\mu_1 - n_1\mu_1^o\right) \langle 0 \text{ or, } \mu_1 \langle \mu_1^o.$$

Thus chemical potential of water in solution (μ_1) is less than the molar free energy of pure water (μ_1^o).

2(c)(ii) Two solid compounds A and B respectively have melting point 67°C and 127°C and the latent heat of fusion 300 cal.g^{-1} and 200 cal.g^{-1}. Which one is better solvent for cryoscopic determination of molecular weight by Rast's methods? Why?   (2)

Ans. In Rast's method, higher K_f value is better solvent. But $K_f = \dfrac{R\left(T_f^o\right)^2}{10^3 l_f^o}$, inserting the data for the

solvents A and B and comparing the value for the two solvents, we have, $K_f(B) = 2.08 \times K_f(A)$.

Thus solvent B is better than solvent A as higher value of K_f means higher ΔT_f and easier to record by ordinary thermometer.

3(a)(i) Derive the Clapeyron equation from Maxwell's equations of thermodynamics. Mention the necessary assumptions and obtain the integrated form of the Clausius-Clapeyron equation from the Clapeyron equation.   (4+4)

Ans. See the text and start from Maxwell's equation, $\left(\partial P / \partial T\right)_V = \left(\partial S / \partial V\right)_T$ and proceed.

(ii) At 0°C the heat of fusion of ice is 333.5 J g^{-1} and the densities of water and ice are 0.9998 g cm^{-3} and 0.9168 g cm^{-3} respectively. Show that an increase of pressure by 1 bar lowers the freezing point of water by 0.0075 K.   (4)

Ans. The Clapeyron equation is $\dfrac{dP}{dT} = \dfrac{L}{T(V_2 - V_1)}$ or, $dT = \dfrac{T(V_2 - V_1)\times dP}{L}$. Inserting the data for 1 g, we get

$$dT = \frac{273K\left(0.9998^{-1} - 0.9168^{-1}\right)cm^3 g^{-1}\times 1\,bar}{333.5\,J\,g^{-1}} = \frac{273K\left(0.9998^{-1} - 0.9168^{-1}\right)cm^3 \times 1\,bar}{333.5\times\left(83.1/8.31\right)cm^3\times bar} = -0.0075K.$$

3(d)(i) What are colligative properties? Deduce the relationship for the molecular weight of a non-volatile solute and the depression in freezing point of the solvent on addition of the solute.   (2 + 6)

Ans. These properties of the solution do not depend on the nature of the solute but these depend on the number of solute particles dissolved in a given amount of the solvent. These properties are relative lowering of vapor pressure, elevation of boiling point, depression of the freezing point and osmotic pressure of the solution.

See the text for the deduction of the relation, $M_2 = K_f \times \dfrac{w_1 \times 10^3}{w_2 \times \Delta T_f}$

(ii) The vapor pressure of a solution containing 6.69 g of $Mg(NO_3)_2$ dissolved in 100 g water is 747 torr at 100^oC. Calculate the degree of dissociation of the salt. (4)

Ans. The observed relative lowering of vapor pressure of a solution is $\left(\dfrac{p_1^o - p_1}{p_1^o} \right)_{obs} = \dfrac{760 - 747}{760} = 0.017$.

The calculated relative lowering of vapor pressure is

$$\left(\dfrac{p_1^o - p_1}{p_1^o} \right)_{cal} = x_2 = \dfrac{n_2}{n_1 + n_2} = \dfrac{\left(\frac{w_2}{M_2} \right)}{\left(\frac{w_1}{M_1} \right) + \left(\frac{w_2}{M_2} \right)} = \dfrac{\left(\frac{6.69}{148.31} \right)}{\left(\frac{100}{18} \right) + \left(\frac{6.69}{148.31} \right)} = 0.00805 .$$

The Van't Hoff factor, $i = \dfrac{observed\ colligative\ property}{calculated\ colligative\ property} = \dfrac{0.017}{0.00805} = 2.112$.

But, $i = 1 + (n-1)\alpha$ or, $2.112 = 1 + (3-1)\alpha$ or, $\alpha = 0.556$ or $\alpha = 55.6\%$.

BU, 2013

1(d) Mention the theory that comes readily to explain the abnormal colligative property of electrolyte solution. What does the theory state? (2)

Ans. The colligative property of a solution is the property that depends on the collection of solute particles (i.e. number of particles) in a fixed amount of the solvent. The property is increased with the increase of solute particles in the solution.

In the electrolyte solution, the solute molecules are dissociated and so number of solute particles is increased in the given amount of the solvent resulting an increase of the colligative property.

Thus the value shows abnormal from the point of view of the relating laws in which the solute is considered non-dissociated molecules.

2(d)(i) From molecular point of view mention the criteria for a solution, B twined by mixing two compounds, A and B, to be ideal and hence arrive at the thermodynamic criteria for this case. (4)

Ans. When the interaction between the molecules A – A and B – B is same with A – B, the solution is ideal. The escaping tendency of both A and B component in solution to the vapour phase will be same and each component obeys Raoult's law.

This uniform interaction among A and B gives the following thermodynamic criteria:

(m) The volume change due to mixing, $\Delta V_{mixing} = 0$ and the molar volume of each component is same as its partial volume i.e., $\overline{V}_i = \overline{V}_i^o$.

(n) There is neither evolution or absorption of heat when A and B are mixed i.e., $\Delta H_{mixing} = 0$.

(o) The chemical potential of each component can be expressed as, $\mu_i(T, P) = \mu_i^o(T, P) + RT \ln x_i$.

(ii) Show that for a binary solution of A and B, molefraction of solute (x_B) can be expressed as

$x_B = \dfrac{m_B M_A}{1 + m_B M_A}$, where M and m are the molar mass and molality respectively. (2)

Ans. The molality (m_B) of a solution of B in A means that m_B moles of B is dissolved in 1 kg of the solvent A. Thus the molefraction of B, $x_B = \dfrac{n_B}{n_A + n_B}$, where n are the mole numbers.

So for m_B molal solution, $x_B = \dfrac{m_B}{\left(\dfrac{1}{M_A}\right) + m_B} = \dfrac{m_B M_A}{1 + m_B M_A}$.

3(c)(i) Deduce the relation between osmotic pressure (π) and mole fraction of solvent (x_1) in solution,

$\pi V_1^o + RT \ln x_1 = 0$, mentioning the necessary assumptions there in. Taking $c_2 = \dfrac{n_2}{V}$ and

$V = n_1 V_1^o + n_2 V_2^o$ (V_1^o and V_2^o and n_1 and n_2 are molar volumes and mole numbers of solvent and solute respectively).

I. Compute $x_1 = \dfrac{n_1}{n_1 + n_2}$ in terms of V_1^o , V_2^o and c_2 ,

II. evaluate $\left(\dfrac{\partial \pi}{\partial c_2}\right)_T$ and show that at $c_2 = 0$, $\left(\dfrac{\partial \pi}{\partial c_2}\right)_T$ is equal to RT. (9)

Ans. See the text for derivation of osmotic pressure up to $\bar{V}_1^o \pi = -RT \ln x_1$ or, $\bar{V}_1^o \pi + RT \ln x_1 = 0$.

I. Now, $x_1 = \dfrac{n_1}{n_1 + n_2} = 1 - \dfrac{n_2}{n_1 + n_2} = 1 - \dfrac{n_2 \bar{V}_1^o}{n_1 \bar{V}_1^o + n_2 \bar{V}_1^o} = 1 - \dfrac{n_2 \bar{V}_1^o}{V}$, taking $V = n_1 \bar{V}_1^o + n_2 \bar{V}_1^o$ (approx.).

But, $\dfrac{n_2}{V} = c_2$, so $x_1 = 1 - c_2 \bar{V}_1^o$. This is the expression of x_1 in terms of c_2 and $\bar{V}_1^o$.

II. We have $\bar{V}_1^o \times \pi + RT \ln x_1 = 0$ or, $\bar{V}_1^o \pi + RT \ln\left(1 - c_2 \bar{V}_1^o\right)$ or, $\bar{V}_1^o \pi = -RT \ln\left(1 - c_2 \bar{V}_1^o\right)$.

Expanding the ln term, we have $\bar{V}_1^o \pi = -RT\left(-c_2 \bar{V}_1^o - \dfrac{1}{2}\left(c_2 \bar{V}_1^o\right)^2 - - -\right)$

or, $\pi = RT\left(c_2 + \dfrac{1}{2} c_2^2 \bar{V}_1^o - - -\right)$. Now, $\left(\dfrac{\partial \pi}{\partial c_2}\right)_T = RT + c_2 RT \bar{V}_1^o + - - -$,

but, if $c_2 = 0$, then all c_2 bearing terms become zero and $\left(\dfrac{\partial \pi}{\partial c_2}\right)_T = RT$.

CU, 2000

6(a): The vapor pressure at 40°C of pure carbon tetrachloride and cyclohexane are 0.2844 and 0.2461 bar respectively. A solution of these two having 0.4753 mole fraction of CCl_4 in composition in equilibrium with

the vapor at 40°C. Calculate assuming ideal behavior the total vapor pressure and mole fraction composition of the vapor at equilibrium. (4)

Solution: The total vapor pressure, $P = p_2^o + \left(p_1^o - p_2^o\right)x_1$, assuming ideal solution and subscript 1 for CCl_4

and 2 for C_6H_{12}. Inserting the values given, $P = 0.2461 + \left(0.2844 - 0.2461\right) \times 0.4753 = 0.2643\,bar$.

Mole fraction of CCl_4 in the vapor phase, $y_1 = \dfrac{p_1}{P} = \dfrac{p_1^o \times x_1}{P} = \dfrac{0.2844 \times 0.4753}{0.2643} = 0.51$.

CU, 2001

2(a): Derive thermodynamically a relationship between the osmotic pressure of the solution and the mole fraction of the solute in the in a dilute solution and hence relate osmotic pressure with molar conc. (5)

Ans. See the text for derivation, $\pi = \dfrac{RT}{\bar{V}_1^o}$ and hence $\pi = cRT$.

2(c): The total vapor pressure at 25°C of a mixture of benzene and toluene in which the two mole fraction are equal, is 62 mm Hg. The vapor pressure of pure benzene at 25°C is 95 mm Hg. Calculate mole fraction of benzene in the vapor at equilibrium with the liquid mixture (assume ideal behavior of the mixture). (3)

Solution: The molefraction of benzene in the vapor phase, $y_b = \dfrac{p_b}{P} = \dfrac{p_b^o \times x_b}{P} = \dfrac{95 \times 0.5}{62} = 0.766$.

CU, 2002

2(a): Derive thermodynamically Raoult's law of relative lowering of vapor pressure. (4)

Ans. See the text for derivation, $\dfrac{p_1^o - p_1}{p_1^o} = x_2$, the terms have their usual meaning.

CU, 2003

2(a): Derive thermodynamically a relation between the elevation of boiling point and conc. of a dilute solution of a non-volatile, non-electrolyte and non-associated solute. (5)

Ans. See the for derivation, $\Delta T_b = K_b \times m$, where m = molality conc. of the solute in the dilute solution.

6(d): What is the thermodynamic criteria for an ideal solution? (2)

Ans. $\Delta V_{mixing} = 0,\ \Delta H_{mixing} = 0$ and the chemical potential of any component, $\mu_i(T,P) = \mu_i^o(T,P) + RT \ln x_i$.

CU, 2004

2(a): Derive thermodynamically a relation between the depression of freezing point and molality of a solute in dilute solution, clearly mentioning the assumptions involved. (5)

Ans. See the text for derivation, $\Delta T_f = K_f \times m$ and state the assumptions.

2(c): The vapor pressure of A is 939.4 mm Hg and that of B is 495.8 mm Hg at 140°C. Assuming that they form an ideal solution, what will be composition of a mixture, which boils at 140°C and under 1 atm? What will be composition of the vapor at this temperature? (3)

Solution: $P = p_B^o + \left(p_A^o - p_B^o \right) x_A$. But the total pressure is 1 atm i.e. 760 mm of Hg, Inserting the data,

$760 = 495.8 + \left(939.4 - 495.8 \right) \times x_A$ or, $x_A = 0.5956$ i.e. mole fraction of A in the mixture is 0.5956.

The mole fraction of A in the vapor phase, $y_a = \dfrac{p_A^o \times x_A}{P} = \dfrac{939.4 \times 0.5956}{760} = 0.7364$.

6(d): "Colligative properties are intensive in nature." – Comment. (2)

Ans. The statement is correct. These properties do not depend on the amount of the solution taken for the experiment.

<center>CU, 2005</center>

2(a) The question is repeated in **CU' 2001, 2(a).**

<center>CU, 2006</center>

1(a) The question is repeated in **CU' 2003, 2(a).**

1(c): Calculate the Van't Hoff factor and the apparent degree of dissociation of a 0.2 molal aqueous solution of $NaNO_3$ which freezes at – 0.675°C. [Given, $K_f = 1.86$ K molal^{-1}] (2)

Solution: $\Delta T_f = T_f^o - T_f = 0 - (-0.675) = 0.675\,^o C$, The depression of freezing point of an electrolyte solution

is given as, $\Delta T_f = i \times K_f \times m$.

Inserting the values given in the problem, $0.675\,^o C = i \times 1.86\,^o C\ molal^{-1} \times 0.2\ molal$

or, the Van't Hoff factor, i = 1.81. Now the apparent degree of dissociation (α) of $NaNO_3$ in aqueous solution is given by the relation, $i = 1 + (n-1)\alpha$ or, $1.81 = 1 + (2-1)\alpha$

or, $\alpha = 0.81$ or 81 %.

2(b)(ii): "Freezing point of a solution of a non-volatile and non-electrolyte solute in a solvent is always less than that of the pure solvent." – Comment on the statement. (2)

Ans. The statement is partially true. When the solvent in the solution separates as pure solid solvent, the statement is true. But when the solute is separates with the solvent and solute is more soluble in the solid solvent, the statement is not true and the freezing point of the solution is greater than that of the pure solvent.

<center>CU, 2007</center>

1(b) The question is repeated in CU'2001, 2(a).

2(b): A certain solution of benzoic acid in benzene has a freezing point of 3.1°C and boiling point of 82.6°C at 1 atm pressure. Explain the observations and suggest structure of the solute particles at the two temperatures. [Normal FP of benzene = 5.5°C, normal BP of benzene = 80.1°C, $K_f = 5.12$ °C/m and $K_b = 2.53$ °C/m] (4)

Solution: Observations show that FP of the solution is depressed whole BP of the solution is elevated.

From the Raoult's law of depression of FP, $\Delta T_f = K_f \times m$ or, $m = \dfrac{\Delta T_f}{K_f} = \dfrac{5.5 - 3.1}{5.12} = 0.47$ molal.

Again from the Raoult's law of elevation of BP, $\Delta T_b = K_b \times m$ or, $m = \dfrac{\Delta T_b}{K_b} = \dfrac{82.6 - 80.1}{2.53} = 0.99$ molal.

The molality of the same solution differs in the two experiments. The molality of the solution in FP experiment is greater than that in FP experiment. Since the conc. is inversely proportional to the molar mass of the solute, hence molar mass of the solute is greater at the FP of the solution than at the BP. This suggest that benzoic acid in benzene remains in the associated form at the FP and remains in normal form at the BP of the solution.

1(a): The question is repeated in **CU'2003, 2(a).**

2(a): In a single graph, draw the $\mu - T$ plots for solid and liquid phases of (i) pure solvent and (ii) solvent in solution. Mention the thermodynamic basis for the depression of freezing point.
Elevation of freezing point is observed sometime in some solutions. – Justify.   (4 + 2)
**Ans.** The reason for drawing the curves is given bellow:

Chem. pot. of the solvent is related with temp. as $\left(\partial\mu_1 / \partial T\right)_P = -\bar{S}_1$

$$= (-)ve.$$

So the curve μ_1 vs. T has $(-)$ve slope always and the slope is more

$(-)$ve for liquid than for solid as, $\bar{S}_1(l) \rangle \bar{S}_1(s)$.

Again, $\mu_1(l) \langle \mu_1^0(l)$ i.e. chemical potential of the solvent in solution
is always less than that of pure solvent at any temperature.
At the FP of the pure solvent (T_f^0), $\mu_1^0(s) = \mu_1^0(l)$,

but at this temperature, solution will not freeze as $\mu_1(l)$ is less than

$\mu_1^0(s)$. As temperature is lowered, $\mu_1(l)$ will increase more than

$\mu_1^0(s)$ and at FP of the solution (T_f), they are equal and solution will freeze.
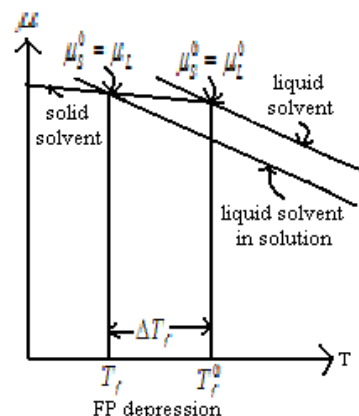
This shows that there occurs depression of freezing point of the solution.
In some solutions, solute is separated with the solvent as solid solution and when the solute is more soluble in solid solvent than in liquid solvent, freezing point is elevated and there occurs elevation of freezing point of these solutions.

1(c) The question is repeated in **CU'2001, 2(a).**

2(c): The melting point of phenol is 40°C. A solution containing 0.172 gm acetanilide (C_8H_9ON) in 12.54 gm phenol freezes at 39.25°C. Calculate the freezing point constant and the latent heat of fusion of phenol.   (4)
Solution: The depression of freezing point of the solution, $\Delta T_f = T_f^o - T_f = 40 - 39.25 = 0.75^o C = 0.75 K$.

Molecular weight of acetanilide, C_8H_9ON is, $M_2 = 8 \times 12 + 9 \times 1 + 16 + 14 = 135$.

Raoult's law of depression of freezing point of dilute solution is, $\Delta T_f = K_f \times m = K_f \times \dfrac{w_2 \times 1000}{w_1 \times M_2}$.

Inserting data, we have, $0.75 K = K_f \times \dfrac{0.172\ gm \times 1000\ gm\ Kg^{-1}}{12.54\ gm \times 135\ gm\ mol^{-1}}$ or, K_f = 7.38 K Kg mol^{-1}.

Again the cryoscopic constant of the solvent, $K_f = \dfrac{R\left(T_f^o\right)^2}{1000\ l_f^o}$.

Now inserting the data $\qquad 7.38 K\ Kg\ mol^{-1} = \dfrac{8.31\ J\ mol^{-1} K^{-1}\left(273 + 40\right)^2 K^2}{1000\ gm\ Kg^{-1} \times l_f^o}$,

we get latent heat of fusion of phenol (l_f^o) = 110.31 J mol^{-1}.

1(a): 1ˢᵗ part is repeated in **CU'2004, 2(a). 2ⁿᵈ part:** Why is the conc. have expressed in molality and not molarity?

(5 + 1)

Answer for the 2ⁿᵈ part: Molality is temperature independent but molarity is temperature dependent. In this experiment, there occurs a change in temperature and so molality is used.

1(c): The BP of ethanol at 1 atm pressure is 78.3°C with $\Delta H_{m,vap} = 39\ kJ\ mol^{-1}$. At what pressure would it boil at 25°C? Mention the assumption, if any, used in the calculation.

Solution: The Clausius-Clapeyron equation is $\ln\left(\dfrac{P_2}{P_1}\right) = \dfrac{\Delta H_{m,vap}}{R}\left(\dfrac{T_2 - T_1}{T_2 T_1}\right)$. Inserting the data given in the problem,

$$\ln\left(\frac{1\ atm}{P_1}\right) = \frac{39\ kJ\ mol^{-1}}{8.31 \times 10^{-3}\ kJ\ mol^{-1} K^{-1}}\left(\frac{351.3 - 298}{351.3 \times 298}\right) K^{-1}.$$ Solving the equation, we get, $P_1 = 0.092$ atm.

2(c): The lowering of chemical potential of the solvent in presence of solute is an entropy effect. – Comment. (3)

Ans. For pure solvent, $\mu_1^o = \bar{H}_1^o - T\bar{S}_1^o$, terms have their usual meanings.

For solvent in solution, $\mu_1 = \bar{H}_1 - T\bar{S}_1$, But for ideal solution, there is no enthalpy effect due to mixing i.e. $\bar{H}_1^o = \bar{H}_1$. In presence of solute, entropy of the solvent is increased due to more randomness in the system. That is, $\bar{S}_1 \rangle \bar{S}_1^o$ and hence, $\mu_1 \langle \mu_1^o$. Thus lowering of chemical potential is an entropy effect.

2(d): Two liquids A and B form an ideal solution. At a particular temperature, the vapor pressure of pure A is 200 torr while that of pure B is 75 torr. If the vapor over the solution consists of 50 mole percent A, what is the mole percent of A in the liquid? (3)

Solution: Given, $p_A^o = 200\ torr$, $p_B^o = 75\ torr$, $y_A = 0.5$ and $x_A = ?$. We have $P = p_B^o + \left(p_A^o - p_B^o\right)x_A$

and $y_A = \dfrac{p_A}{P} = \dfrac{p_A^o \times x_A}{P}$, now inserting the expression of P, we have, $y_A = \dfrac{p_A^o \times x_A}{p_B^o + \left(p_A^o - p_B^o\right)x_A}$.

Inserting the data given, $0.5 = \dfrac{200 \times x_A}{75 + (200 - 75)x_A}$. Solving the equation, we get, $x_A = 0.273$.

