

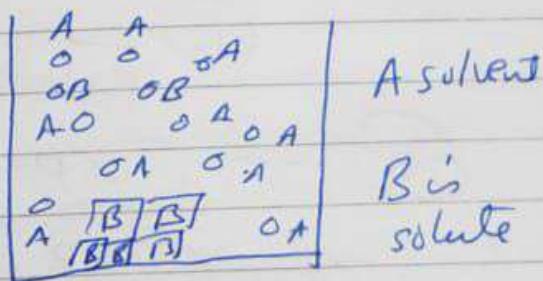
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Solubility Behavior of Ideal Solution

When a solute is dissolved in a solvent a homogeneous solution is formed. If more & more solute is added a saturation point is reached where a dynamic equilibrium is obtained i.e. rate of dissolution is equal to rate of crystallization. There exists an equilibrium between pure solute and solute in solution.

At equilibrium the chemical potential of pure solute is equal to the chemical potential in solution.

$$\mu_s(\text{solution}) = \mu_2^* \text{pure}$$



In pure state of a substance the chemical potential depends on temp. & pressure $\mu_i^* = \mu_i(T, P)$

While in solution the chemical potential depends upon T, P, mole fraction $\mu_i = \mu_i(T, P, x_i)$

$$\text{At equilibrium } \mu_i^*(T, P) = \mu_i(T, P, x_i) \quad \text{--- (1)}$$

If there are small changes then eq. (1) becomes

$$d\mu_i^*(T, P) = d\mu_i(T, P, x_i) \quad \text{--- (2)}$$

For solute since 2 is used. Therefore eq (2) can be written as

$$d\mu_2^*(T, P) = d\mu_2(T, P, x_2) \quad \text{--- (3)}$$

For solid solute 's' is used and 'l' for liquid phase solution therefore

$$d\mu_2^s = d\mu_2^l$$

$$d\mu_2^s = \left(\frac{\partial \mu_2}{\partial T} \right)_P^s dT + \left(\frac{\partial \mu_2}{\partial P} \right)_T^s dP$$

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$$= -(S_{2,m})^s dT + (V_{2,m})^s dP \quad \text{--- (4)}$$

$\therefore \mu = f(T)$
for pure solid solute

For the solute in solution $\mu_2^l = \mu_2^e(T, P, x_2)$ (2)

$$d\mu_2^l = \left(\frac{\partial \mu_2}{\partial T}\right)_{P, x_2}^e dT + \left(\frac{\partial \mu_2}{\partial P}\right)_{T, x_2}^e dP + \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T, P}^l dx_2$$

$$= -(S_{2,m})^l dT + (V_{2,m})^l dP + \left(\frac{\partial \mu_2}{\partial x_2}\right)_{T, P}^l dx_2 \quad (3)$$

When P is const $dP = 0$

eq.(4) becomes $d\mu_2^s = -S_{2,m}^s dT \quad (4)$

eq.(5) becomes $d\mu_2^l = -S_{2,m}^l dT + \left(\frac{\partial \mu_2}{\partial x_2}\right)^l dx_2$

At equilibrium eq. (4) = eq (7)

$$d\mu_2^s = d\mu_2^l$$

$$-S_{2,m}^s dT = -S_{2,m}^l dT + \left(\frac{\partial \mu_2}{\partial x_2}\right)^l dx_2$$

$$(S_{2,m}^l - S_{2,m}^s) dT = \left(\frac{\partial \mu_2}{\partial x_2}\right)^l dx_2 \quad (8)$$

$$\Delta S_{2,m} dT = \left(\frac{\partial \mu_2}{\partial x_2}\right)^l dx_2 \quad (9)$$

Entropy of solution

Since saturated solution is a state of equilibrium

$$\Delta G = 0 = \Delta H - T\Delta S$$

$$\Delta S = \frac{\Delta H}{T} \quad (10)$$

Substitute (10) in (9)

POCO $\frac{dH_{2,m} dT}{dT} = \left(\frac{\partial \mu_2}{\partial x_2}\right)^l dx_2 \quad (11)$