Thus, the mole percent of A in the liquid, $x_A = 27.3$.

1(a): The question is repeated in **CU'2001, 2(a).**

1(d): A certain mass of a substance when dissolved in 100 gm of benzene lowers the freezing point by 1.28°C. The same mass of solute dissolved in 100 gm of water lowers the freezing point by 1.40°C. If the substance has a normal molecular weight in benzene and is completely dissociated in water, into how many ions does it dissociate in water? [Given, K_f(water) = 1.86, K_f(benzene) = 5.12 in K Kg mol⁻¹ unit] (4)

Solution: The Raoult's law of depression of freezing point is given by, $\Delta T_f = K_f \times \dfrac{w_2 \times 1000}{w_1 \times M_2}$.

In benzene solvent, $1.28 = 5.12 \times \dfrac{w_2 \times 1000}{100 \times M_2}$ and in water solvent, $1.40 = i \times 1.86 \times \dfrac{w_2 \times 1000}{100 \times M_2}$.

Dividing the two equations, we get $\dfrac{1.28}{1.40} = \dfrac{5.12}{i \times 1.86}$ or, $i = 3.01$.

This Van't Hoff factor, 'i' is related with the degree of dissociation (α) as $i = 1 + (n-1)\alpha$.

Putting the values, $3.01 = 1 + (n-1) \times 1$ or, $n = 3$.

The substance dissociates into three ions in water solvent.

2(b): For an ideal solution which of the following thermodynamic properties will be zero:

$$\Delta V_{mix}, \Delta G_{mix}, \Delta S_{mix}, \Delta H_{mix} ?$$

Ans. ΔV_{mix} and ΔH_{mix} have zero value.

Calcutta University, 2012

Q. 1(b): Derive thermodynamically a relation between the elevation of boiling point of a dilute
  solution and molal concentration of the solute. State assumptions and approximations
  involved. [4]

Ans. See the Text.

Q. 1(c): Calculate the van't Hoff factor and the apparent degree of dissociation of a 0.2 molal
  aqueous solution of $NaNO_3$ which freezes at -0.675 °C. [$K_f = 1.86$ K kg mol^{-1}] [2]

Ans. $\left(\Delta T_f\right)_{cal} = K_f \times m = 1.86$ K kg mol^{-1} $\times$ 0.2 mol kg^{-1} = 0.372 K.

Given, $\left(\Delta T_f\right)_{obs} = 0.675$ K. Thus, van't Hoff factor, $i = \dfrac{\left(\Delta T_f\right)_{obs}}{\left(\Delta T_f\right)_{cal}} = \dfrac{0.675 \, K}{0.372} = 1.81$.

The apparent degree of dissociation, $\alpha = \dfrac{i-1}{n-1} = \dfrac{1.81-1}{2-1} = 0.81 = 81$ %.

Q. 1(d): The lowering of chemical potential of the solvent in presence of a solute is an entropy
  effect. – Comment. [2]

Ans. See C.U. 2010, Q. 2(c), page 290.

Q. 1(e): Two liquids A and B form an ideal solution. At a particular temperature the vapour
  pressure of A is 200 torr, while that of pure of B is 75 torr. If the vapour pressure over
  the solution consists of 50 mole percent A, what is the mole percent of A in the liquid?
  State the assumption involved. [3+1]

Ans. **1st part:** See C.U. 2010, Q. 2(d).

  2nd part: Both Raoult's law of vapour pressure and Dalton's law partial pressure are
    assumed to be valid for this ideal solution.

TIFR Adm. to Int. M Sc and Ph D, 2014

Q 5: The partition of a compound between two immiscible solvents A and B is 10. Solvent A is preferred over
  solvent B. You are given 10 ml of 0.1 M solution of the compound in solvent B. This solution is vigorously
  shaken and equilibrated with 10 ml of solvent A. After phase separation, the concentration of the
  compound in solvent B is
  (A) 0.09 M (B) 0.099 M   (C) 0.009 M   (D) 0.05 M   **[Correct answer is (C)]**

Q 38: When 10 ml of each liquid pairs listed below are mixed and then allowed to stand, which pair is most
  likely to separate into two layers?
  (A) carbon tetrachloride and hexane   (B) ethanol and methanol
  (C) carbon tetrachloride and methanol   (D) hexane and pentane   **[Correct answer is (A)]**

Q 39: Vapor pressure of a liquid in a closed container depends upon
  (A) the volume of the container   (B) the volume of the liquid   (C) the temperature (D) both B and C
                                                                       [Correct answer is (C)]

An American scientist, Willard Gibbs in 1876 deduced a relation from thermodynamical consideration among the number of phases (P), components (C) and degrees of freedoms (F) of the system at equilibrium. This relation is called phase rule and

Phase rule it is stated as,

$$F = C - P + 2$$

The numeral 2 is added to account for the influence of temperature (T) and pressure (P). The beauty of the relation lies in its simplicity and ability to explain the various divergent and unrelated multi-phase equilibria.

Definition of the terms involved in the Phase rule:

(1) Phase (P): It is a part of the system, homogeneous in itself and mechanically separable

Definition of phase. from other homogeneous parts of the system. Each phase is separated from other phases by definite boundary surface, called phase boundary.

  (a) For gaseous system: Only one phase is possible since the gases are completely miscible with each other in all proportions.

  (b) For liquid system: The number of phases is equal to the number of layers formed in the system. Completely miscible liquids form only one phase. Solution is also one phase system.

  (c) For solid system: Each solid constitutes a single phase except for solid solution. Thus, the number of phases in the solid system is equal to the number of solids present. Allotropic modifications and polymorphic forms constitute separate phases.

(2) Component (C): It is the smallest number of independent chemical constituents by

Definition of component. means of which the composition of each and every phase of the system can be described.

Independent chemical constituent is the one whose concentration can be varied independent of other constituents present in the system.

The properties of a system at equilibrium are determined not by what constituents have been selected as its components, but by their number i.e. by the number of components only.

While expressing the composition of a phase, in terms of selected constituents i.e. components, every one of the selected constituents must be included.

Non-reacting system. (i) One component system: Only one chemical constituent is present in non-reacting system. Such as, water(s) $\rightleftharpoons$ water(l), water(s) $\rightleftharpoons$ water(v), water(l) $\rightleftharpoons$ water(v) and water(s) $\rightleftharpoons$ water(l) $\rightleftharpoons$ water(v).

All this equil^m. systems constitutes one–component only.

Reacting system: Dissociation of $NH_4Cl(s)$ in evacuated vessel constitutes one component system.

Reacting system.
$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g).$$

There are three chemical constituents but all are not independent.

No. of components(C) = No. of chemical constituents(C') — No. of restrictions(r).

In the example, one restriction is the chemical equil^m. and other restriction is due to equal conc. of NH_3 and HCl existing in the system. and so, $p_{NH_3} = p_{HCl}$.

The no. of components, $C = 3 - 1 - 1 = 1$, it is one-component two-phase system. NH_3 and HCl are present in the gaseous phase in the same proportion as in the solid NH_4Cl. The phase rule does not make a distinction between chemical compound and its chemical constituents in a mixture in the same proportion, so long that mixture is homogeneous.

(ii) Two-component system: Two chemical constituents in non-reacting system comprises two-component system.

(a) An aqueous solution of common salt, NaCl is a two-component system. Though the solution contains three chemical species Na^+, Cl^- and H_2O, yet it is a two-component system as there is one restriction of electroneutrality, so number of components, $C = 3 - 1 = 2$.
If the species are taken Na^+, Cl^-, H^+, OH^- and H_2O, the restrictions are then three as $c_{H^+} = c_{OH^-}$, $c_{Na^+} = c_{Cl^-}$ and $H_2O \rightleftharpoons H^+ + OH^-$ so number of components,
$$C = 5 - 3 = 2.$$

Aqueous solution of common salt.

(b) Another example is H_2, I_2 and HI system at equil^m. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is one phase system. But the component in the gas phase is determined by any two arbitrarily selected constituents, while the conc. of the third one is definite and can be known from the other two. The number of component, $C = 3 - 1 = 2$, as there is one equil^m. restriction.
But if H_2 and I_2 are taken initially equal then it is one-component system as
$$c_{H_2} = c_{I_2} .$$
Similarly, system containing $NH_4Cl(s)$ along with initially taken $NH_3(g)$ or $HCl(g)$ reacting vessel is a two-component system at equil^m. as in that case, $p_{NH_3} \neq p_{HCl}$.

H_2, I_2 and HI at equil^m.

(c) Decomposition of $CaCO_3(s)$ at equil^m., $CaCO_3 (s) \rightleftharpoons CaO(s) + CO_2(g)$. is a three-phase system but it is a bi-component one, since there is one restriction of equil^m. and three chemical constituents.
Though number of moles of CaO and CO_2 are same but conc. of the two are different as they are not in the same phase. That is,
$$n_{CaO(s)} = n_{CO_2(g)} \quad \text{but } c_{CaO(s)} \neq c_{CO_2(g)} .$$

Decomposition of $CaCO_3(s)$ with products at equil^m.

(3) Degree of freedom (F): It is the smallest number of independent variables such as pressure (P), temperature (T), concentration (x) which can be varied independently without altering the number of phases of the system.
Let us illustrate with one-component water system with different phases at equil^m.

Definition of degree of freedom.

One component water system with different phases.

C = 1, P = 1, F = 2
Bivairant
I

C = 1, P = 2, F = 1
Monovariant
II

C = 1, P = 3, F = 0
Non-variant
III
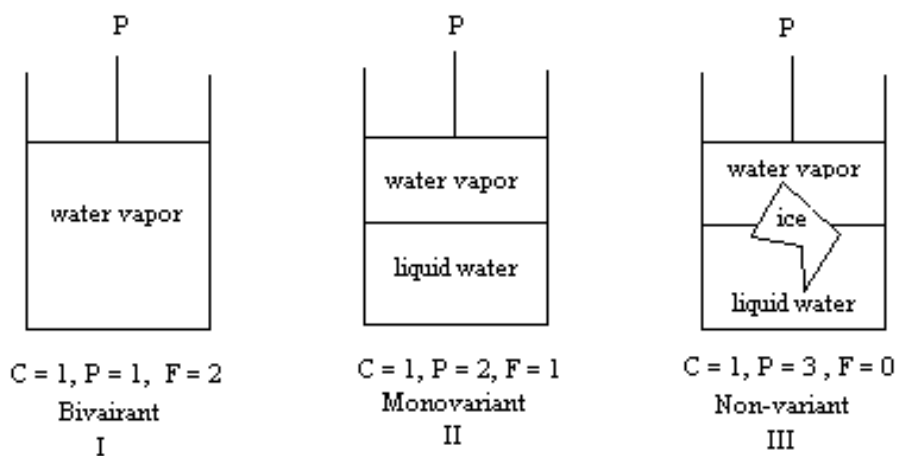
In I, both T and P can be varied independently, in II, only T can be varied independently, P is automatically fixed. In II, neither T nor P can be varied. These are fixed and it is called 'triple point'.

We may illustrate with systems having two components.

(a) The system consists of solid sucrose in equil^m. with aqueous solution of sucrose.

$$sucrose(s) \rightleftharpoons sucrose(aq).$$

Phase rule for saturated solution
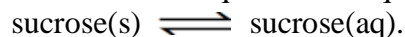
Number of components, C = 2, Number of phases = 2 so, the degrees of freedom (intensive variables),

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

Two degrees of freedom signifies that once T and P are specified the equil^m. mole fraction (solubility) of sucrose in saturated solution is fixed.

The other properties like solution density, refractive index, thermal expansivity and specific heat capacity all are fixed, but the volume of the solution is not fixed.

(b) Let us consider a mixture of H$_2$(g), O$_2$(g) and H$_2$O(g). There is no chemical equil^m. in this case and the number of components is 3. Now if the mixture is heated in the presence of a catalyst, a chemical equil^m. is attained.

Phase rule for H$_2$(g), O$_2$(g) and H$_2$O(g) reacting system

$$2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g).$$
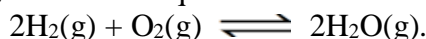
The number of components = 3 − 1 = 2, as there is one chemical equil^m. condition,

$$\mu_{CaCO_3(s)} = \mu_{CaO(s)} + \mu_{CO_2(g)}$$

The degrees of freedom, $F = C - P + 2 = 2 - 1 + 2 = 3$.

If the equil^m. is attained by starting with H$_2$O(g) in a closed vessel, the number of components would become 1 and in that case, $F = 1 - 1 + 2 = 2$.

(c) Another system is considered with aqueous solution of weak acid HCN. Let us find the restrictions, components and degrees of freedom.

Phase rule for aqueous solution of HCN

The system has five chemical species H$_2$O, HCN, H$^+$, OH$^-$, and CN$^-$, so $C' = 5$. But there are two independent chemical equil^m. conditions,

$$\mu_{H_2O} = \mu_{H^+} + \mu_{OH^-} \text{ and } \mu_{HCN} = \mu_{H^+} + \mu_{CN^-}$$

In addition to, there is another restriction of electroneutrality, $x_{H^+} = x_{CN^-} + x_{OH^-}$.

Thus no. of components, $C = C' - r = 5 - 3 = 2$, and, $F = 2 - 1 + 2 = 3$.

These intensive variables of the system are P, T and x_{H_2O} or x_{HCN}

Exercise: Calculate the number of phases (P), components (C) and degrees of freedom (F) of the following systems at equil^m..

(1) NH$_4$Cl(s) $\rightleftharpoons$ NH$_3$(g) + HCl(g), (a) when $p_{NH_3} = p_{HCl}$ and (b) when $p_{NH_3} \neq p_{HCl}$.

Ans. (a) P = 2, C = 1, F = 1, (b) P = 2, C = 2, F = 2.

(2) I$_2$(s) $\rightleftharpoons$ I$_2$(water) $\rightleftharpoons$ I$_2$(benzene). Ans. P = 3, C = 3, F = 2, [T, $c_{I_2(w)}$ or $c_{I_2(b)}$].

(3) Water at its freezing point. Ans. P = 2, C = 1, F = 1 (T or P).

(4) Aqueous solution of H$_2$SO$_4$. Ans. P = 1, C = 2, F = 3 (P, T and $x_{H_2SO_4}$ or x_{H_2O}).

(5) Aq. solution of H$_2$SO$_4$ and HAc. Ans. P = 1, C = 3 and F = 4 (P, T, $x_{H_2SO_4}$ and x_{HAc}).

(6) H$_2$O(l) and H$_2$O(v) in equil^m. at 1 atm. Ans. P = 2, C = 1, F = 0 (as P = fixed).

(7) N$_2$O$_4$(g) $\rightleftharpoons$ 2 NO$_2$(g). Ans. P = 1, C = 1, F = 2 (T, x_{NO_2}).

(8) Pure partly frozen acetic acid. Ans. P = 2, C = 1 and F = 1.

(9) A liquid at its critical point. Ans. P = 2, C = 1, F = 0 (liquid and vapor are alike).

(10) A binary azeotrope. Ans. P = 2, C + 2 and F = 0 (two restrictions, P = fixed and liquid and vapor have same composition).

(11) A saturated solution of Na$_3$PO$_4$ which is completely dissociated to its component ions, contains an excess of the salt. Ans. P = 2, C = 2, F = 2 (P and T).

Thermodynamic criteria of phase equilibria.

Let us consider a system in which a pure substance (one component) is present in two phases (α and β) in equil^m. with each other.

Let μ^α and μ^β are the chemical potentials of the substance in phase α and β respectively. The free energy of the system is thus given as,

$$G = f(T, P, n^\alpha, n^\beta).$$

where, n^α and n^β are the mole number of the substance in the phases α and β respectively. The change in free energy of the system as a result of changes in T, P, n^α and n^β is given by

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n^\alpha,n^\beta} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n^\alpha,n^\beta} dP + \left(\frac{\partial G}{\partial n^\alpha}\right)_{T,P,n^\beta} dn^\alpha + \left(\frac{\partial G}{\partial n^\beta}\right)_{T,P,n^\alpha} dn^\beta.$$

Or, $dG = \left(\frac{\partial G}{\partial T}\right)_{P,n^\alpha,n^\beta} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n^\alpha,n^\beta} dP + \mu^\alpha dn^\alpha + \mu^\beta dn^\beta.$

If dn mole of the substance is transferred from phase α to β at constant T and P, we get,

$$dG = \mu^\alpha(-dn) + \mu^\beta(+dn) = (\mu^\beta - \mu^\alpha) dn.$$

If the above transfer takes place reversibly (i.e. under equil^m. condition), then $dG = 0$ and so the equation reduces to

$$(\mu^\beta - \mu^\alpha) dn. = 0, \text{ since } dn \neq 0, \text{ it follows that } \mu^\beta = \mu^\alpha.$$

It signifies that if a substance remains in equil^m. between the two phases, its chemical potential must have the same value in both the phases.

The above criterion of a substance present in two phases in equil^m. may be generalized for a system containing more than one phase and each phase containing more than one substance. If a closed system at a given T and P contains n_1, n_2, n_3..moles of components 1, 2, 3, … remain in equil^m. in each of the phases $\alpha, \beta, \gamma, ...$, then the above criterion can be extended to,

Generalized criteria for equil^m.

$$\mu_1^\alpha = \mu_1^\beta = \mu_1^\gamma = ...$$
$$\mu_2^\alpha = \mu_2^\beta = \mu_2^\gamma = ...$$
$$\mu_3^\alpha = \mu_3^\beta = \mu_3^\gamma = ...$$

That is, if the system remains in equilibrium, the chemical potential of any one component must have the same value in each phase in which it exists.

Derivation of the phase rule, F = C – P + 2:

Let us consider a multiphase system containing P phases at equil^m. and each phase contains all the C components at pressure, P and temperature, T. The system is a closed one and non-interactive. The system can be completely defined by specifying the following variables:

(1) pressure (P) – one variable (2) temperature (T) – one variable

and (3) concentration of each component in each phase.

Let us take the mole fraction as the mode of expressing the conc. of the components. For each phase we require (C – 1) mole fraction terms since the last one is fixed from the remaining. Since there are P phases, hence total conc. terms required, is P (C –1).

Again, components in all the P phases are in thermodynamic equil^m., so chemical potential of each component is same in all the phases in which it exists.

Since chemical potential is related to the mole fraction (x_i) linearly, $\mu_i = \mu_i^0 + RT \ln x_i$,

hence conc. of a particular component in one phase if known, the same in other phases are fixed. Thus the number of conc. variables fixed for the system = C (P – 1).

So, the conc. variables required to define the system = P (C –1) – C (P – 1).

Including P and T variables, we have the total degrees of freedom,

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

This is the Gibbs phase rule equation and valid for any heterogeneous equilibria.

The influence of electric, magnetic, gravitational or surface force are ignored. The equation does not depend on the nature or amount of the substances present in the system.

It does not assume anything regarding the constitution of the matter or molecular complexity. It simply depends on the number of components and phases present in the system.

However, phase rule is qualitative in nature. Complete study of heterogeneous equilibria can be made with the help of (i) law of mass action (ii) Nernst distribution law (iii) Clapeyron equation and (iv) the Phase rule.

The phase rule predicts qualitatively the effect of temperature, pressure and conc. on the polyphase equilibria.

The rule states that systems having same number of degrees of freedom shall behave similarly. Thus it enables to classify the different types of physical or chemical equilibria.

To illustrate, let us take three different systems viz.

(i) H$_2$O(l) $\rightleftharpoons$ H$_2$O(v), (ii) solid tin(α) $\rightleftharpoons$ vapor and (iii) CaCO$_3$(s) $\rightleftharpoons$ CaO(s) + CO$_2$(g).

The last one is chemical equil^m. while the first two are physical equilibria.

Each system has one degree of freedom i.e. monovariant. The effect of P and T on the phases of the systems is given below.

Intensive variables

Limitations

Systems having same degree of freedom behave similarly.
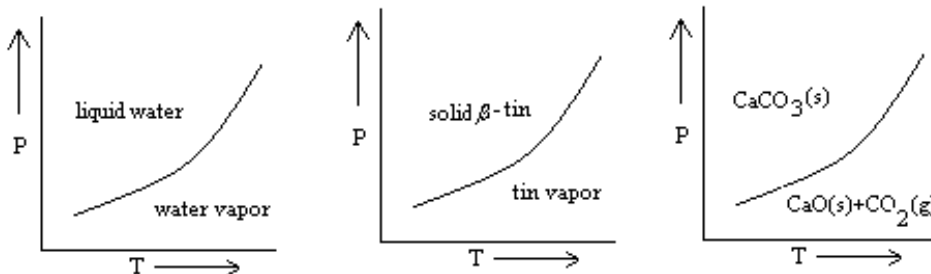
Effect of temperature (T) and pressure (P) on the stability of phases:

The basic equation relating to the chemical potential, $d\mu = -\bar{S}\, dT + \bar{V}\, dP$,

where, $\bar{S}$ and $\bar{V}$ are the molar entropy and molar volume of the substance respectively.

The equation gives, $\left(\dfrac{\partial \mu}{\partial T}\right)_P = -\bar{S} = (-)\text{ve}$, since molar entropy is always (+)ve.

That is, μ decreases with T at constant P. The slope of μ vs. T curve is highest for gas, lowest for solid and in-between for liquid.

Effect of T on the stability of different phases
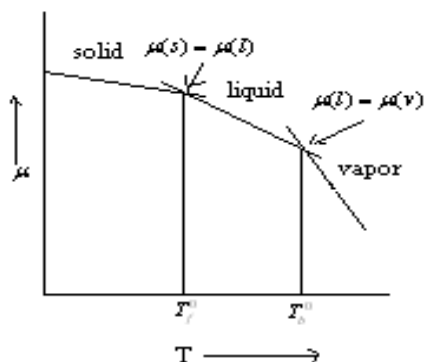
The curves of μ vs. T for solid, liquid and gas are given here.
The following conclusions, we can draw from the diagram:
When,

(1) T > T_b, vapor phase is stable.
(2) T = T_b, liquid and vapor phase co-exist.
(3) T < T_b, liquid phase is stable.
(4) T = T_f, liquid and solid phase co-exist.
(5) T < T_f, solid phase is stable.

Effect of P on the stability of different phases

Again, $\left(\dfrac{\partial \mu}{\partial P}\right)_T = \bar{V} = (+)\text{ve}$, since molar volume is always (+)ve

The chemical potential of a substance always increases with increase of pressure at constant temperature.

Since the equil^m. condition at constant T and P is the minimization of G, the stable phase at any point of one component in P –T diagram is the one with the lowest μ.
Thus at point A in the figure, liquid vapor coexist and have equal chemical potential
i. e. μ (l) = μ (v).

Since $\left(\dfrac{\partial \mu}{\partial P}\right)_T = \bar{V}$ and $\bar{V}(g) \ggg \bar{V}$ (l), an isothermal decrease of P lowers substantially the $\mu(v)$ but

has only a small effect on the $\mu(l)$. Therefore lowering of P makes vapor to have lower chemical potential and thus vapor is the stable phase at point A.
That is, when P is lowered at constant T, $\mu(v)$ decreases more than μ (l), so vapor state is more favored.
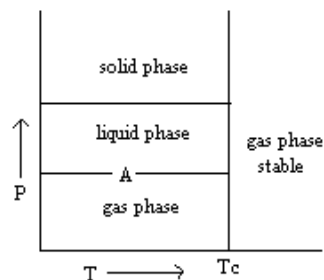
Problem: The following graph shows the variation of chemical potential, μ as a function of pressure, P at constant temperature for diamond (solid line) and graphite (dotted line).
Which of the following statements does not follow from the graph.
(a) Below 15 Kbar, graphite is more stable then diamond.
(b) The molar volume of graphite is less than that of diamond.
(c) The molar volume of graphite is greater than that of diamond.
(d) Diamond is more stable than graphite above 15 Kbar.

[Ans. (c)]
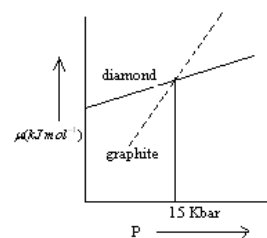
Phase diagram:

Phase diagrams are the graphs showing the effect of pressure, temperature and concentration on the different phases of heterogeneous equilibria.

Co-existence of different phases can be studied in the phase diagram of the system.

When two variables such as (P and T), (P and x) or (T and x) are chosen, two-dimensional phase diagrams are used. But when three variables are chosen, solid diagrams are needed.

Time is not a variable since it concerns with system at equil^m.

For example, in one-component system, C = 1, so the phase rule, F = C – P + 2

or, F = 3 – P.

If, P = 1, F = 2, if P = 2, F = 1 and when P = 3, F = 0. Thus, maximum F = 2.

For a one-component system, at least two intensive variables are required to describe the state of the system. We can represent any state of one-component system by a point in a two-dimensional P vs.T diagram (mole fraction of one-component system is always one). Each point corresponds to a definite value of P and T.

Such diagram is called phase diagram.

The graph shows the P – T phase diagram of pure water.

The effect of P on T for transition of one phase to another of a substance is guided by Clapeyron equation.

Lines are the locus of the points of P and T on the coexistence two phases (F = 1). Areas bounded by the lines indicate the existence of a single homogeneous phase (F = 2). The point of intersection of any two curves indicates the coexistence of three phases (F = 0) and the point is called triple point.

It could be shown from the Clapeyron equation, that sublimation curve (S $\rightleftharpoons$ V) is steeper than the vaporization curve (L $\rightleftharpoons$ V).

The slope of the sublimation curve according to the Clapeyron equation is

$$\frac{dP}{dT} = \frac{\bar{L}_{sub}}{T\left(\bar{V}_{vapor} - \bar{V}_{solid}\right)} \quad \text{and} \quad \text{that for the vaporization curve is} \quad \frac{dP}{dT} = \frac{\bar{L}_{vap}}{T\left(\bar{V}_{vapor} - \bar{V}_{liquid}\right)}.$$

But, $\bar{L}_{sub} = \bar{L}_{fus} + \bar{L}_{vap}$ thus, $\bar{L}_{sub} \rangle \bar{L}_{vap}$ and $\left(\bar{V}_{vapor} - \bar{V}_{solid}\right) \approx \left(\bar{V}_{vapor} - \bar{V}_{liquid}\right)$.

This explains that $\left(\dfrac{dP}{dT}\right)_{sublimation} \rangle \left(\dfrac{dP}{dT}\right)_{vaporisation}$

i.e. the sublimation curve is steeper than the vaporization.

Again by the use of Clapeyron equation, it is possible to show that melting curve is steepest and slightly tilted towards the pressure axis.

$$\frac{dP}{dT} = \frac{\bar{L}_{fusion}}{T\left(\bar{V}_{liquid} - \bar{V}_{solid}\right)} \quad \text{and} \quad \left(\bar{V}_{liquid} - \bar{V}_{solid}\right) \text{ is very small and (–)ve for water system.}$$

This shows that $\left(\dfrac{dP}{dT}\right)_{fusion}$ is very high and negative.

Problem: The graph above shows the P – T phase diagram of pure water.

Indicate which of the following statement about the figure is not true.

(a) At the point Y, water has one degree of freedom.

(b) Point X is the triple point of water.

(c) The molar entropy of water at Q is greater than at Z.

(d) Solid liquid water coexist at the point R. [Ans. (a)]
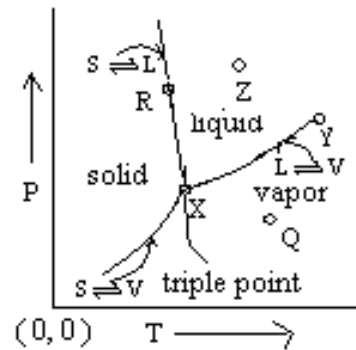
Phase diagram of water system:

It is one component system and the possible phases are three – solid (s), liquid (l) and vapor (v). The degree of freedom, F = 3 — P.

Phase rule of the system

F is 2 for single phase, 1 for two phases in equil^m. and 0 for three phases in equil^m.
The phase diagram of water system is given below.

Phase diagram of water system
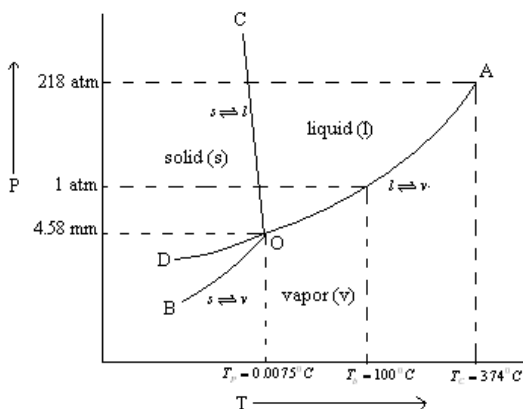
BO → sublimation curve, s ⇌ v
OA → vaporization curve. l ⇌ v
OC → melting curve, s ⇌ l
 O → triple point representing the coexistence of s ⇌ l ⇌ v
OD → super cooled water ⇌ vapor
Three curves BO, OA and OC divide the diagram into three curves:
 BOC → single solid phase (ice)
 AOC → single liquid phase
 BOA → single vapor phase.

Experimental set-up →
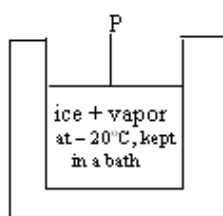
An evacuated vessel fitted with a movable piston is placed in a thermostat of temperature much below of 0°C, let it be – 20°C. The piston can be placed at any position by a set of stops. The solid water (ice) is placed in the vessel. The behavior of the system at various temperature and pressure is shown by the above phase diagram.

(a) Sublimation curve: (solid ⇌ vapor):

Univariant system

Initially the vessel contains ice and its vapor in equilibrium at – 20°C. The system has two phases so degree of freedom is one. The system has a fixed pressure at the temperature. The intensive state of the system is indicated by the point B in the diagram.

Isochoric heating

Now T is increased at constant volume. The vapor pressure (P) of the ice is increased along the line BO. The curve shows the relation of P and T for ice ⇌ vapor equil^m. following the Clapeyron equation.

Isothermal expansion

At any temperature of the curve BO, if the volume is increased by moving the piston upwards, pressure is decreased. But at a given T, pressure is fixed (F = 1). So to keep the P fixed, a little bit ice is vaporized. If the process of isothermal expansion be continued, whole of ice is vaporized and the system contains only the water vapor (one phase). It occurs at a pressure below of that given by the curve BO at temperature of expansion.

Isothermal compression

Similarly isothermal compression at any point along BO leads to only solid state, ice when the piston will be directly in contact with the solid phase at a pressure greater than indicated by the curve BO. Thus the area above BO curve is solid (ice) and below BO is vapor. This curve extends to 0K.

Isochoric heating along the BO curve

If the temperature of the system containing ice and its vapor is increased at constant volume, vapor pressure is increased until the vapor pressure of ice becomes equal to that of liquid water. At this temperature, called triple point, ice starts melting and the system contains three phases at equil^m., ice ⇌ water (l) ⇌ water (v).

The system is invariant (F = 0) and both T and P are fixed and can not be changed.
If any of the variables is tried to change, one phase will disappear and becomes two-phase system.
The state is shown by the point O in the diagram. The temperature and pressure and P of the
point are 0.0075°C and 4.58 mm of Hg respectively.

(b) Vaporization curve (liquid $\rightleftharpoons$ vapor):

Isochoric
heating along
the curve OA
that extends to
T$_C$

If the system is heated at O keeping volume constant, whole ice melts
and the system contains water and vapor only. Now isochoric increase of temperature,
vapor pressure of liquid water also increases and it is shown by the vaporization curve OA.
The curve will extend up to the critical temperature (T$_C$) at which liquid and vapor become
indistinguishable (F = 0).

The system containing liquid water and vapor is univariant (F = 1)
and only one variable out of P and T can be altered. At a given T, vapor pressure of liquid water
is fixed. When P = 1 atm (760 mm of Hg), the liquid starts boiling, and corresponding
temperature is called normal boiling point of water (100°C).

The slope of BO is greater than that of AO at the triple point (T$_P$).
This can be shown by approximate calculation.

$$\left(\frac{dP}{dT}\right)_{sublimaation} = \frac{18\times(80+540)\,cal\,mol^{-1}}{273K\times22.4\,lit\,mol^{-1}}\times\frac{0.082\,lit\,atm}{2\,cal} = 0.075\,atm\,K^{-1} = 5.7 \text{ cm of Hg K}^{-1}$$

$$\left(\frac{dP}{dT}\right)_{vaporization} = \frac{18\times540\,cal\,mol^{-1}}{273K\times22.4\,lit\,mol^{-1}}\times\frac{0.082\,lit\,atm}{2\,cal} = 0.065\,atm\,K^{-1} = 4.9 \text{ cm of Hg K}^{-1}.$$

At a given temperature of AO curve, if the system is subjected to isothermal
expansion, liquid water is vaporized to keep vapor pressure fixed. If the process is continued all
liquid is vaporized and system contains only the vapor phase.
Thus at pressure below the curve OA the system will contain single phase vapor and at pressure
above the curve OA, it will contain single phase liquid water.
These single phases are shown by area below and above OA respectively.

(c) Melting curve (solid $\rightleftharpoons$ liquid):

If the system containing only the solid phase (ice) at high pressure,
is gradually heated, its temperature rises till a stage is reached when it starts melting.
At this stage, temperature of the system remains constant till whole of the solid phase is
converted into liquid. The temperature at which solid phase melts depends on the pressure over

the solid phase. The line OC represents the variation of T and P at which solid and liquid are in
equil^m. with each other.

The slope of the melting curve OC is given by the Clapeyron
equation and the approximate value of the slope is calculated as,

$$\left(\frac{dP}{dT}\right)_{melting} = \frac{18\times80\,cal\,mol^{-1}}{273\,K\times\left(-0.09\times10^{-3}\right)lit\,mol^{-1}}\times\frac{0.082\,lit\,atm}{2\,cal} = -134\,atm\,K^{-1}.$$

(d) Metastable state (super cooled liquid water $\rightleftharpoons$ water vapor):

If the system containing liquid water $\rightleftharpoons$ vapor is rapidly cooled, it may
happen that ice fails to appear at the triple point, O and the vapor pressure of the liquid continues

to move along OD. It represents the metastable equil^m. involving super cooled water $\rightleftharpoons$ vapor.
Similarly, if the system containing ice and vapor is heated rapidly, ice fails to melt and
metastable equil^m. is reached as super heated ice $\rightleftharpoons$ vapor and the curve extends beyond O.

Since at the triple point, the slope of solid-vapor is greater than that of
liquid-vapor curve, the metastable curve OD remains above of OB and vapor pressure of the

metastable equil^m. is greater than that of stable equil^m. at the same temp. The metastable state is
unstable and a slight disturbance shifts it to the stable state of the system.

Thermodynamically, it can be shown that metastable state (ms) → stable state (s) is a spontaneous process since for the process, $\Delta G \langle 0$.

$\Delta G = \mu_s - \mu_{ms}$. But $\mu_s = \mu_v = \mu_v^0 + RT \ln p_s$ and $\mu_{ms} = \mu_v = \mu_v^0 + RT \ln p_{ms}$.
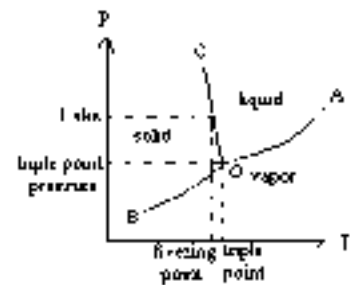
Inserting the values, we get, $\Delta G = \mu_s - \mu_{ms} = RT \ln \left(\dfrac{p_s}{p_{ms}} \right)$,

but, $p_s \langle p_{ms}$ so, $\Delta G = (-)ve$, hence, the process is spontaneous.

Comparison of triple point (T_p) and freezing point (T_f) of a pure substance:

(1) At the triple point, three phases of a substance remain at equil^m. under the vapor pressure of the substance. For water, at the triple point, the system contains solid water (ice) $\rightleftharpoons$ liquid water $\rightleftharpoons$ water vapor in equil^m

At the triple point, the system is three phasic (F = 0)

The degree of freedom (F) = 0, i.e. the system is invariant. Both pressure and temperature are fixed at 4.58 mm of Hg and 0.0075°C.

(2) At the normal freezing point (melting point), a substance remains in two phases under one atm pressure.
For water, the system contains liquid water $\rightleftharpoons$ vapor.

At the freezing point, the system is two phasic (F = 1)

The degree of freedom (F) = 1, the system is univariant.
If pressure of the system is changed the freezing point is also changed.
If pressure is kept at 1 atm, the freezing point of water is 0°C.
From Clapeyron equation it can be shown that the freezing point of water changes by 1°C, when external pressure is changed by about 134 atm. So at 4.58 mm pressure, the freezing point is raised to +0.0075°C.

However, T_p is close to T_f

Since the effect of external pressure on the freezing point of liquid is very small, the normal freezing point of a substance is very close to its triple point and in all practical purposes; the triple point of a substance may be referred to its freezing point.

Sublimation:

What is called sublimation?

When a substance changes its phases from solid to vapor under atmospheric pressure without melting i.e. without passing through the liquid state, the process is called sublimation.

$$(solid \rightleftharpoons vapor).$$

The vapor exerted by the solid is usually small but some substances like naphthalene, camphor, iodine, solid CO_2 (dry ice) have vapor pressure even at ordinary temperature high and it increases with the increase if temperature. If the vapor pressure of the solid reaches the atmospheric pressure before it reaches its melting point,

Condition for a substance to sublime → triple point pressure is greater than 1 atm.

In other words, such solids would be found to sublime when its triple point pressure is higher than the external pressure of the system. In such case, vapor pressure of the solid reaches the external pressure before the solid melts.
Liquid CO_2 does not appear at 1 atm pressure, so it remains dry and this is why it is called dry ice.
However, when the external pressure is kept higher than the triple point pressure, the solid melts.

These solids can be melted.

Triple point pressure of iodine system is 1.06 atm.

(Phase diagram pf dry ice)

Phase diagram of Sulphur system:

Sulphur is one component system (C = 1).

It has polymorphic forms, some of which are unstable. It can exist in four phases.

(1) Rhombic Sulphur (S_α), (2) Monoclinic Sulphur (S_β),

(3) Liquid Sulphur (S_L) and (4) Sulphur Vapor (S_V).

The phase rule states, $F = C - P + 2$, but for the system, C = 1, so $F = 3 - P$.

Thus the following information can be drawn for the existence of its different equilibria.

(a) Single phase equilibria: P = 1, so F = 2, the system is bivariant. There will be four single phases ($^4C_1$) and represented by the area in the phase diagram.

(b) Two phase equilibria: P = 2, so, F = 1. The system is univariant and could be specified by one variable (P or T). There are six two-phase equilibria ($^4C_2$), and these are:

$$S_\alpha \rightleftharpoons S_\beta, S_\alpha \rightleftharpoons S_L, S_\beta \rightleftharpoons S_L, S_\alpha \rightleftharpoons S_V, S_\beta \rightleftharpoons S_V, S_L \rightleftharpoons S_V,$$

The equilibria are represented by lines.

(c) Three phase equilibria: P = 3, so, F = 0, i.e. the system is invariant and there are four three phase equilibria ($^4C_3$). These are represented by points and called triple points. The variables are automatically adjusted. The four equilibria are:

$$S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_L, S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_V, S_\alpha \rightleftharpoons S_L \rightleftharpoons S_V, S_\beta \rightleftharpoons S_L \rightleftharpoons S_V,$$
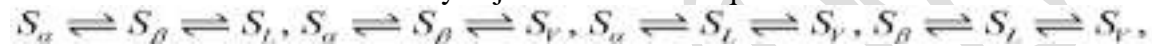
(d) Four phases can not exist in equil^m., when P = 4 , F = – 1 and this is meaningless.

With the use of the above information, the following phase diagram of the sulphur system can be drawn.

Description of the phase diagram:

Areas → ABEF(S_α), ABCD(S_V), FECD(S_L), EBC(S_β)

Lines indicating stable curves:

(i)   AB → sublimation curve for $S_\alpha \rightleftharpoons S_V$.

(ii) BC → sublimation curve for $S_\beta \rightleftharpoons S_V$

(iii) CD → vaporization curve for $S_L \rightleftharpoons S_V$.

(iv) BE → transition curve for $S_\alpha \rightleftharpoons S_\beta$.

(v) CF → melting curve for $S_\beta \rightleftharpoons S_L$.

(vi) EF → melting curve for $S_\alpha \rightleftharpoons S_L$.
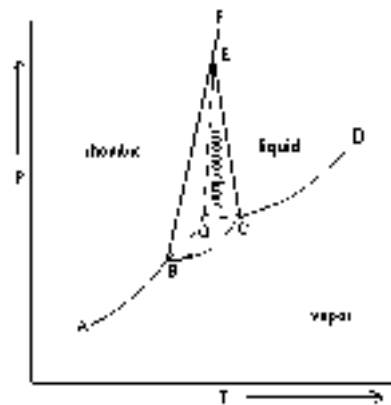
Lines showing curves:

(i) BG → metastable sublimation curve of rhombic sulphur, $S_\alpha \rightleftharpoons S_V$

(ii) CG → metastable vaporization curve of liquid sulphur, $S_L \rightleftharpoons S_V$.

(iii) BH → metastable sublimation curve of monoclinic sulphur, $S_\beta \rightleftharpoons S_V$.

(iv) EG → metastable melting curve of rhombic sulphur, $S_\alpha \rightleftharpoons S_L$.

The system has three stable triple points and one metastable triple point.

(i) B point represents the stable equil^m. of $S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_V$.

(ii) C point represents the stable equil^m. of $S_\beta \rightleftharpoons S_L \rightleftharpoons S_V$.

(iii) E point represents the stable equil^m. of $S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_L$

(iv) G point represents the metastable equil^m. of $S_\alpha \rightleftharpoons S_\beta \rightleftharpoons S_V$.

Data for triple points are →

Triple points →	B	C	E	G
Pressure (P →	0.01 mm	0.025 mm	1290 atm	0.03 mm
Temp.(t°C) →	95.5	120	151	114

--- 0 ---

TWO – COMPONENT SYSTEM

The phase rule states, $F = C - P + 2$. For two-component system, $C = 2$, so the rule becomes, $F = 4 - P$. Since, $F_{mini} = 0$, so $P_{max} = 4$.
This shows that 4-phases of 2-component system can coexist
Again, $F_{max} = 4 - P_{min}$ so $F_{max} = 3$ as $P_{min} = 1$

So to describe the of a two-component system we need three degrees of freedoms. Thus if we like to draw phase diagram of this system, three independent co-ordinates are required resulting 3-d (solid) phase diagram. This is rather difficult to draw, instead, we generally keep one degree of freedom (either T or P) constant and then we draw 2-d diagram either P vs. x_1 (composition) keeping T constant or T vs. x_1 at P constant.