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If solution is ideal then the chemical potential of the solute is $\mu_2^l = \mu_2^* + RT \ln x_2^l$

$$\left(\frac{\partial \mu_2}{\partial x_2}\right)_{T, P} = \frac{RT}{x_2} \quad \rightarrow (12)$$

Sub. (12) in (11)

$$\frac{RT}{x_2} dx_2 = \frac{\Delta H_{2,m}}{T} dT$$

$$d \ln x_2 = \frac{\Delta H_{2,m} dT}{RT^2} \quad (13)$$

$\Delta H_{2,m}$ in eq (13) is molar enthalpy change. When a solute is dissolved in a solvent to get a saturated solution or it can be called heat of fusion of solid solute either by breaking up of the order of crystalline form to obtain a liquid or solid is melted or dissolved, same disordering process have undergone. eq. (13) can be written as

$$d \ln x_2 = \frac{\Delta H_{2,fus}}{RT^2} dT \quad (14)$$

Eq (14) gives relationship between the dependence of solubility on temp. and heat of fusion of solid solute. (a) Higher ΔH_{fus} , greater is barrier to breaking of crystalline order. More solute dissolves with increase of temperature.

If $\Delta H_{fus} = 0$, no barrier is to be overcome the solubility is independent of temperature.

on interpretation eq (14)

$$\ln n_2 = \frac{\Delta H_{2, \text{fus}}}{R} \int_{T_0}^T \frac{dT}{T^2}$$

$$\ln n_2 = \frac{\Delta H_{2, \text{fus}}}{R} \left[\frac{1}{T_0} - \frac{1}{T} \right] + 15$$

T_0 = equilibrium temp. when $n_2 = 1$ i.e. it is
the temperature at which solid solute is in
equilibrium with a solution so concentrated
that it is the only component there.
This is pure liquid of component 2 hence it
is melting point of T_0 . Eq (15) is called
ideal solubility law of expression.

Acc to ideal solubility law, the solubility of
a solute if expressed as mole fraction at a
given temperature is same in all solvents
with which it forms an ideal solution.

Solubility of a substance in an ideal solution
depends on the properties of that substance
only.

If there are two solutes with equal heat
of fusion, the solubility of the solute with lower
mpt will be higher in a given solvent at
const temperature

Limitations of Ideal solubility law

The solubility law is not accurate at temps

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far below the mpt of the solid since ΔH_{fus} would not independent of temp.

② The law is not valid for solutions of ionic solute present in aqueous medium because their saturated solutions are not ideal due to ionic interactions.

8. Calculate the ideal solubility of naphthalene at 25°C . $\Delta H_{\text{fus}} = 19.29 \text{ kJ/mole}$, $T_0 = 353 \text{ K}$.

Ans eq. (15) is used.

$$\log x_2 = \frac{\Delta H_{\text{fus}}}{2.303R} \left[\frac{1}{T_0} - \frac{1}{T} \right]$$
$$= \frac{19290 \text{ J/mole}}{2.303 \times 8.314 \text{ J/K/mole}} \left[\frac{1}{353\text{K}} - \frac{1}{298\text{K}} \right]$$

$$x_2 = 0.298$$

x_2 is mole fraction of naphthalene in any ideal sol. whatever is the solvent.

C_6H_6	0.298
Toluene	0.286
CH_3COCH_3	0.224
C_6H_{12}	0.125

But this is not always true for all types of solvent-solute pair. Ideal solubility law is valid only if the solvent has similar physical & chemical properties of solute.

Colligative Properties - This is property which depends only on number of particles of the solute in the solution & not on the nature of the particles.

Colligative means bound together. It is used as a group name for several properties, e.g. lowering of v.p., elevation of Bpt, depression of freezing pt, osmotic pressure.

There is a connecting relationship between each of the colligative properties.

If one property is measured, others can be calculated using same mathematical relationships but there are some assumptions to be taken into account.

- 1) Added solute should be non-volatile & should not appear in vapour phase.
- Non volatile solute is insoluble in the solid solvent i.e. on cooling solution, only pure solvent separates as solid at freezing pt.