We shall discuss four two-component systems keeping in mind that one degree of freedom is kept constant, the phase rule in that case is $F = 4 - P - 1$ or,

$$F = 3 - P$$

Systems to be discussed

The systems of our discussion are given as,
1. partially miscible liquid-pair in equilm. with special emphasis to critical solution temperature (CST).
2. completely immiscible liquid pair in equil^m. with their vapors with an application to steam distillation.
3. Completely miscible liquid-pair in equil^m. with their vapors with special reference to azeotropic mixture.
4. Solid-liquid equil^m. with special reference to eutectic point.

PARTIALLY MISCIBLE LIQUID PAIR

Two liquids are partially miscible means that each is soluble in the other to limited extent. We shall discuss two liquid pairs – (1) phenol-water system and (2) nicotine-water system.

(1) PHENOL-WATER SYSTEM:

These liquids are mutually soluble to certain extent depending on temperature. Therefore, in this system we shall keep pressure constant at one atmosphere and use T and x_p to draw the phase diagram.

Content of the system

Let us take roughly equal amount of phenol and water in a system at constant P of 1 atm and at low temperature. These two liquids form two layers – one (say, 1st layer) contains saturated solution of phenol in water and the other (say, 2nd layer) contains saturated solution of water in phenol. The vapor of the liquids are neglected as at 1 atm pressure, phenol and water remain exclusively in liquid phase and no vapor is formed.

P = 1 atm

layer 1
phenol in water
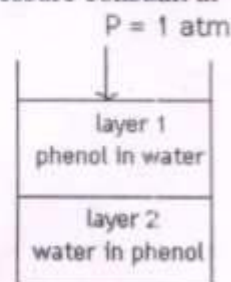
layer 2
water in phenol

Effect of T on mutual solubilities.

Now let at temperature, say 40°C, the composition of the 1st layer is $x_{p,1}$ and that of the 2nd layer is $x_{p,2}$. As the temperature is increased, more phenol is dissolved in water and so $x_{p,1}$ increases while more water is dissolved in phenol and so $x_{p,2}$ is decreased.

|	The mutual solubility in both the layers is increased and so the immiscibility is reduced. If the temperature is further increased, the two solubility curves meet at C at which both conjugate solutions have same composition and it becomes homogeneous (one phasic).
Concept of CST.	This temperature is called critical solution temperature (CST) above which phenol and water are completely miscible. The points along AC and BC represent two-phase and two-component system, so the degree of freedom along the lines, $F = 3 - P = 3 - 2 = 1$, when P is kept constant.
Value of F along AC and BC, and at C	Since the degree of freedom ($F = 1$), the system is monovariant ie, if T is kept fixed, the composition of the two layers remain fixed. But at C, there is another physical restriction, both the layers have same composition and $F = 0$.
Temp and comp^n. at CST	The system at C is invariant - both temperature and composition are fixed at a constant P. If P is 1 atm, for phenol-water system, CST = 66°C and composition at the CST is 33%(w/w) phenol in water. However if P is changed, the above values are also changed.
Comparison with liquid-vapor equil^m. of a pure substance	This point is similar to the critical point of liquid-vapor equil^m. of a pure substance at which both the liquid and vapor phases in equil^m. gets more and more alike. And at the critical point, both phases become indistinguishable yielding one phasic system. The degree of freedom at the critical point (T_c) is $F = C - P + 2 = 1 - 2 + 2 - 1 = 0$, as there is one more restriction for the two phases are identical in density at the critical point of a pure substance ($C = 1$).
Effect of addition of phenol at constant T	Now let us take temperature constant at say 40°C and see the effect of adding phenol in water at this constant T. Let the system contains only pure water at the start and so $x_p = 0$. Now as phenol is added gradually to the system, x_p increases until the point L is reached in the phase diagram when the system contains the saturated solution of phenol in water. Further addition of phenol creates two phasic system – one is saturated solution of phenol in water (1st phase) and other is saturated solution of water in phenol (2nd phase). These are conjugated solutions. At constant T, the composition of both the solutions (phases) are fixed ($F = 1$). If now more phenol is added, the relative amount of the two phases will change keeping the composition of these phases unchanged. The relative amount of the two phases
Liver rule	is known by the liver rule. The liver rule is so called because a similar rule relates the masses of two ends of a liver to their distances from a pivot. The liver rule states that a point in the two-phase region of a phase diagram indicates not only qualitatively both the phases are present, but represent quantitatively the relative amount of each by the relation.

$$n_1 \times l_1 = n_2 \times l_2 \qquad\qquad\qquad m_1 \times l_1 = m_2 \times l_2$$

where, l_1 and l_2 are the distances along the horizontal tie line from the balanced point.

n_1 and n_2 are mole number of the 1st phase and 2nd phase that are in equil^m.
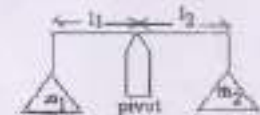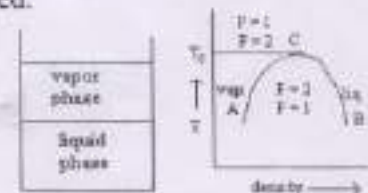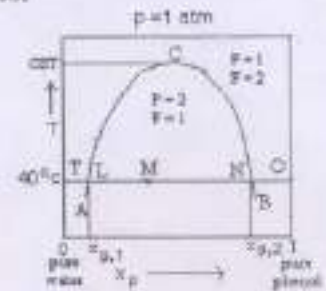
At the point M in the phase diagram, let $MN = l_2$ and $ML = l_1$, then $\dfrac{n_2}{n_1} = \dfrac{ML}{MN}$.

Relative amount of the two phases are given by liver rule

The liver rule is $\dfrac{n_2}{n_1} = \dfrac{l_1}{l_2}$

As more phenol is added, M shifts towards N, l_1 increases and l_2 decreases so $\dfrac{n_2}{n_1}$ increases, that means amount of water in phenol phase increases and amount of phenol in water phase decreases. At the point N, $l_2 = 0$ and $l_1 = LN$, so $\dfrac{n_1}{n_2} = \dfrac{l_2}{l_1} = 0$.

The 2nd phase is present with a trace amount of the1st phase i.e. the system is saturated solution of water in phenol only. Further addition of phenol, the system contains the unsaturated solution of water in phenol. At the point O, infinite amount of phenol is added so that water content is negligible and $x_p = 1$, i.e. almost pure phenol.

So long the system contains two phases, the degree of freedom, $F = 3 - P = 3 - 2 = 1$. It means that at a given T, composition of both the conjugate solutions is fixed. Both phases are saturated solutions in the system

NICOTINE – WATER SYSTEM

another ~~This is another~~ important system of partially miscible liquid pair.

Two CST values of this system

The system has two critical solution temperatures (consolute temperatures); above the upper CST and below the lower CST, two liquids are completely miscible; but between the two temperatures they are partially miscible.

For the nicotine-water system,
upper CST = 208°C and lower CST = 61°C.

CST values and the comp^n. at CST

The composition at the two CST is same and is 34% (w/w) nicotine in water.
At 94°C to 95°C, nicotine is least soluble in water, while at 129°C to 130°C, water is least soluble in nicotine.

One interesting information regarding the system is that if pressure above this system

Effect of P on the CST

is increased, the two CST come closure; the area of the egg-shaped figure decreases and at a sufficient high pressure the area vanishes and two liquids become completely miscible.

However it is worth noting that CST values of these liquid pairs are highly sensitive towards any impurity present. Very often purity of a liquid is checked by noting its CST value, with another liquid with which it is partially miscible.
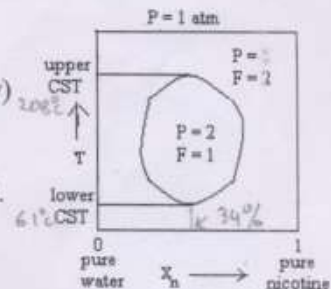
Presence of impurity on CST

(1) When the impurity is soluble in one liquid, mutual solubilities of the liquids are decreased resulting an increase of CST.
(2) When the impurity is soluble in both the liquids, the mutual solubilities are increased and CST is lowered.

THERMODYNAMICS OF GENERAL PHASE EQUIL^M. — N C DEY   14

Immiscible liquids are mutually insoluble. When such liquid pair is brought together, each liquid behaves independent of the other. Consequently the vapor pressure of a mixture of two immiscible liquids at any temperature is the sum of the vapor pressures of the individual pure components at the same temperature.

Immiscible liquid pair behaves independently

More over, the vapor pressure above the mixture will be independent of the amount of each liquid present.

If P is the total pressure and, p_1 and p_2 are the partial vapor pressures of the two components, then, $P = p_1 + p_2$.

At a given T, vapor composition is fixed

Since $p_1 = \dfrac{n_1}{n_1 + n_2} P$ and $p_2 = \dfrac{n_2}{n_1 + n_2} P$, so $\dfrac{p_1}{p_2} = \dfrac{n_1}{n_2}$,

where, n_1 and n_2 are the mole number of the two components in the vapor phase. At a given temperature, vapor pressure of the two

components are fixed, i.e. $\dfrac{p_1}{p_2}$ = constant and so $\dfrac{n_1}{n_2}$ is also fixed.

It means that the vapor composition is always the same so long as the two components are present at a given temperature. If w_1 and w_2 are the weights of the components in the

vapor phase, then $\dfrac{p_1}{p_2} = \dfrac{w_1/M_1}{w_2/M_2} = \dfrac{w_1 \times M_2}{w_2 \times M_1}$. Thus, $\boxed{\dfrac{p_1}{p_2} = \dfrac{w_1 \times M_2}{w_2 \times M_1}}$

Distillate has fixed composition when the liquid pair is distilled - principle of steam distillation.

If the liquid pair is distilled, then the distillate contains the weights that depend on the vapor pressures and molecular weights of the components.
This principle is applied in STEAM DISTILLATION.
As the temperature is increased, the vapor pressure of the liquid pair, in which one component is water, is also increased. When the vapor pressure over the liquid pair is equal to the external pressure (say, 1 atm), the mixture boils and distillation goes on with constant composition of the distillate. The boiling point will be lower than the boiling point of either of the two liquids.

Let a liquid which is immiscible with water is to be separated from other non-volatile impurities, it is often distilled with steam. The process becomes particularly useful when the substance boils at high temperature and decomposes near its boiling point. In steam distillation, the substance is distilled with water at a temperature considerably below its normal boiling point (near $100°C$), and hence the danger of decomposition is avoided.

purification of decomposable substances

To illustrate the utility, let us take iodobenzene (BP, $185°C$) which is purified at about $98°C$ by the steam distillation. At this temperature,

One example for illustration

$p_{water} = 712 \, mm$ and $p_{iodobenzene} = 48 \, mm$, total vapor pressure = 760 mm.
The liquid is taken with water and heated to boiling. The vapor is condensed and the distillate contains the weight ratio as,

$$\frac{w_1}{w_2} = \frac{p_1 \times M_1}{p_2 \times M_2} = \frac{48 \times 204}{712 \times 18} = \frac{7}{9}$$

That is out of every 16 gm of the distillate, 7 gm would be iodobenzene.

This relation may also be used to determine the molecular weight of the liquid from the other data.

Problem 1: A mixture of water and nitrobenzene boils at 98.5°C at 1 atm pressure. The distillate collected after a time shows that water content is 10.0 gm. What is the nitrobenzene content in the distillate? [CU '92].

[Vapor pressure of water = 73.3 cm of Hg at 98.5°C, mol. wt. of nitrobenzene = 123].

Solution: $p_{nitrobenzene} = 76.0 - 73.3 = 2.7\, cm$ of Hg. The content ratio in the distillate,

$$\frac{w_{water}}{w_{nitrobenzene}} = \frac{p_{water} \times M_{water}}{p_{nitrobenzene} \times M_{nitrobenzene}} \quad or, \quad \frac{10\, gm}{w_{nitrobenzene}} = \frac{73.3\, cm \times 18}{2.7\, cm \times 123} \quad or,\ w_{nitrobenzene} = 2.52\, gm.$$

Problem 2: A mixture of quinoline and water boils at 98.9°C under a pressure of 740 mm of Hg. The distillate contains 78 gm of quinoline and 1000 gm water. The vapor pressure of quinoline at 98.9°C is 8 mm of Hg. Calculate the molar mass of quinoline. [CU'96].

Solution:

$$\frac{w_{water}}{w_{quinoline}} = \frac{p_{water} \times M_{water}}{p_{quinoline} \times M_{quinoline}} \quad or, \quad \frac{1000\, gm}{78\, gm} = \frac{(740-8)cm \times 18\, gm\, mol^{-1}}{8\, cm \times M_{quinoline}}$$

So, the molar mass of quinoline, $M_{quinoline} = 128.5\, gm\, mol^{-1}$.

COMPLETELY MISCIBLE LIQUID PAIR IN EQUIL^M. WITH THEIR VAPORS

The system is a two–component two-phase of liquid –vapor equil^m. at constant temperature.
The total vapor pressure of the liquids is P.
The liquid pair is completely miscible.
The composition of the system is expressed by

x_1 = mole fraction of the 1st component in the liquid phase

$P = p_1 + p_2$

vapors of the liquid pair

miscible liquid pair

constant T bath

Composition of liquid, vapor and overall

$$= \frac{n_1(l)}{n_1(l) + n_2(l)} \text{ and } x_1 + x_2 = 1.$$

y_1 = mole fraction of the 1st component in the vapor phase

$$= \frac{n_1(v)}{n_1(v) + n_2(v)} \text{ and } y_1 + y_2 = 1.$$

z_1 = overall mole fraction of the 1st component of the entire system

$$= \frac{n_1(l) + n_1(v)}{[n_1(l) + n_1(v)] + [n_2(l) + n_2(v)]} \text{ and } z_1 + z_2 = 1.$$

P vs. x_1 plot at constant T

When the solution is ideal, it obeys Raoult's law.

$p_1 = p_1^o x_1$, $p_2 = p_2^o - p_2^o x_1$ and $P = p_2^o + (p_1^o - p_2^o) x_1$

When the pressure over the piston is greater than the equil^m. vapor pressure, the system contains only the liquid phase.
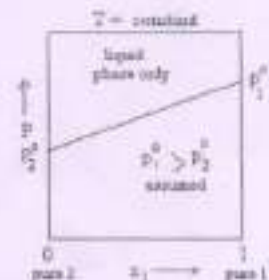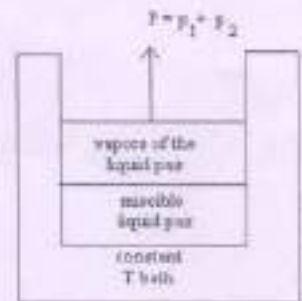
Vapor phase is always rich with more volatile component

Again, for the composition of the vapor phase,

$y_1 = \frac{p_1}{P} = \frac{p_1^o x_1}{P}$ or, $x_1 = \frac{P}{p_1^o} y_1$. But $p_1^o > P$ since 1st liquid

is assumed more volatile, this shows that vapor phase is always rich with more volatile component (here, 1st component).

z = constant

liquid phase only

$p_1^o > p_2^o$ assumed

* $[p_1^o, z_1 > x_1]$

Again, $P = p_2^v + (p_1^v - p_2^v)x_1$, putting the value of x_1, we have

$$P = p_2^v + (p_1^v - p_2^v)\frac{P}{p_1^v}y_1, \text{ rearranging the equation, } P = \frac{p_1^v p_2^v}{p_1^v - (p_1^v - p_2^v)y_1}$$

This is not a linear relation between P and y_1.

However, the above equation can be reshuffled as,

$$\frac{1}{P} = \frac{1}{p_2^v} - \left(\frac{p_1^v - p_2^v}{p_1^v p_2^v}\right)y_1.$$

p_1^v and p_2^v are fixed for the liquids at a given temperature.

$\frac{1}{P}$ is linearly related with y_1.

When the pressure over the piston is below the vapor curve, the system contains only the vapor phase.

The curve starts at p_2^v (when, $y_1 = 0$) and ends at p_1^v

(when, $y_1 = 1$). This is not a linear plot of P vs. y_1.

When the two curves are combined, it gives the plot of P vs. z_1 (overall mole fraction of the 1st component).

The upper curve is called liquid curve and the lower curve is vapor curve. When the pressure over the piston is above the liquid curve, the system contains only the liquid phase. But when the pressure is below the vapor curve, the system contains only the vapor phase.

When the pressure is within the two curves, the system contains liquid and vapor phase both in equil[m]. with each other. The degree of freedom of this two-component and two-phase system is $F = C - P + 1 = 2 - 2 + 1 = 1$.

The system is univariant at constant temperature.

It means that P and composition are inter-dependent. If P is changed, the composition of the liquid and vapor phases is also changed. But if P is kept fixed at say, P', the composition of the liquid and vapor phases are fixed at x_1' and y_1'.

Let the pressure of the system is reduced isothermally from the state point A with fixed overall composition, z_1'.

At the point, the system is entirely liquid and remains so as the pressure is reduced until the B point is reached.

At B, the first trace of vapor appears with composition, y_1'.

This first vapor is considerably richer with more volatile 1st component than the less volatile 2nd component.

As the pressure is further reduced, the point reaches to C, more liquid is vaporized with composition, y_1'' in the vapor phase and x_1'' in the liquid phase with overall composition, z_1'. The amount of the two phases are obtained by the liver

rule, $\frac{n_l}{n_v} = \frac{\overline{CV}}{\overline{CL}}$. This could be expressed and becomes same

with the mass-ratio of the two phases.
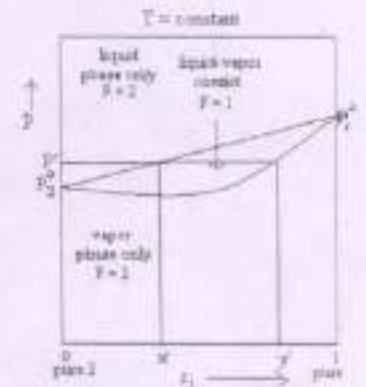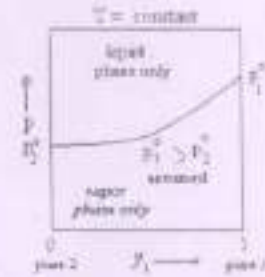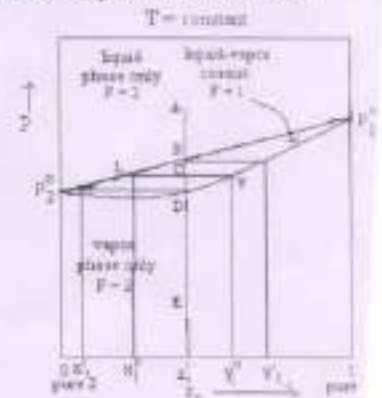
A point in a two-phase region of a phase diagram gives the system's overall composition, and the compositions of the two phases in equil^m. are given by the points at the ends of the tie line through that point.

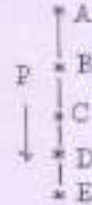Further reduction of pressure, more liquid is vaporized and point comes down to D when last drop of the liquid vaporizes with liquid composition, x'_1 and vapor composition, virtually z'_1. Further if P is reduced, the point falls to E, below the vapor curve and the system contains entirely vapor phase.

This is the basis of isothermal distillation.

Isopleth situation in brief

Two component liquids can be separated by this process completely. Thus as P is lowered, the system's state point is changed from A to E. At A, only liquid exists, at B, first vapor appears, at C, liquid and vapor coexist, at D, last liquid vaporizes and at E, only vapor exist.

For NON-IDEAL solutions, both the liquid components do not obey the Raoult's law. Vapor pressure of the components are given as,

Non-ideal solutions with (+)ve and (-)ve deviations

$$p_1 = x_1 \, p_1^\circ \, e^{\alpha x_2^2} , \quad p_2 = x_2 \, p_2^\circ \, e^{\alpha x_1^2} \quad \text{and} \quad \text{total pressure, } P = x_1 p_1^\circ e^{\alpha x_2^2} + p_2 = x_2 \, p_2^\circ \, e^{\alpha x_1^2}$$

α is constant which has the same value for the both the components. For ideal solution, $\alpha = 0$ and for non-ideal solutions, $\alpha \neq 0$, and it means that there is interaction between the component liquids. For non-ideal solution with (+)ve deviation, $\alpha > 0$ and for non-ideal solution with (-)ve deviation, $\alpha < 0$.
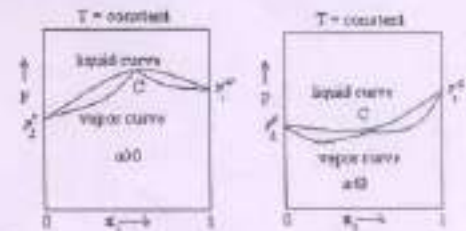
At the point C, liquid and vapor have the same composition. This mixture is called AZEOTROPIC mixture.

DUHEM - MARGULES EQUATION

Let us start with Gibbs-Duhem equation, $\sum n_i \, d\mu_i = 0$ -------(1)

For binary system, $n_1 d\mu_1 + n_2 d\mu_2 = 0$, n_1 and n_2 are the mole number of the two components in the liquid phase and μ_1 and μ_2 are their chemical potentials in that phase. Since each component in liquid phase is in equil^m. with its vapor phase, hence,

$\mu_1(l) = \mu_1(v) = \mu_1^\circ(v) + RT \ln p_1$, or $d\mu_1 = RT \, d \ln p_1$ and similarly, $d\mu_2 = RT \, d \ln p_2$. Dividing equation (1) by $(n_1 + n_2)$ and replacing $d\mu_1$ and $d\mu_2$ in terms of p_1 and p_2,

we have, $\dfrac{n_1}{n_1 + n_2} RT \, d \ln p_1 + \dfrac{n_2}{n_1 + n_2} RT \, d \ln p_2 = 0$ or, $x_1 d \ln p_1 + x_2 d \ln p_2 = 0$.

Again dividing by dx_1, $\dfrac{x_1}{dx_1} d \ln p_1 + \dfrac{x_2}{dx_1} d \ln p_2 = 0$ But $x_1 + x_2 = 1$ or, $dx_1 + dx_2 = 0$

or, $dx_1 = -dx_2$. Putting this, $\dfrac{d \ln p_1}{\left(\dfrac{dx_1}{x_1}\right)} = \dfrac{d \ln p_2}{\left(\dfrac{dx_2}{x_2}\right)}$ or, $\boxed{\dfrac{d \ln p_1}{d \ln x_1} = \dfrac{d \ln p_2}{d \ln x_2}}$

This is Duhem-Margules equation which relates the composition of the components in the liquid phase with the vapor pressure in the vapor phase. This equation can show that α is same for both the components in the system, hence they behave in the same manner.

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(a) If one component behaves ideal and obeys Raoult's law, $p_1 = x_1 p_1^o$, then,

$\ln p_1 = \ln x_1 + \ln p_1^o$ or, $d \ln p_1 = d \ln x_1$ or, $\dfrac{d \ln p_1}{d \ln x_1} = 1$, hence, $\dfrac{d \ln p_2}{d \ln x_2} = 1$

or, $d \ln p_2 = d \ln x_2$, integrating, $\ln p_2 = \ln x_2 + IC$.

But, when $x_2 = 1 (pure\ 2)$, $p_2 = p_2^o$. Putting we get $IC = \ln p_2^o$.

Thus, $\ln p_2 = \ln x_2 + \ln p_2^o$ or, $p_2 = x_2 p_2^o$.

This shows that if one component behaves ideal then other component also behaves ideal.

(b) If one component behaves non-ideal with (+)ve deviation, then $p_1 > x_1 p_1^o$

or, $\ln p_1 > (\ln x_1 + \ln p_1^o)$ or, $d \ln p_1 > d \ln x_1$ or, $\dfrac{d \ln p_1}{d \ln x_1} > 1$. The equation gives $\dfrac{d \ln p_2}{d \ln x_2} > 1$

This leads to $p_2 > x_2 p_2^o$, that is, second component also shows (+)ve deviation with respect to Raoult's law.

KONOWALOFF'S RULE

Duhem-Margules equation

Let us begin with Duhem-Margules equation $\dfrac{d \ln p_1}{d \ln x_1} = \dfrac{d \ln p_2}{d \ln x_2}$ or, $\dfrac{x_1}{p_1} \dfrac{dp_1}{dx_1} = \dfrac{x_2}{p_2} \dfrac{dp_2}{dx_2}$.

But, $dx_2 = - dx_1$, hence, $\dfrac{x_1}{p_1} \dfrac{dp_1}{dx_1} = -\dfrac{x_2}{p_2} \dfrac{dp_2}{dx_1}$ or, $\dfrac{dp_1}{dx_1} = -\left(\dfrac{p_1}{p_2}\right)\left(\dfrac{x_2}{x_1}\right)\dfrac{dp_2}{dx_1}$.

Now the total vapor pressure, $P = p_1 + p_2$ or, $\dfrac{dP}{dx_1} = \dfrac{dp_1}{dx_1} + \dfrac{dp_2}{dx_1}$.

putting the expression of $\dfrac{dp_1}{dx_1}$, we get, $\dfrac{dP}{dx_1} = \dfrac{dp_2}{dx_1}\left(1 - \dfrac{p_1}{p_2} \dfrac{x_2}{x_1}\right)$. But $\dfrac{p_1}{p_2} = \dfrac{y_1}{y_2}$,

composition of the components in the vapor phase. This leads to the Konowaloff's rule,

Konowaloff's equation

$$\dfrac{dP}{dx_1} = \dfrac{dp_2}{dx_1}\left(1 - \dfrac{y_1}{y_2} \dfrac{x_2}{x_1}\right)$$

Konowaloff's equation can be used to explain the fraction distillation and formation of azeoetrope.

Type – I, ideal liquid pair: ($p_2^o < P < p_1^o$). 1st liquid is taken more volatile than 2nd liquid.

Ideal solution-component iquids can e separated

$\dfrac{dP}{dx_1} = (+)$ve and $\dfrac{dp_2}{dx_1} = (-)$ve, so $\left(1 - \dfrac{y_1}{y_2} \dfrac{x_2}{x_1}\right) < 0$, so, $\dfrac{y_1}{y_2} > \dfrac{x_1}{x_2}$

That is, the vapor phase (distillate in fractional distillation) contains more of the 1st component (more volatile liquid). The repeated distillation produces pure 1st component in the distillate and pure 2nd component in the residue.

Thus ideal solution of two liquids can be completely separated by fractional distillation.

Type II liquid pair: non-ideal solution with (+)ve deviation.

P attains max^m.at $x_1 = x_M$ and $P > p_1^o > p_2^o$.

(i) When $x_1 = x_M$, azeotrope composition liquid mixture.
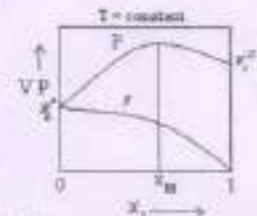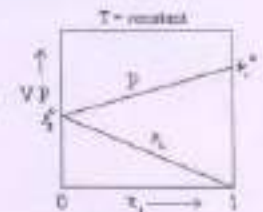
Non-ideal solution – component liquids can not be separated

$\frac{dP}{dx_1} = 0$, since P attains max^M. at $x_1 = x_M$, $\frac{dp_2}{dx_1} = (-)$ve, so $\frac{y_1}{y_2} = \frac{x_1}{x_2}$

Repeated distillation can not separate the liquid components as the vapor phase and liquid phase both have same composition.

The liquid mixture boils with constant composition at constant minimum boiling point.

(ii) When $x_1 < x_M$ taken, $\frac{dP}{dx_1} = (+)$ve, $\frac{dp_1}{dx_1} = (-)$ve, and $\frac{y_1}{y_2} > \frac{x_1}{x_2}$

The distillate will be rich in 1st component and residue rich in 2nd component. Fractional distillation produces azeotrope in the distillate and pure 2nd component in the residue.

(iii) When $x_1 > x_M$ taken, $\frac{dP}{dx_1} = (-)$ve, $\frac{dp_1}{dx_1} = (-)$ve, and $\frac{y_1}{y_2} < \frac{x_1}{x_2}$.

Repeated distillation produce azeotrope in the distillate as vapor phase contains less and less of the 1st component and ends with azeotrope. The residue contains more and more of the 1st component and ends with pure 1st component.

Type III liquid pair: non-ideal solution with (−)ve deviation.

P attains minimum at $x_1 = x_M$ and $P < p_1^s < p_1^o$.

(i) When $x_1 = x_M$, azeotropic composition liquid mixture.

$\frac{dP}{dx_1} = 0$, since P attains minimum, $\frac{dp_2}{dx_1} = (-)$ve, so $\frac{y_1}{y_2} = \frac{x_1}{x_2}$

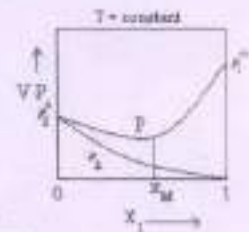Non-ideal solution – component liquids can not be separated

Repeated distillation can not separate the liquid components as the vapor phase and liquid phase both have same composition. The liquid mixture boils with constant composition at constant maximum boiling point.

(ii) $x_1 < x_M$ taken, $\frac{dP}{dx_1} = (-)$ve, $\frac{dp_2}{dx_1} = (-)$ve, $\frac{y_1}{y_2} < \frac{x_1}{x_2}$.

Repeated distillation enriches the residue with 1st component and ends with azeotrope. Distillate ends with pure 2nd component.

(iii) When $x_1 > x_M$ taken, $\frac{dP}{dx_1} = (+)$ve, $\frac{dp_1}{dx_1} = (-)$ve, and $\frac{y_1}{y_2} > \frac{x_1}{x_2}$.

Repeated distillation enriches distillate with 1st component and residue with 2nd component. That is, residue contains less and less of the 1st component (x_1 decreases to x_M). Residue ends with azeotrope and distillate with pure 1st component.

Reducing pressure at constant temperature is one way of doing distillation but it is more common to distill at constant pressure by raising the temperature. So we require a temperature (T) – composition (z_1) diagram.

For ideal solution which obeys Raoult's law, we have, $P = p_2^o + \left(p_1^o - p_2^o \right) x_1$

Process of drawing curves of T vs. x_1 and T vs. y_1

or, $x_1 = \dfrac{P - p_2^o}{p_1^o - p_2^o}$. Again, $y_1 = \dfrac{p_1^o x_1}{P}$ or, $y_1 = \dfrac{p_1^o}{P} \cdot \dfrac{P - p_2^o}{p_1^o - p_2^o}$.

At a temperature T, p_1^o and p_2^o are known from Clausius-Clapeyron equation. So x_1 and y_1 can be calculated at various T at constant known pressure (usually 1 atm). These calculations can be used to draw T vs. x_1 and y_1, $T = f(x_1)$ and $T = g(y_1)$, but the relations are not linear. The point of differences in this diagram from P vs. z_1 at constant T are :

Difference with P vs. comp^n.

(i) the curve looks like a lense within which liquid and vapor remain in equil^m. and the degree of freedom is one (F = 1), since the curves T vs. x_1 and T vs. y_1 are not linear.

(ii) outside this zone, there is one phase (F = 2).
← Vapor phase is stable at high T and liquid is stable at low T, so vapor phase is above the lense and liquid phase is below the lense.

(iii) at a given pressure, boiling point (BP) of a liquid depends on its volatility, the more volatile liquid (liquid having high vapor pressure) will boil at lower T. So solution with different compositions will boil at different temperatures.
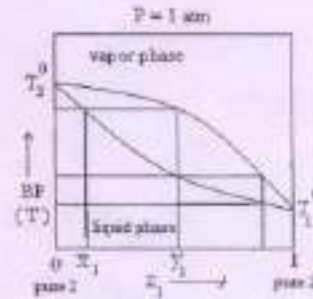
The BP vs. comp^n. diagram is discussed for three different types of miscible liquid pairs.

(a) Solutions either ideal or very little deviation from ideality. The total pressure (P) of the liquid mixture lies between those of the pure components, ($p_2^o \langle P \langle p_1^o$).

Ideal solutions → components can be separated

Example: benzene – toluene pair.

T_2^o and T_1^o are the BP of pure 2nd and 1st liquids respectively. Since at BP, liquid – vapor exist in equi^m., F = 1 and so comp^n. and BP are mutually dependent. At a given T, the comp^n of liquid and vapor are fixed at x_1 and y_1 respectively.

The vapor phase is rich with more volatile 1st component, and this vapor is condensed into liquid and again it is evaporated. This vapor becomes richer with the 1st component and the residue is rich with less volatile 2nd component. Repeated distillation gives distillate (condensed vapor phase) pure 1st component and residue contains pure 2nd component. Thus for ideal solution, both components can be separated by repeated distillation. This repeated distillation is done efficiently by fractional distillation in which the boiling and condensation cycle is repeated successively. The technique is used to separate volatile liquids.

(b) Solutions with large (+)ve deviation from ideality, $P_{max} \rangle p_1^o \rangle p_2^o$.

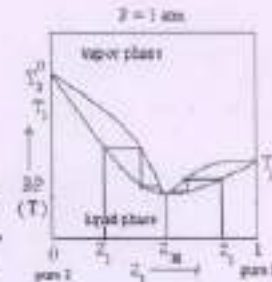Example, ethyl alcohol and water with minimum boiling point at azeotropic comp^n. z_M is the point indicating the comp^n. of azeotropic mixture .

(i) If liquid mixture is taken initially having composition (z_1) less than azeotropic mixture (z_M) then by fractional distillation,

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Non-ideal solutions with +ve deviation. components can not be separated

we get pure 2nd component in the residue and azeotropic mixture in the distillate.

(ii) If the liquid mixture is taken as that of azeotropic composition, then it distills with same composition and separation of any component is not possible.

(iii) If the liquid mixture comp^n. (z_1) is taken greater than azeotropic comp^n. (z_M) then by fractional distillation, we get pure 1st in the residue and azeotropic mixture in the distillate.

Example → ethyl alcohol and water (BU'2001)

Water and ethyl alcohol mixture forms the miscible liquid pair with large (+)ve deviation and thus it forms azeotropic mixture with minimum BP (78.2°C) and composition, 96.8% w/w ethyl alcohol in water. When a dilute solution of ethyl alcohol is fractionally distilled, it separates as pure water in the residue and azeotrope in the distillate. When concentrated ethyl alcohol solution is fractionally distilled, we obtain pure ethyl alcohol in the residue and azeotrope in the distillate. Complete separation of alcohol and water in not possible. The rectified spirit sold in the market is the azeotropic mixture. This pair forms azeotrope with minimum BP and it means that it is more volatile than water and ethyl alcohol.

BP of ethyl alcohol → 78.5°C, BP of water → 100°C and BP of azeotrope → 78.2°C.

(c) Solutions with large (−)ve deviation from ideality, $P_{min} \langle p_2^c \langle p_1^r$.

Example: hydrochloric acid and water with maximum boiling point at azeotropic comp^n.

z_M is the point indicating the comp^n. of azeotropic mixture.

Non-ideal solutions with large (-)ve deviation. The components can not be separated.

Since this pair of liquids forms max^m. BP azeotropic mixture so it is less volatile than both the components.

(i) If the liquid mixture of composition (z_1) is taken less than azeotropic mixture (z_M), then fractional distillation gives pure 2nd component in the distillate and azeotropic mixture in the residue. Complete separation is not possible.

(ii) If the liquid mixture is taken as that of azeotropic composition, then it distills with same composition and separation of any component is not possible.

(iii) If the liquid mixture comp^n. (z_1) is taken greater than azeotropic comp^n. (z_M) then by fractional distillation, pure 1st component separates in the distillate and azeotropic mixture in the residue.
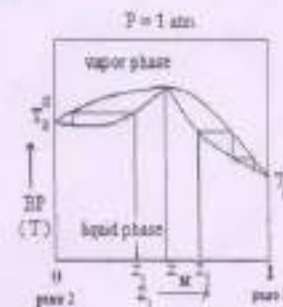
This is due to the fact that azeotropic mixture is of having max^m. BP and so least volatile.

Example → HCl and H$_2$O (BU'2001)

This mixture forms azeotrope with max^m. BP, 108.6°C. and composition 20.22% w/w HCl in H$_2$O.

Any solution of HCl is boiled and residue ends with azeotrope. BP of HCl is − 80°C. In analytical work where very accuracy is intended, standard solution are prepared by the help of azeotropy wherever it is possible. Thus in highly accurate analytical work, standard HCl solution is prepared by boiling HCl and H$_2$O together till azeotrope residue appears at 1 atm pressure. Evaporation of this solution removes both the acid and water in the same proportion and the solution retains its composition intact.

Composition however can be changed by altering the pressure above the liquid. But fluctuation in the atmospheric pressure, being usually small, have practically little effect upon the azeotropic composition.

	Azeotropes boils at a definite temperature and the liquid and vapor have identical composition and this may appear that the azeotropes would be a true compound. But this is not so, because
Azeotropes is not a true compound	

(i) the composition of constant boiling mixture depends on the pressure (P) over the mixture. If P is changed, the comp^n. of the mixture alters.

(ii) the comp^n. does not correspond to any stoichiometric ratio of the components.

(iii) there is no spectroscopic evidence of the formation of a compound between the components.

The separation of the components in the azeotropic mixture is made possible by any of the methods given below:

Azeotrope mixture can be separated

(1) by distillation with a third substance. For example, absolute alcohol can be recovered by distilling rectified spirit (azeotrope) with benzene.

(2) by chemical reaction or absorption of one component from the azeotrope mixture. For example, nitration will remove aromatic component from azeotrope mixture with saturated hydrocarbons, or lime may be used in removing water from rectified spirit.

(3) by solvent extraction, one component may be removed by adding suitable immiscible solvent.

THE FRACTIONATING COLUMN

The process of fractional distillation is extremely tedious and involves more time and labour as the separation is carried out in batches and in a discontinuous manner. However, these difficulties can be overcome by employing a fractionating column, which essentially carries the distillation in a continuous manner. Figure 4.7.9 displays one such column commonly
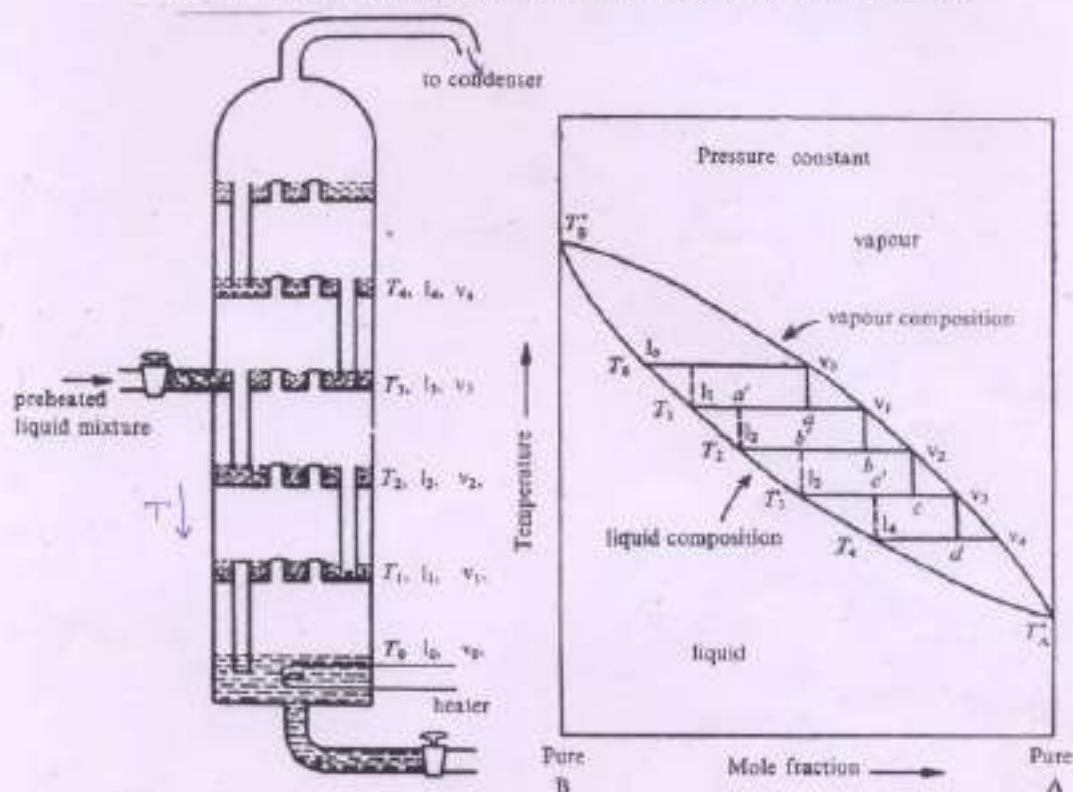
$$T_0 > T_1 > T_2 > T_3 > T_4$$

Fig. 4.7.9 Bubble-cap distilling column

Fig 4.7.10 Scheme of redistribution of constituents in the distilling column

employed in industry. This is known as the *bubble-cap column*. It consists of a long tube carrying a large number of bubble-cap plates and is attached to a boiler at the bottom and to a condenser at the top. Each plate can hold a thin layer of liquid and has an overflow mechanism through which the excess liquid can pass to the plate just below it. It also has many bubble-caps through which the vapour passes upward after bubbling through the liquid. There is a temperature gradient along the length of the column, the top being cooler than the bottom. The various plates are thus situated at different temperatures and also hold the liquid at that temperature. The principle of bubble-cup column can be illustrated very nicely with the help of temperature-composition diagram (Fig. 4.7.10).

Let the liquid be boiled at the bottom, say at temperature T_0. The vapour issuing has composition v_0. When this vapour is passed through the first plate, it is cooled to temperature T_1 and thus its state is moved to the point a. At this state, some of the vapour condenses to form liquid of composition l_1 and the remaining vapour has composition v_1. The liquid formed contains more of the less volatile constituent and thus the remaining vapour has more of the more volatile constituent. Next, the vapour of composition v_1 is passed through the second plate whose temperature is $T_2(T_2 < T_1)$.

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Here the vapour is cooled to T_2 and thus the state of system is moved from v_1 to b. At this state, again part of the vapour is condensed to give liquid of composition l_2 and the remaining vapour has composition v_2. Now the vapour has become more enriched in the more volatile constituent. This happens at every plate of the column as is also shown in Fig. 4.7.10. As the vapour moves up the column, it is being cooled; this cooling condenses the less volatile component preferentially, so that the vapour becomes increasingly enriched in the more volatile component as it passes upward from one plate to another.

Similarly, as the liquid flows down, its temperature is increased and again there is a redistribution of the constituents. For example, the liquid of composition l_3 has flown from the plate 3 to plate 2. The liquid has been heated from T_3 to T_2 and thus the state of the system has moved from l_3 to b'. Thus part of the liquid vaporizes to yield vapour of composition v_2 containing more of the more volatile constituent. The resultant liquid has a composition of l_2 and thus contains more of the less volatile constituent. This happens at every plate of the column as shown in Fig. 4.7.10. As the liquid moves down the column, it is being heated; this heating vaporizes the more volatile constituent preferentially, so that the liquid becomes increasing enriched in the less volatile component as it moves downward from one plate to another.

If sufficient number of plates are used, it is possible to separate the two constituents of a binary liquid mixture; the more volatile constituent in the vapour form is collected from the top of the distilling column and that of lesser volatile constituent from the bottom of the column. The vapour from the top of the column is fed into a condenser where it is liquified. Part of this liquid is drawn off and the rest is returned to the column in order to maintain the stock of essentially pure distillate on the upper plates. In order to make the separation continuous, the preheated liquid mixture is introduced somewhere within the column as shown in Fig. 4.7.9.

SOLVED NUMERICALS

1. Suppose that the vapour over an ideal solution contains n_1 mol of 1 and n_2 mol of 2 and occupies a volume V under the pressure $p = p_1 + p_2$. If we define $V_{1,m}^* = RT/p_1^*$ and $V_{2,m}^* = RT/p_2^*$, then show that Raoult's law implies that $V = n_1 V_{1,m}^* + n_2 V_{2,m}^*$.

The pressure p over a solution as calculated by making use of Raoult's law is given by Eq. (4.7.13), i.e.,

$$\frac{1}{p} = \frac{1}{p_2^*} + \left(\frac{1}{p_1^*} - \frac{1}{p_2^*} \right) y_1$$

Replacing p's in terms of V's we get

$$\frac{V}{(n_1+n_2)RT} = \frac{V_{,m}^*}{RT} + \left(\frac{V_{1,m}^*}{RT} - \frac{V_{2,m}^*}{RT} \right) \left(\frac{n_1}{n_1+n_2} \right)$$

or

$$V = (n_1+n_2)V_{2,m}^* + n_1(V_{1,m}^* - V_{2,m}^*)$$

or

$$V = n_1 V_1^* + n_2 V_{2,m}^*$$

Thermal analysis method

To study the two-component solid-liquid equil^m at constant pressure, we may approach thermal analysis method. In this method, we study the cooling rate curve (temperature-time curve). The liquid is cooled and temperature (T) at different time (t) is noted. Finally T is plotted against t.

First, a pure liquid (C = 1) is taken and its T vs. t curve is drawn.

At the beginning, the liquid is at A. The system is one component. The degree of freedom, is one component. The degree of freedom, F = 1, as pressure is fixed. T is variable and it falls along AB with time.

At B, the liquid begins to freeze, solid separates. It becomes one-component two-phase system.

Cooling of pure liquid and cooling rate curve

F = 0, T is not changed till solidification is complete at C. The entire mass becomes solid at C and again F = 1 so T decreases with t.
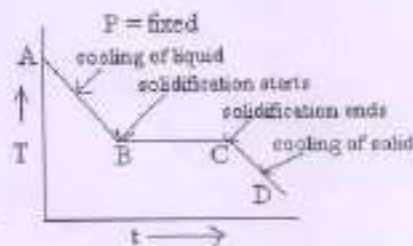
Cooling curve becomes different if two-component liquid mixture of a definite composition is taken. The substances are completely soluble in the liquid state.

Cooling of two miscible liquids of a fixed composition
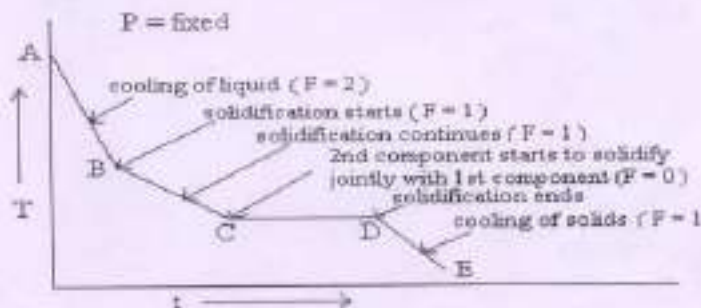
Let the liquid solution is at A of a definite composition and cooled, the degree of freedom, F = 2 – 1 + 1 = 2. Both T and composition are independent variables.

At B, one component begins to solidify and it becomes two-component two-phase system, F = 2 – 2 + 1 = 1. T and composition are inter-dependent. As one solid separates, composition of the solution is changed and so T is also changed. For a liquid solution of definite composition, the T at which solid first appears is fixed. This temperature is called 'initial arrest'.

At C, another solid comes out and the system is a three phase one, F = 2 – 3 + 1 = 0. T and composition remains fixed and T does not change with t. This break point at C is called 'final arrest'.

At D, entire liquid becomes solidified and it is two-phase solid system, F = 2 – 2 + 1 = 1. The system becomes univariant and T changes with t.

It shows that any break-point in the cooling curve means appearance of a new phase.

The above curve is drawn for a liquid mixture of a given composition. Cooling curves for liquid mixtures of different composition can be drawn. It could be seen that temperature for the initial arrest is different but temperature of the final arrest is same for every mixture of different compositions.

One particular curve of a definite composition resembles that of pure liquid. This liquid mixture is called eutectic mixture. It has definite composition and definite temperature for solidification of both the substances together forming a solid solution.

Cooling curves of Bi – Cd system of solution of different composition are given here:

Cooling curves of Bi – Cd system of different compositions
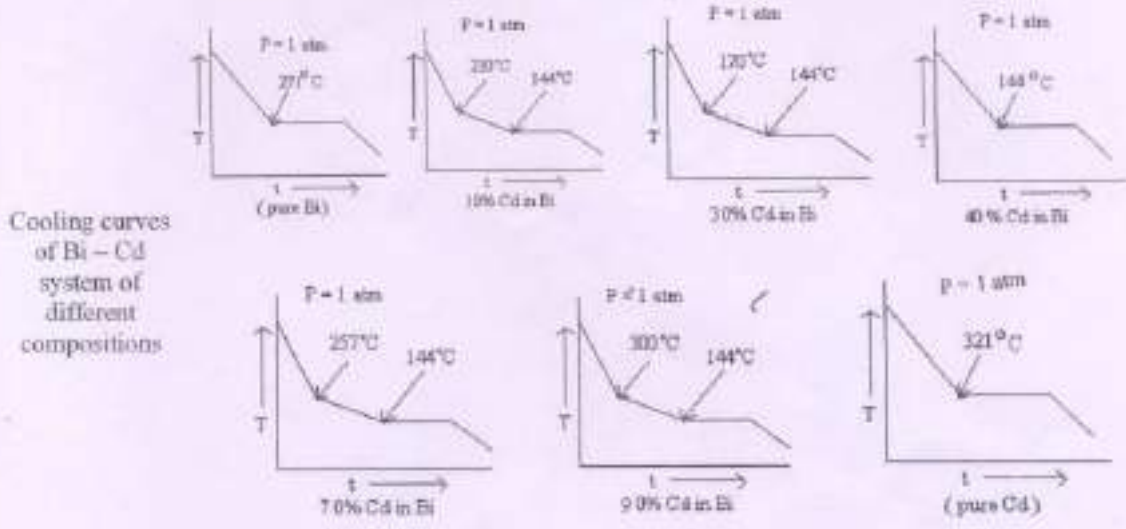
Our next attempt is to draw the phase diagram by using the cooling curves of Bi – Cd system. Temperature of the initial arrest and final arrest is plotted against the composition at constant pressure (P). The following phase diagram is obtained.

T – comp⁰. curve of Bi – Cd system
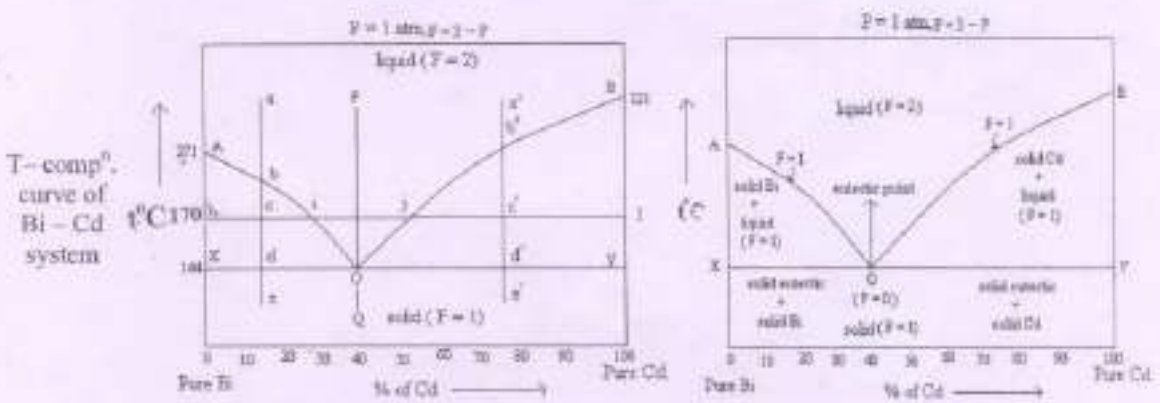
Three isopleths are discussed

The points A and B represent the freezing points of pure Bi and pure Cd respectively and O is the final arrest that represents the eutectic point of the system.

We shall discuss the phase diagram by drawing three isopleths [it is a vertical line of constant overall composition, meaning equal abundance (Greek word)] — abcde having composition less than , POQ equal to and $a'b'c'd'e'$ greater than the eutectic mixture.

(a) abcde is the isopleth of the system of composition less than that of the eutectic mixture (O).

The state point 'a' represents the liquid state of overall composition of the system.

The liquid solution is cooled to reach the state point 'b' when Bi starts to solidify (1st arrest). The system now contains two phases (F = 1) and it means that T and comp^n. are inter-dependent.

Further cooling of the system, state point 'c' is reached. More of Bi solidifies. The system becomes richer with Cd, FP decreases and solution comp^n. corresponds to 'i'.

As T is lowered down, amount of solid Bi increases and conc. of solution (% of Cd in Bi) increases, FP is also lowering down.

When the state point 'd' is reached by further cooling, final arrest occurs and (Bi – Cd) together with eutectic comp^n. begins to separate as solid from the solution.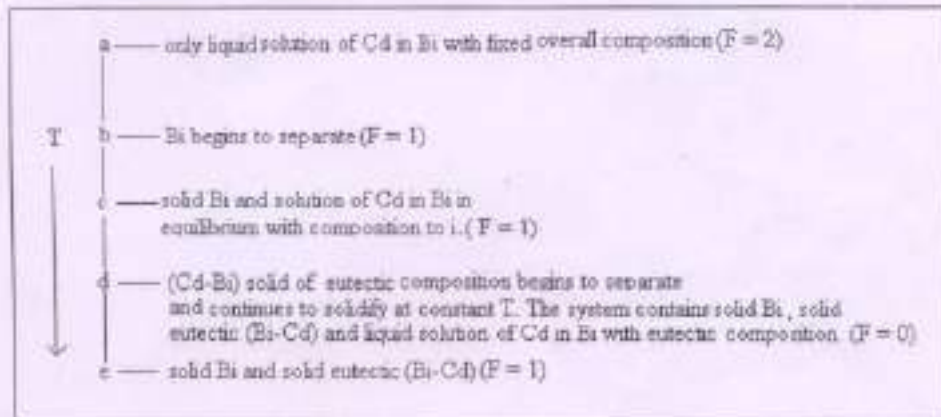 The system now contains solid Bi, solid (Bi-Cd) eutectic and liquid solution of Cd in Bi with comp^n. corresponding to eutectic point O. F = 3 – 3 = 0.

The system is invariant, both T and comp^n. are fixed and have definite value. So, on further cooling, only the solution freezes at a constant T (here, 144°C) with fixed comp^n. (40 % Cd in Bi) corresponding to O. This T is called eutectic temperature and solidification of whole solution is complete at 'd'.

The point 'd' comes down to 'e' which represents the two solid phases (F = 1), T lowers down on further cooling.

T

a ——— only liquid solution of Cd in Bi with fixed overall composition (F = 2)

b —— Bi begins to separate (F = 1)

c ——— solid Bi and solution of Cd in Bi in
equilibrium with composition to i. (F = 1)

d —— (Cd-Bi) solid of eutectic composition begins to separate
and continues to solidify at constant T. The system contains solid Bi , solid
eutectic (Bi-Cd) and liquid solution of Cd in Bi with eutectic composition. (F = 0)

e —— solid Bi and solid eutectic (Bi-Cd) (F = 1)

(b) Another isopleth, $a'b'c'd'e'$ represents line of comp^n. (% of Cd in Bi) greater than the eutectic mixture (point, O). Same occurrence happens with a difference that at b' , pure solid Cd begins to appear and this continues to d' at which solid Bi-Cd of eutectic comp^n. appears and F = 0.

(c) The isopleth, POQ is at the eutectic composition. At P, the solution is in liquid phase and F = 2. When the solution is cooled, the state point 'O' is reached, the solution begins to solidify with the comp^n. of the solution. FP remains fixed.

Since the liquid phase and solid phase have the same comp^n., F = 3 – 2 – 1 = 0. (another restriction for equal comp^n. in both the phases).

When all the liquid solidifies, further cooling is the lowering of temperature of the solid with eutectic comp^n.

If the process is reversed, by taking solid of eutectic comp^n. and T is raised, the state point 'Q' goes to 'O' and the solid begins to liquefy with same comp^n. of the solid. This solid mixture has the lowest melting point and this is why it is called eutectic (easily melted). Further heating, we get liquid of the state point 'P'.

In the similar manner, other two isopleths abcde and $a'b'c'd'e'$ could be reversed by taking solid Bi and Cd corresponding to the respective composition.

28

Now, we may consider the isothermal behavior of the system at 170°C along the horizontal line hcij c'l .

The point, 'h' represents pure Bi at 170°C. Now, sufficient Cd is added to bring the comp⁰. to the state point 'c'. This point lies in the region of solid Bi and solution of Cd in Bi, therefore solid Bi coexists with liquid solution of comp⁰. 'i'. All the added Cd melts and the molten Cd dissolve enough of solid Bi to bring the liquid solution to the comp⁰. 'i'. The liver rule shows that the relative amount of liquid present at point 'c' is given by the rule

$$\frac{mass\ of\ solid\ Bi}{mass\ of\ solution\ of\ Cd\ in\ Bi} = \frac{c\ i}{c\ h}.$$

On further addition of Cd, Cd continues to melt and dissolves more of solid Bi and forms the solution of same comp⁰. 'i'. This is due to degree of freedom, F = 1 and so at the given T of 170°C, the comp⁰. of the solution remains unchanged.

The state point moves horizontally from 'c' to 'i'. When the state point reaches 'i', sufficient Cd is added to dissolve all of original Bi present to form a saturated solution of Cd in Bi.

Further addition of Cd simply dilutes the solution. Amount of liquid increases, state point reaches to 'j', the initial arrest point, when Cd starts to solidify from the melt. Further addition of Cd does not produce any change. The state point meanwhile moves to 'c''.

If we had reached ' c' ' by starting with pure Cd at 'l' (i.e. pure Cd) and adding Bi, all the Bi would have melted and would dissolve sufficient Cd to form the melt of comp⁰. 'j'.

To conclude, the following points can be outlined :

(1) AXOA area represents the system of solid Bi in equil⁰. with liquid whose comp⁰ lies on the curve AO.

(2) BYOB area represents solid Cd in equil⁰. with liquid whose comp⁰. lies on the curve BO.

(3) Along the line AO and BO, and within areas AXOA and BYOB, F = 3 – 2 = 1. It means that for a given T, comp⁰. of liquid phase is fixed.

(4) A point on XY, F = 2 – 3 + 1 = 0, indicating the presence of three phases except at the point 'O' at which the system contains two phases – one liquid phase and other solid phase both with same composition. This point is the eutectic point corresponding to the lowest freezing point

(5) AOB is called liquid curve above which only liquid phase is present.

(6) XOY is called solid curve below which only solid phase is present.

CU'1990

Q4(a) Apply phase rule to determine the 'degree of freedom' for a binary alloy system at the 'eutectic point'
and for a partially miscible pair at the 'critical solution temperature.' (m = 5)

Ans. The phase rule is $F = C – P + 2$. It is the two-component two-phase system with solid
and liquid are in equil^m. But at the eutectic point, both the phases are of same composition.
So, $F = 2 – 2 + 2 – 1 = 1$. But usually the pressure is kept constant, so $F = 1 – 1 = 0$.
Similarly, at the CST, the degree of freedom, $F = 2 – 2 + 2 – 1 – 1 = 0$ as pressure is kept
constant and both the conjugate solutions have same composition.

CU'1991

Q3(a) How many degrees of freedom are there in each of the following systems?
Suggest variables that could correspond to these degrees of freedom. (m = 2 × 3)
 (i) Liquid water with its vapor in equil^m. at a pressure of 1 atm. **Ans.** $F = 1 – 2 + 2 – 1 = 0$.
 (ii) I_2 dispersed between liquid water and liquid CCl_4 at 1 atm. **Ans.** $F = 3 – 2 + 2 – 1 – 1 = 1$. T is variable.
 (iii) NH_4Cl vapor in equil^m. with $NH_3(g)$ and $HCl(g)$. **Ans.** $F = 2 – 1 + 2 = 3$.
 T and mole fraction of any two components are variables.

CU'1992

Q5(a) Define number of components and degrees of freedom in connection with phase equil^m. Show that
the greatest number of phases that can co-exist in equil^m. in one component system is three. (m = 4)
Ans. See the note.
 (b) Explain why a solution of NaCl in water has two components in spite of the fact that it has actually
three species.
Ans. It has 3 species H_2O, Na^+ and Cl^- but there is one restriction of electro-neutrality so, $C = 3 – 1 = 2$.
 (c) Is four phase sulphur system possible? Compute the degree of freedom of three sulphur system. (m = 4)
Ans. No. In that case $F = – 1$ which is absurd. For 3 phase S system, $F = 1 – 3 + 2 = 0$.
 (d) A mixture of water and nitrobenzene boils at 98.5°C under 1 atm pressure. The distillate collected after a
time shows that the water content to be 10.0 gm. What is the nitrobenzene content in the distillate?
(VP of water = 73.3 cm of Hg at 98.5°C, mol. wt. of nitrobenzene = 123). (m = 4)
Ans. See note.

CU'1993

Q4(a) Calculate the degree of freedom for each of the following systems: (m = 3)
 (i) $HCl(g)$ and $NH_3(g)$are equil^m. with $NH_4Cl(s)$ when the equil^m. is approached by starting with the two gases
only. **Ans**. There are 3 chemical constituents but one equil^m. restriction. So $C = 3 – 1 = 2$ and $F = 2$.
 (ii) $HCl(g)$ and $NH_3(g)$are equil^m. with $NH_4Cl(s)$ when the equil^m. is approached by starting with the solid.
Ans. Besides one equilm restriction, mole fraction of $HCl(g)$ and $NH_3(g)$ are equal in the gas phase
so, $C = 3 – 1 – 1 = 1$ and $F = 1$.
 (b) Derive Gibb's phase rule. (m = 6). **Ans.** See the note.
 (c) What is consolute temperature? Can we have systems with (i) upper (ii) lower (iii) upper and lower
consolute temperatures? If so, give one example for each. (m = 4)
Ans. When two partially miscible liquids are mixed with approx. equal amounts, two conjugate
solutions are formed. At the consolute temperature, both the conjugate solutions are completely
miscible. Yes. The examples are: (i) phenol – H_2O (ii) Triethylamine – H_2O (iii) nicotine – H_2O.

Q5(b) What are meant by (i) a triple point and (ii) an eutectic point? How many triple points do you expect in the sulphur system? (m = 4)

Ans. For definition, see the note, page, 2 and 28. Four triple points ($^4C_3$) are possible in the S–system.

(c) Discuss how the phase diagram of a binary alloy system may be constructed by thermal analysis. (m = 7)
Ans. See the note.

CU'1995

Q3(a) Assuming the general thermodynamic condition of equil^m. between different phases to hold, deduce the relation between the number of phases, components and degrees of freedom for the cases of C components distributed over P phases. (m = 6). **Ans.** See the note.

(b) What are meant by the upper and lower consolute temperatures? Illustrate with diagram. (m = 5)
Ans. Draw the diagram of T vs. x_n for nicotine - water system and define the two consolute temperatures. See the note.

(c) Deduce thermodynamically Duhem – Margules equation. (m = 5). See the note.

CU'1996

Q4(a) For the dissociating equil^m. system, $X(s) \rightleftharpoons Y(g) + Z(g)$, find out the number of phases, number of components and number of degrees of freedom.

Obtain and explain the number of degrees of freedom at the triple point and normal freezing point of water. (m = 6)

Ans. C = 3 – 1 – 1 = 1, P = 2 and F = C – P + 2 = 1 – 2 + 2 = 1. See the note.

F = 0 at the triple point and F = 1 at the normal freezing point of water. See the note, page 10.

(b) Explain 'lever rule' and its importance. (m = 2). **Ans.** See note.

(c) A mixture of quinoline and water boils at 98.9°C under a pressure of 740 mm of Hg. The distillate contains 78 gm quinoline and 1000 gm of water. The vapor pressure of quinoline at 98.9°C is 8 mm of Hg. Calculate the molar mass of quinoline. (m = 4) **Ans.** See the note.

CU'1997

Q4(a) Starting from the appropriate form of the Duhem – Margules equation, obtain Konowaloff's rule and use this to construct BP – composition curve to explain the distillation of binary liquid pairs with minimum BP. What argument would you put forward to ascertain that azeotrope is a mixture and not a compound?
(3 + 3 + 1)

Ans. Start with Duhem – Margules equation, $\dfrac{d \ln p_1}{d \ln x_1} = \dfrac{d \ln p_2}{d \ln x_2}$ and arrive at $\dfrac{dP}{dx_1} = \dfrac{dp_2}{dx_1}\left[1 - \dfrac{y_1}{y_2}\cdot\dfrac{x_2}{x_1}\right]$.

When miscible liquid pair is non-ideal with large (+)ve deviation, like a mixture of ethanol and water, pressure (P) attains max^m. value at a certain $x_1 = x_M$ of the

solution and then, $\dfrac{dP}{dx_1} = 0$. So, $1 - \dfrac{y_1}{y_2}\cdot\dfrac{x_2}{x_1}$ or, $\dfrac{x_1}{x_2} = \dfrac{y_1}{y_2}$.

It means that the liquid composition (x_1/x_2) and vapor composition (y_1/y_2) are identical when the mixture at this composition (x_M) is distilled. The distillation occurs at constant BP, if pressure is kept fixed and F = 0. This forms azeotropic mixture.
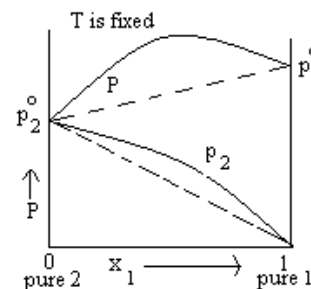
If this type of liquid mixture is distilled at constant pressure of say at 1 atm, the BP is increased as

x_1 of the solution is decreased. When the liquid mixture attains the composition x_M, it boils at minimum temperature and liquid and vapor phase have identical composition.
See the BP vs. composition phase diagram for liquid mixture with minimum BP in the note.

Though azeotropic boils at constant T at fixed pressure with unchanged composition, it is not a compound. If pressure is fixed at some other value, the composition of the azeotropic is changed. If it would be a true compound, then with changing pressure, its composition would not be changed. Thus it is not a compound but a mixture only.

(b) Depict, stating the salient features, the approximate phase diagram of nicotine – water system. (m = 5)
Ans. See the note.

Q4(c) What is meant by upper critical solution temperature (UCST)? Draw a T – comp^n. diagram for a system showing UCST. Apply phase rule to find the number of degrees of freedom in the different regions of the plot and explain the result. (m = 6). **Ans.** See the note.

Q6(a) Define degrees of freedom and components in connection with phase equil^m. Show that greatest number of phases that can co-exist in one-component system is three. (m = 3)
Ans. See the note.
(b) Derive the Gibb's phase rule. (m = 5). Ans. See the note.
(c) Draw the phase diagram of carbon dioxide system. How does it differ from the water system?
What is dry ice? (m = 6).
Ans. For the diagram, see the note, page 10. The difference from water system is that the triple point pressure of CO_2 is greater than that 1 atm so, $CO_2(s)$ sublimes if heated at 1 atm pressure. Another difference is that the melting curve is having (+)ve slope indicating that melting point of $CO_2(s)$ is increased with increase of pressure unlike water in which MP is decreased with increase of pressure. For last part, see again the note

Q6(a) Draw the phase diagram (T vs. mole % of B) of a system consisting of solids A and B forming a stable compound A_2B with congruent melting point. Show the different phases present in the different regions of the diagram. State the degrees of freedom at the eutectic point.
(Given: M.pt. of A_2B < M.pt of A < M.pt of B). (m = 6). **Ans.** Not included in the BU syllabus.

Q2(b) Explain Konowaloff's rule. (m = 2) **Ans.** See the note.

Q2(c) Explain the phase diagram of a two-component liquid-liquid system – phenol, water system. (m = 4).
Ans. See the note.

Q2(c) Sketch the phase diagram of a two-component solid, liquid system with a simple eutectic. Briefly explain what happens when the state point moves down an isopleth (a straight line reflecting the same comp^n.) from one phase region to a two phase region. (m = 4). **Ans.** See the note.

Q2(b) Water and phenol are partially miscible at 323K. When these two liquids are mixed at 323K and 1 atm then at equilibrium one phase is 89 % water by weight and the other is 37.5 % water by weight. If 6.00 g of phenol and 4.00 g of water are mixed at 323K and 1 atm, find the mass of water and the mass of phenol in each phase at equil^m. (m = 2)

Ans. Let total amount of the two phases in the system = 200 g out of which water = 89 +37.5 = 126.5 g and phenol = 11 + 62.5 = 73.5 g. Now when 6 g phenol and 4 g water are added,

amount of water in the 1st phase = $\dfrac{89}{126.5} \times 4 = 2.81\,g$ and in the 2nd phase = 4.00 – 2.81= 1.19 g

And the amount of phenol in the 1st phase = $\dfrac{11}{73.5} \times 6 = 0.898\ g$

and in the 2nd phase = 6.00 – 0.898 = 5.102 g.

Q2(b) Draw the phase diagrams for H_2O and CO_2 systems. Indicate the differences between the two diagrams. (m = 4). **Ans**. See CU'99, Q 6(c).

Q1(d) Draw the phase diagram (T vs. mole % of B) of a system containing of solid A and B forming a stable compound A_2B with congruent melting point. Show the different phases present in the different regions of the diagram. State the degrees of freedom at eutectic point.
(Given, M. pt. of A_2B ⟨ M. pt. of A ⟨ M. pt. of B).

Ans.   O = 1st Eutectic point , O' = 2nd Eutectic point

AO = Freezing point curve of liquid A
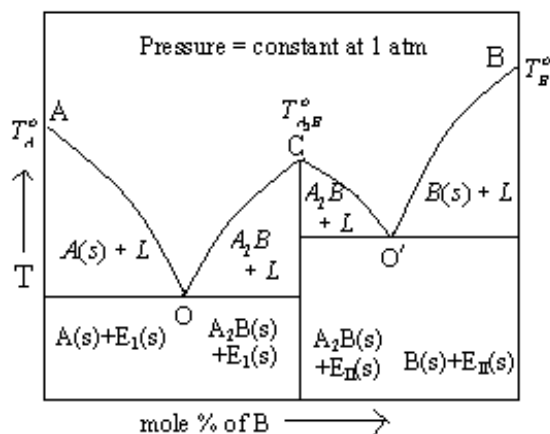
CO = Freezing point curve of A_2B compound

CO' = Freezing point curve of A_2B compound

BO = Freezing point curve of liquid B

Degree of freedom at the Eutectic point,
F = C – P + 1, (since pressure is constant)
F = 2 – 2 + 1 – 1 = 0, as both liquid phase and solid phase have same composition.

2(b)(i) A mixture of quinoline and water (immiscible pair) boils at 98.9°C under a pressure of 740 mm of Hg. The distillate contains 78 g quinoline and 1000 g water. The vapor pressure of quinoline at 98.9°C is 8 mm of Hg. Calculate the molar mass of quinoline. (4)
Ans. See the text.

2(c)(i) Find the degree of freedom at the triple point of water (2). Ans. F = C – P + 2 = 1 – 3 + 2 = 0.

(ii) Starting from the approximate form of the Duhem – Margules equation, deduce Konowaloff's rule and discuss its significance.   (4)

Ans. See the text for derivation from Duhem – Margules equation.

Significance: (i) For ideal solution of two completely miscible liquids, each component can be separated by fractional distillation.

(ii) For non-ideal solution, the two components can not be separated.
At a certain composition, the solution forms azeotropic mixture and it distills with equal composition of distillate and residue.

CU'2007

1(d) Derive Duhem – Margules equation stating clearly the assumptions. Show that if Raoult's law is applicable to one of the constituents of a binary liquid mixture, at all compositions, it must be equally applicable to the other constituent.   (4 + 2)

**Ans.** The equation is applicable for both ideal binary liquid mixture and non-ideal binary liquid mixture. The only assumption taken in the derivation is that the vapor over the liquid mixture is ideal.

2(e) Solid 'X' has m. pt. = 630°C and 'Y' has m. pt. = 346°C. X and Y exhibit a simple eutectic at 246°C with eutectic composition being 30 weight % of X. Draw and explain the cooling curves of

(i) liquid having the eutectic composition and (ii) liquid having composition where the weight % of X = 50. Find the degrees of freedom at the eutectic point.   (5)

Ans. (i)
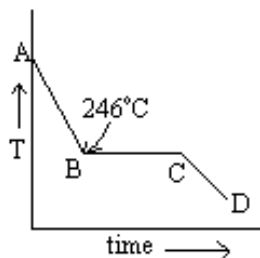
AB → cooling of liquid having composition.
At B, solidification of eutectic composition starts.
BC → solidification continues.
At C, solidification ends.
CD → cooling of solid of eutectic composition.

(ii)

cooling of liquid.
solidification starts and X separates as solid.
solidification of eutectic solid at 246°C.
eutectic solidification ends.
cooling of solid.
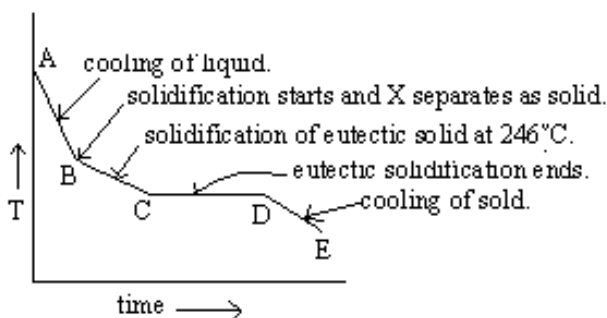
Last part: At the eutectic point,
Degree of freedom,
$F = C - P + 2$.
But Pressure is constant.
So the reduced phase rule, $F = C - P + 1$.
$C = 2$, $P = 2$ and there is one restriction that solid and liquid have the same composition.

So, the degree of freedom at the eutectic point is, $F = 2 - 2 + 1 - 1 = 0$, invariant.
Both temperature of solidification (246°C) and composition (30% wt. of X.) remain fixed.

1(b)(i) Sketch the phase diagram of water and mark the following in the diagram: Normal boiling point and normal freezing point, triple point, critical point. (1 + 2)

Ans.
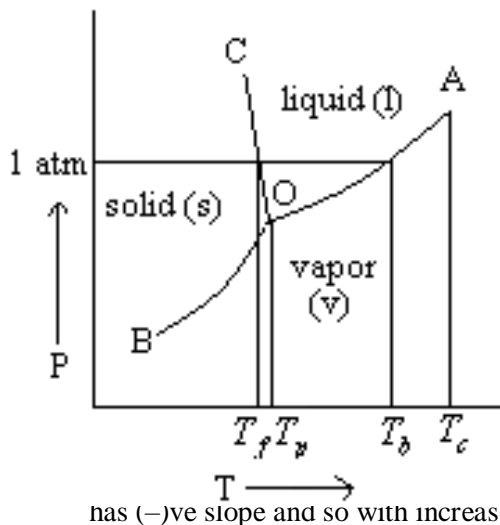
(ii) Find the number of degrees of freedom at the freezing point and the triple point of water. (2)
Ans. At the freezing point of water, the degree of freedom, $F = C - P + 2 = 1 - 2 + 2 = 2$.
At the trjiple point of water, the degree of freedom, $F = 1 - 3 + 2 = 0$.

(iii) How does the phase diagram of water differ from that of carbon dioxide? (1)
Ans. For carbon dioxide, the solid ⇌ liquid equilibrium curve has (+)ve slope so the with increase of pressure, the m. pt. of solid CO_2 is increased.
But for water system, the above curve has (−)ve slope and so with increase of pressure, the m. pt. of solid water (ice) is decreased.

2(a) In a single diagram, draw the $\mu - T$ plots for solid and liquid phases of (i) pure solvent and (ii) solvent in solution. Mention the thermodynamic basis for the depression of freezing point.
Elevation of freezing point is observed sometime for some solutions – justify. (4 + 2)
Ans. See the answer of CU'2008, 2(a) in the chapter "Thermodynamics of Two – phase Equilibrium."

2(c) 100 gm of a 1:1 (by weight) mixture of water and phenol is taken at 40°C. It shows two layers:
(i) phenol (9.2 %) in water and (ii) water (35 %)in phenol. Find the amount of the two layers. Also mark the above three % values of phenol (w/w) in proper T – weight % of phenol diagram. (2 ½ + 2 ½)

Ans.
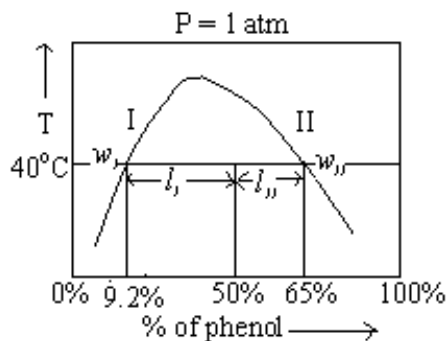
According to the liver rule,
$$\frac{w_{II}}{w_I} = \frac{l_I}{l_{II}} \text{ or, } \frac{w_{II}}{w_I} = \frac{50-9.2}{65-50} = 2.72.$$
But, $w_I + w_{II} = 100 \text{ } gm$, solving the two equations we have,
$$w_I = 26.88 \text{ } gm \text{ and } w_{II} = 73.12 \text{ } gm.$$

1(a) Derive Duhem – Margules equation. (4) **Ans.** See the text or CU'2007, 1(d).

2(d) What do you understand by Eutectic mixture? Illustrate it with a simple labeled phase diagram. (4)
Ans. If the solid eutectic mixture is heated at constant pressure, it melts at a temperature less than the m. pt. of either of the two solid constituents and the melted liquid have the same composition of the solid.
The degree of freedom at the point, $F = C - P + 1$, since pressure is kept constant.
It is a two-component and two-phase system with the two phase have the same composition. So,
$$F = 2 - 2 + 1 - 1 = 0, \text{ invariant}$$
For labeled diagram, see the text.

2(d) The question is given in the chapter " Thermodynamics of Two – phase Equilibrium."

CU'2011

1(c) Draw labeled phase diagram for a two – component solid – liquid equilibrium system and hence explain what is meant by an eutectic mixture. (4)

Ans. See the text for two-components A and B in solid – liquid equilibrium.

2(c) What do you understand by an azeotrope? Calculate the degree of freedom for an azeotrope in a two – component liquid – vapor equilibrium.

Ans. When two completely miscible liquids form a solution and this solution is vaporized with same composition of liquid solution, it is called azeotrope mixture. These two components could not be separated by fractional distillation as both distillate and residue have the same composition.

At the azeotrope mixture, the degree of freedom, $F = C - P + 1$, as the pressure is kept constant. It is two-component two-phase system with both liquid and vapor has same composition. This is another restriction, so $F = 2 - 2 + 1 - 1 = 0$, invariant.

2(d) Find out the number of components in the following chemical equilibrium,
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$
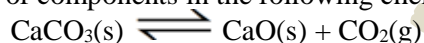
" Four phases of sulphur can not exist simultaneously at equilibrium." – Justify. (2 + 2)

Ans. For the above equilibrium, there are 3 chemical constituents and one equilibrium restriction. The number of components(C) = number of chemical constituents – number of restrictions = 3 – 1 = 2.

For sulphur system, if there exist four phases at equilibrium, then the degree of freedom,
$$F = C - P + 2 = 1 - 4 + 2 = -1.$$
But the degree of freedom of a system can never be negative.

Calcutta University, 2012

Q. 2(a): Derive Duhem-Margules equation stating clearly the assumptions. Show that if Raoult's law is applicable to one of the constituents of a binary liquid mixture at all compositions, it must be equally applicable to the other constituents. (4+2)

Ans. See C.U. 2007, Q. 1(d).

Q. 2(c): Draw the phase diagram for H_2O system and find the number of degrees of freedom at the triple point of water . (3+1)

Ans. See the Text.

BU'2000

Q1(o) What condition must be satisfied for a binary liquid mixture to show azeotropism?   (m = 1).

Ans: The binary liquid mixture must behave as non-ideal solution with large (+)ve or (−)ve deviation from Raoult's law so that $\left(\frac{\partial P}{\partial x_1} \right)_T = 0.$

Q5(e) Explain the principle behind steam distillation.   (5)

Ans. See the note.

Q6(d)(i) Derive Gibbs phase rule, explaining clearly the terms involved.   (5)

Ans. See the note.

BU' 2001

Q1(c) I_2 usually sublimes, but it can be melted. How?   (1)

Ans. The vapor pressure of solid I_2 reaches the atmospheric pressure before it reaches its triple point, so it sublimes. But if the external pressure is kept greater than its triple point pressure, it can be melted.

(n) How many phases and components are there in a closed vessel where the following equilibrium exists?

$$NH_4Cl \text{ (s)} \rightleftharpoons NH_3 \text{ (g)} + HCl \text{ (g)}.$$

(1)

Ans. It is a two-phase system and the number of components (C) = 3 − 1 − 1 = 1.
There is one equil^m. restriction and other is the equal conc. of NH_3 and HCl in the gas phase.

(o) It is not possible to get pure ethanol from 50% aqueous ethanol by distillation only. Why?   (1)

Ans. If fractional distillation is done with 50% aqueous ethanol solution at 1 atm pressure, it separates into pure water as residue and azeotrope in the distillate which contains 95.6% w/w ethanol in water.

Q2(f) All the four phases of sulphur can not co-exist in equilibrium. − Why?   (2)

Ans. The phase rule states as F = C − P + 2, but it is one component system so C = 1. Thus F = 3 − P.
If P = 4, then F = 3 − 4 = − 1, which is not possible as F can never be (−)ve. So four phases of sulphur can not co-exist at equilibrium.

Q5(a) Explain with necessary diagrams, what is meant by eutectic point.

Ans. The necessary phase diagram for a pair of solid-liquid equil^m.
is given here.

Two liquids A and B are taken which are completely miscible in liquid state. O point is the eutectic point in the diagram. It means that if we take a liquid solution of A and B at C and cooled down, then it solidifies with same composition and at lowest temperature. This mixture is called eutectic mixture.
      Again if we take a solid solution of A and B with eutectic composition, then it melts down at the lowest temperature.
This is why it is called eutectic and it means easy melting.
The degree of freedom, F = 2 − 2 + 1 − 1 = 0. It states that both T and composition are fixed at this eutectic point if pressure is kept constant.
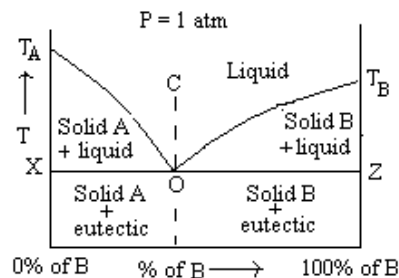
Q5(c) Draw the necessary vapor pressure – composition diagram and explain the formation of azeotropic mixture of two liquids.   (5)

Ans. Let the two miscible liquids 1, 2 are in equil^m. with its vapors and let the liquid 1 is more volatile than liquid 2, then

Konowaloff equation is $\dfrac{dP}{dx_1} = \dfrac{dp_2}{dx_1}\left[1 - \dfrac{y_1}{y_2}\cdot\dfrac{x_2}{x_1}\right]$. When miscible liquid pair is non-ideal with large
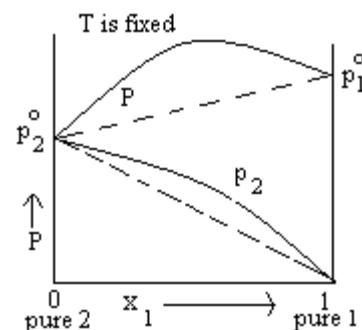
(+)ve deviation, pressure (P) attains maximum value at a certain

then, $\dfrac{dP}{dx_1} = 0$. So, $1 - \dfrac{y_1}{y_2}\cdot\dfrac{x_2}{x_1}$ or, $\dfrac{x_1}{x_2} = \dfrac{y_1}{y_2}$.

It means that the liquid composition (x_1/x_2)

and vapor composition (y_1/y_2) is identical.

This forms azeotropic mixture. When T is constant, F = 0
at the azeotropic point.

T is fixed

BU'2002

Q1(d) Find the maximum number of degrees of freedom of one component system. (1)
    Ans. The phase rule is, F = C – P + 2, but for one component system, C = 1, so F = 3 – P.
         But for $F_{max} = 3 - P_{min}$. As, $P_{min} = 1$, so $F_{max} = 2$

 (e) Find the degree of freedom of an aqueous solution of sucrose and ribose. (m = 1)
    Ans. The number of component, C = 3, number of phase, P = 1, degrees of freedom, F = 3 – 1 + 2 = 4

Q6(b)(ii) Draw the phase diagram of water system and explain the slopes of various lines. (5)
    Ans. See the note.

BU'2003

Q1(j) Find the number of components in the reaction mixture, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.
(1)
    Ans. There are 3 chemical constituents but it has one equilibrium restriction so, C = C' – r = 3 – 1 = 2.

    In the system, CaO and CO_2 are not in one phase so, $x_{CaO(s)} \neq x_{CO_2(g)}$.

 (n) Explain whether a pure system with 4 phases can co-exist. (1)
    Ans. F = C – P + 2 or, P = C – F +2. For pure system, C = 1, so P = 3 – F. But, if P = 4, then F = -1.
    It is absurd so four phases of a pure system can not co-exist.

Q6(b) What are azeotropic mixture? Draw the BP – composition diagram for such a system and explain the
    results of distillation by taking solution with conc. (i) lower (ii) higher (iii) equal in relation to the
    azeotropic conc. What should be degree of freedom of an azeotrope and why? (10)
    Ans. Azeotropic mixture is a complete miscible liquid pair which boils at constant temperature with
        unchanged composition. (m = 1)


        The diagram is given here.
        1st liquid is considered more volatile
        than the 2nd liquid.
        In both the cases, M indicates azeotropic
        point. The composition corresponding
        to M is the azeotropic composition.
        1st figure is for non-ideal solution with
        large (+)ve deviation and the azeotropic
    solution boils at minimum temperature. 2nd figure is for non-ideal solution with large (–)ve
    deviation and the azeotropic mixture boils at maximum temperature.(m = 2)
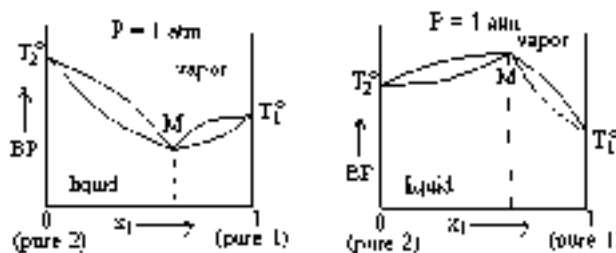
(i) When the conc. is lower than the azeotropic composition, after distillation the distillate contains the azeotropic mixture and residue contains pure 2nd liquid for the 1st type liquid mixture. But for the 2nd type liquid mixture, distillate contains pure 2nd liquid while residue contains azeotrope. (m = 2)

(ii) When conc. is higher than azeotropic composition, in 1st type liquid mixture contains distillate azeotrope but residue contains pure 1st liquid. (m = 2)
For 2nd type liquid mixture, distillate contains pure 1st liquid and residue contains azeotrope.

(iii) In this case liquid mixture boils with unchanged composition and both distillate and residue have same composition equal to azeotrope. Both types of liquid mixture behave same way. (1)
If P is kept constant, the reduced phase rule is $F = C - P + 2 - 1 = C - P + 1$.
At the azeotrope, C = 2, P = 2 and there is one restriction of being both phases have identical composition. So $F = 2 - 2 + 1 - 1 = 0$.
That is at constant P, both BP and composition are fixed. (2)

BU'2004

Q1(g) Write the number of components at equil^m. in PCl_5 decomposition. (1)
**Ans.** The equilibrium is $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. It has three chemical constituents and two restrictions
— one for equil^m. and other for equal conc. of PCl_3 and Cl_2 in the gas phase. So $C = C' - r = 3 - 2 = 1$
Thus it is one-component system provided PCl_3 or Cl_2 is not added from outside.

(u) How many phases can generally exist for one-component system at STP? (1)
Ans. $F = C - P + 2$. But at STP, T and P are fixed so $F = C - P + 2 - 2 = C - P$. But C = 1 so $F = 1 - P$.
or, $P = 1 - F$. When $F_{min} = 0$ so $P = 1$. One component system can exist in only one phase at STP.

(v) What is meant by 'critical solution temperature'? (1)
Ans. When mixture of two partially miscible liquids is taken, we have two conjugate solutions of different composition. But at CST, two conjugate solutions becomes identical in composition. Above CST, the two partially miscible liquids are completely miscible at any composition. The degree of freedom at CST = 0 when P is kept constant, both T and composition of the solution are fixed.
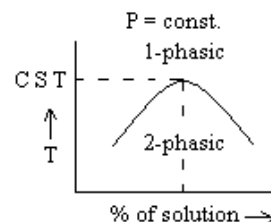
BU'2005

Q1(w) What is the degree of freedom of an unsaturated aqueous solution of sucrose kept in as open beaker.
Ans. C = 2, P = 1 and pressure is constant at 1 atm. So $F = C - P + 2 = 2 - 1 + 2 - 1 = 2$. (1)

(x) Cite an example of a binary liquid system have two critical solution temperatures. (m = 1)
Ans. Nicotine-water system. It has one upper CST and other lower CST.

(y) How can water- ethanol azeotropism be avoided in purifying ethanol? (1)
Ans. The above azeotropism can be avoided by distillation with a third substance like benzene. The pure ethanol is thus obtained by destroying the azeotropism.

BU'2006

Q1(i) What is the number of degrees of freedom (in the context of phase rule) of a gas mixture containing N_2, He, O_2 and CO_2? (m = 1)
Ans. It is four-component one phase system, So, $F = C - P + 2 = 4 - 1 + 2 = 5$.

(o) Define 'upper critical solution temperature' of a binary liquid system.   (1)

Ans. It is the temperature above which the two partially miscible liquids become completely miscible.

Q5(d) Discus the miscibility phase diagram of phenol – water system. What is the number of degrees of freedom of the system at the critical solution temperature (the experiment is carried out in an open hard glass test tube)? (m = 5)

Ans. For the diagram, see the note.

At the CST, the system contains two components and two phases but one restriction is that both the phases have equal composition. Since the experiment is done in open air so pressure is constant at 1 atm. The reduced phase rule is $F = C – P + 2 – 1 = C – P + 1$, and $F = 2 – 2 +1 – 1 = 0$.

Q6(d)(i) Define the terms: phase, number of components and degree of freedom.   (3)

Ans. See the note.

(ii) Derive Gibbs phase rule relating these parameters. (m = 5). Ans. See the note.

(iii) In two separate sealed vessels (I) $NH_4Cl(s)$ and (II) a mixture of $NH_4Cl(s)$ and $HCl(g)$ are taken and heated to attain equil^m. Giving reasons find out the number of components in each case.   (2)

Ans. (I) C = 1, $NH_4Cl(s)$ dissociates as $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$. Though it has 3 chemical constituents but there are 2 restrictions due to one equil^m. condition and the other equimolar conc. of $NH_3(g)$ and $HCl(g)$ in the gas phase. So $C = C' – r = 3 – 2 = 1$.

(II) C = 2 as the product conc. are not equal so only one restriction exists and $C = 3 – 1 = 2$.

BU'2007 (New regulation)

Q1(c) What is meant by triple point of water? Why it is different from the normal melting point of ice?   (2)

Ans. At the triple point of water, three phases – solid liquid and vapor of water co-exist at equil^m. and so $F = 0$. At this point both temperature and pressure are fixed.

But at the normal melting point ice, two phases- solid and liquid phases of water co-exist at equil^m. so $F = 1$ and the normal melting point remains constant so long pressure is at 1 atm.

(d) Define the terms in context with phase rule: (i) number of components, (ii) degrees of freedom.   (2)

Ans. See the note

(h) Sketch the degrees of freedom in each of the following systems. In each case state briefly the basic of your result. (i) An azeotrope in a binary system. (ii) A eutectic mixture in a binary system   . (2)

(i) In an azeotrope, the system contains two components in two phases ─ liquid and vapor with same composition. Thus the degree of freedom, $F = C – P + 2 = 2 – 2 + 2 – 1 = 1$.

But usually pressure is kept constant then $F = 1 – 1 = 0$. That is, the system is invariant.

(ii) At the eutectic mixture, the system contains two components in two phases ─ solid and liquid with same composition. Thus the degree of freedom, $F = C – P + 2 = 2 – 2 + 2 – 1 = 1$.

But if pressure is kept constant then $F = 1 – 1 = 0$. That is, the system is invariant.

Q2(e) Draw the temperature ─ composition (mole fraction) curve of a system of two partially miscible liquids, for example phenol and water.

From the diagram show the points of composition of the two phases and hence draw an expression of the ratio of the moles in the two phases.

Is there any effect of addition of a little NaCl to the system?   (2+2 +1+1 = 6)

Ans. 1St part: Draw the phase diagram of phenol – water system. ─ See the note.

2nd part: Use the Liver rule to find the ratio of moles of the two phases in the horizontal line drawn.

3rd part: CST is increased as NaCl is soluble only in water and not in phenol.

BU'2008

Q1(d) Iodine sublimes usually. Explain the situation under which it can be made to melt.   (2)

Ans. Triple point of pressure of iodine is 1.06 atm so $I_2(s)$ goes to vapor directly when heated at 1 atm.

But if the pressure over $I_2(s)$ is kept above its triple point pressure, it melts into $I_2(l)$.

Q10(a)(i) Triple point of water system is invariant. — Justify .(2)

Ans. At the triple point, water remains in three phases — solid, liquid and vapor at equil^m.

That is, C = 1, P = 3 so, F = C – P + 2 = 1 – 3 + 2 = 0, i.e. the system is invariant.

(ii) Calculate in each of the following examples, the number of phases, components and degrees of freedom: (m) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ (n) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$. (3+3)

Ans. (m) C = 2, P = 3 and F = 2 – 3 + 2 = 1. (n) C = 1, P = 2 and F = 1 – 2 + 2 = 1.— See note.

(b) Criticize or justify: A eutectic has a definite composition and a sharp melting point, yet it is not a compound. (m = 2)

Ans. When pressure is kept constant, a eutectic is invariant so it has definite composition and it melts a definite temperature. As pressure is kept constant, the reduced phase rule is, F = C – P + 1.
So F = 2 – 2 + 1 – 1 = 0 as both solid and liquid at this eutectic point has same composition.
Instead, it is not a compound as, if pressure is changed; the composition of the eutectic is changed.
Thus, it is not a compound but a mixture only.

BU'2009

Q1(c) Define triple point. (2)

Ans. When three phases of one component system co-exist, it is called triple point of the system.

(g) What is meant by critical solution temperature? (2)

Ans. When two partially miscible liquids are mixed up, two conjugate solutions are formed. But at the CST, both the conjugate solutions are completely miscible forming one phase.
Thus CST is the temperature above which the conjugate solutions of two partially miscible liquids are completely miscible.

Q9(i) Derive the Gibbs phase rule, explaining all the terms involved. (5)

Ans. See the note.

(iii) Aniline-water mixture boils at 371.4K and 1atm. At this temperature, vapor pressure of aniline is 42 mm of Hg. If the mass ratio of aniline to water in the distillate is 0.13, calculate the molar mass of aniline.

Ans. The vapor pressure of water at this temperature is 760 – 42 = 718 mm of Hg. (5)

The principle of steam distillation is given as,

$$\frac{p_1^0}{p_2^0} = \frac{w_1 \times M_2}{w_2 \times M_1} \text{ or, } M_2 = M_1 \times \frac{p_1^0}{p_2^0} \times \frac{w_2}{w_1} = 18\, gm\, mol^{-1} \times \frac{718\, mm}{42\, mm} \times 0.13 = 40 \text{ gm mol}^{-1}.$$

BU, 2010

Q1(e) Calculate the number of components for (i) a system containing calcium carbonate at a higher temperature and (ii) a dilute solution of sugar. (2)

Ans. (i) Calcium carbonate at high T remains in equil^m. as $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$.
The number of components, C = 2 as there is one equil^m. restriction.
(ii) The number of components, C = 2.

Q9(d) Mention two azeotropic solutions having maximum and minimum boiling points. (2)

Ans. 20.22% hydrochloric acid in water has maximum BP of 108.6° and 96.8% ethyl alcohol in water has minimum BP of 78.5°C.

Q10(b) Prove that the chemical potential of a component in every phase must be equal at equilibrium. (4)

Ans. See the note, page 4. Modify the last paragraph as: The above criterion of a substance present in two phases in equil^m. may be generalized for a system containing more than two phases.
If a closed system at a given T and P contains one-component in different phases such as α, β, γ,-- at equil^m. , then $\mu_1^{\alpha} = \mu_1^{\beta} = \mu_1^{\gamma} = ...$

That is, if the system remains in equilibrium, the chemical potential of the substance must have

the same value in each phase in which it exists.

1(f) Calculate the number of phases, the number of components and number of degrees of freedom for a eutectic mixture in a binary system. (2)

    Ans. In the eutectic mixture of a binary system, there are two components, and two phases – solid and liquid both having the same composition. Thus, C = 2, P = 2 and the degree of freedom,
                F = C – P + 1, since the pressure is constant.
    Again, there is one restriction as the two phases have the same composition. So, F = 2 – 2 + 1 – 1 = 0.

2(e)(i) Draw the phase diagram of water system and explain the slopes of various curves. (4)
    Ans. See the text for the diagram and the slopes of various curves.

  (ii) Criticize or justify: "A eutectic has a definite composition and a sharp melting point, yet it is not a compound." (2)

    Ans. The eutectic mixture has degree of freedom zero when pressure is kept constant. The solid eutectic mixture thus has a sharp fixed melting point like a compound.
    But the eutectic solid is not a compound as, if pressure is changed, the solid has different composition. Further, spectroscopic data shows that it is not a compound but a mixture.

3(d)(ii) What is steam distillation? Aniline – water mixture boils at 371.4K and 1 atm. At this temperature, vapor pressure of aniline is 42 mm of Hg. If the mass ratio of aniline to water in the distillate is 0.13, calculate the molar mass of aniline. (5)

    Ans. When a completely immiscible liquid of high BP is taken in water and is distilled, it boils at a temperature near the BP of water. The distillate contains immiscible liquid and water. This is called steam distillation.
    This method is widely used to purify the a liquid which is not miscible with water. It is specially used for the liquid when it is distilled alone and decomposed at this high BP.

Solution: Steam distillation relation is, $\dfrac{weight\ of\ aniline}{weight\ of\ water} = \dfrac{vapor\ pressure\ of\ aniline \times molar\ mass\ of\ aniline}{vapor\ pressure\ of\ water \times molar\ mass\ of\ water}$.

    Putting the data given, $0.13 = \dfrac{42\ mm\ of\ Hg \times mol.wt.of\ aniline}{(760-42)\ mm\ of\ Hg \times 18\ g\ mol^{-1}}$.

    Solving the equation we get, mol. wt. of aniline = 40 g mol^{-1}.
   [The wt. ratio is probably given wrong, it should be 0.3 and the mol. wt. of aniline then is 93]

2(b)(i) The following is the miscibility (phase) diagram of phenol water system. What happens when two vigorously stirred solutions I and II, containing x % and y % of phenol respectively at 323 K are allowed to settle at that temperature? (4)

    Ans. The mixed up solution will form two conjugate solutions of 'a' % phenol and 'b'% phenol respectively.
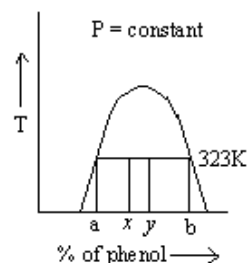
    The solution I contains x gm phenol and $(100 - x)$ gm water, and solution II contains y gm phenol and $(100 - y)$ gm water.
    When the two solutions are mixed, the total phenol content $= (x + y)$ gm
    and water $= 200 - (x + y)$ gm. Total % of phenol in the system $\dfrac{(x+y)}{\{200-(x+y)\}+(x+y)} \times 100 = \dfrac{(x+y)}{2}$.

The amount of the two conjugate solutions can be obtained from the Liver rule.
Ratio of the amount of the two conjugate solutions are given by

$$\frac{wt.\ of\ first\ phase}{wt.\ of\ second\ phase} = \frac{\left(b - \dfrac{x+y}{2}\right)}{\left(\dfrac{x+y}{2} - a\right)}$$

2(b)(ii) When heated under an inverted funnel, iodine sublimes; but it melts when heated under a covered container. – Why? (2)

Ans. When iodine is heated under an inverted funnel means that it is heated under atmospheric pressure and the triple point pressure of iodine is greater than 1 atm so it sublimes and fails to melt..
But when it is heated under a covered container, the vapor pressure of iodine exceeds the triple point pressure and it melts.

3(b)(i) "A pair of completely miscible liquids A and B can not show azeotropism if they obey Raoult's law throughout the entire range of mole fraction." – Justify or criticize. How can you prepare a primary standard solution of HCl by utilizing the phenomenon of azeotropism? Draw schematically the necessary experimental set up for this purpose and explain. (9)

**Ans.** When the liquids A and B in the solution obeys Raoult's law, $p_A = p_A^o\, x_A$ and

$p_B = p_B^o\, x_B = p_B^o(1 - x_A) = p_B^o - p_B^o\, x_A$ and the total vapor pressure, $P = p_A + p_B = p_A^o\, x_A + p_B^o - p_B^o\, x_A$

or, $P = p_B^o + \left(p_A^o - p_B^o\right)x_A$.

If the liquid A is more volatile than A, then $p_B^o \langle P \langle p_A^o$.

Thus at any composition of the solution, the vapor is always rich with more volatile component, A and the liquid is rich with less volatile component, B.
Both liquid and vapor will never have same composition and so azeotropism will not arise for the liquids that obey Raoult's law.
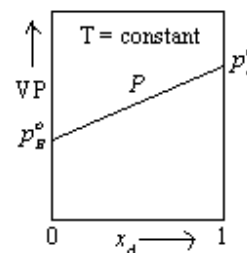
2nd part: Solution of HCl and water forms non-ideal solution with negative deviation and so it behaves as azeotropism at a certain composition of the solution. This azeotropic mixture of HCl and water will keep same composition both in the liquid phase and vapor phase. Therefore, due to vaporization of the solution there will be no change in the conc. and the solution can be used to prepare standard solution of HCl in water.

3rd part: Any solution of HCl in water is boiled, the residue ends with azeotropic mixture and its experimental set up is very easy.

BU, 2013

1(c) Four phases of any one component system cannot coexist in equilibrium. – Criticize or justify. (2)

Ans. The phase rule states, $F = C - P + 2$, for one component system, $C = 1$, so the rule becomes
$F = 1 - P + 2$ or, $P = 3 - F$, for P maximum, F is minimum and it is zero.
Putting, we get maximum number of phases that can coexist is, $P = 3$.

(g) Evaporation of solvent from the surface of a saturated KCl solution at room temperature does not change the concentration of the solution. Explain why? (2)

Ans. Saturated solution of KCl is two-component two-phase system, so $C = 2$ and $P = 2$ and the phase rule is
$F = 2 - 2 + 2 = 2$, but if pressure and temperature are kept constant, then $F = 0$.
The system becomes invariant. and concentration remains unchanged.

2(e)(i) Define fractional distillation. Discuss the principle of fractional distillation from boiling point composition curve for a completely miscible binary liquid mixture. (1+3 = 4)

Ans. When a completely miscible binary liquid mixture is partially distilled, the distillate is richer with more volatile component and the residue is rich in less volatile component. Repeated distillation with the distillate and residue may be used to separate the two components from the mixture. This process is called fractional distillation.

This repeated distillation is done in fractionating column The components in the mixture are separated according to their different boiling points. Vapors from the boiling mixture are passed along a column. The temperature of the column gradually decreases along its length. Components with a higher BP condense on the column and return to the solution; components with a lower BP pass through the column and are collected.

Three types of BP vs. composition curves can be drawn for the mixture forming (i) ideal solution (ii) non-ideal solution with large positive deviation and (iii) non-ideal solution with large negative deviation. For case (i) both components can be completely separated, for (ii) distillate contains azeotropic mixture which is constant boiling liquid mixture and the distillate contains any one pure liquid depending the initial composition of the liquid mixture. For (iii), distillate contains azeotropic mixture and the distillate contains any one pure liquid depending the initial composition of the liquid mixture.

The BP vs. composition curves are shown below:
 See the text for showing fractional distillation in the curves, (i), (ii) and (iii).
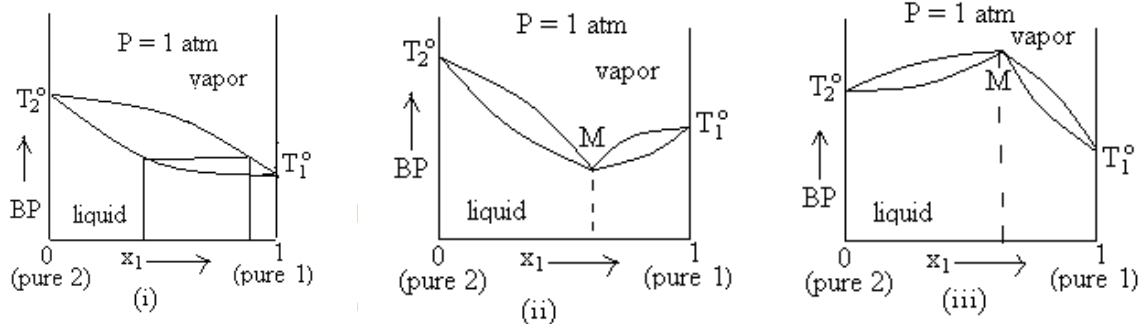
(ii) Phase rule, $F = C - P + 2$, is valid even if some of the components may not be present in all the phases. – Comment. (2)

Ans. The statement is true.

Q3(d)(i) Draw the phase diagram for the water system and explain the various lines. Calculate degree of freedom at the triple point. (6)

Ans. See the text. The degree of freedom at the triple point is 0.

(iii) What are azeotropes ? Can they be regarded as true chemical compounds ? Justify your answer. (1+2)

Ans. See the BU, 2003, Q 6 (b)