Lowering of Vapour Pressure

The difference between the v.p. of a pure component & its partial v.p. in the solution containing non volatile solute is called lowering of v.p.

Let P_1^* be the v.p. of the pure solvent and P_1 the partial vapour pressure. P_1 is called lowering of v.p. & is denoted by ΔP .

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Solvent at given T & P then the V.P. of the solvent is lowered, the chemical potential is also lowered or decreased.

When an equilibrium is maintained, the change in chemical potential of the solvent vapour equals the chemical potential change of solvent in the solution $d\mu_i^l = d\mu_i^u$.

The chemical potential in solution depend upon T , P mole fraction or concentration

$$\mu_i^l = f(T, P, x_i) \quad i \text{ represents solvent}$$

$$d\mu_i^l = \left(\frac{\partial \mu_i}{\partial T}\right)_{P, x_i} dT + \left(\frac{\partial \mu_i}{\partial P}\right)_{T, x_i} dP + \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T, P} dx_i \quad (1)$$

For an ideal solution $\mu_i = \mu_i^0 + RT \ln x_i$

$$\left(\frac{\partial \mu_i}{\partial x_i}\right)_{T, P} = \frac{RT}{x_i} \quad (2)$$

If the solution is assumed to be 1 atm, & T is fixed $dT = dP = 0$ then using (1) & (2)

$$d\mu_i^l = 0 + 0 + \left(\frac{\partial \mu_i}{\partial x_i}\right)_{T, P}^0 dx_i$$

$$d\mu_i^l = RT dx_i = RT d\ln x_i \quad (3)$$

The vapour (solvent) is affected only by change in T & P hence $\mu_i^0 = f(T, P)$

$$d\mu_i^u = \left(\frac{\partial \mu_i^0}{\partial T}\right)_P dT + \left(\frac{\partial \mu_i^0}{\partial P}\right)_T dP \quad (4)$$

When T is fixed i.e $dT = 0$, & $\left(\frac{\partial \mu_i^0}{\partial P}\right)_T = V_{1,m}$

$$d\mu_i^u = V_{1,m} dP \quad (5)$$

$$d\mu_i^u = \frac{RT}{P} dP = RT d\ln P \quad (5)$$

At equilibrium

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$$\frac{RT d \ln P}{P_i} = RT d \ln x_1, \quad \text{--- (7)} \quad (8)$$

$$\ln \frac{P_i^*}{P_i} = \ln x_1 \Rightarrow \frac{P_i^*}{P_i} = x_1$$

$$P_i = P_i^* x_1 = P_i^*(1-x_2)$$

$$P_i = P_i^* - P_i^* x_2$$

$$P_i^* - P_i = -P_i^* x_2 \Rightarrow x_2 = \frac{P_i^* - P_i}{P_i^*} \quad (8)$$

$(P_i^* - P_i)$ is lowering of v.p & $\frac{P_i^* - P_i}{P_i^*}$ relative lowering of v.p.

Eq.(8) shows that the relative lowering of v.p is equal to the mole fraction of the solute in the solution & hence is a colligative property

Eq.(8) can be used to calculate the molecular weight of solute. For a dilute solution $x_2 = m_2 M_1$ where m_2 is molality M_1 is molecular mass of solvent in kg

$$\frac{P_i^* - P_i}{P_i^*} = m_2 M_1$$

$$\frac{P_i^* - P_i}{P_i^*} = \left(\frac{\omega_2}{M_1 \times \omega_1} \right) M_1 \quad \text{--- (9)}$$

(9) can be used (1) to calculate molecular weight of non volatile solute.

calculate the mass ω_2 of given solute to get a known lowering of v.p

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Q When 2 g of non rotatile hydrocarbon is dissolved in 10g of C_6H_6 , v. P. of C_6H_6 at $20^\circ C$ is lowered from 74.66 mm Hg to 74.01 mm Hg. Calculate the molecular mass of hydrocarbon. If the given hydrocarbon contains 94.4% carbon, what should be molecular formula of the hydrocarbon.

$$w_2 = 2 \text{ g}, w_1 = 10 \text{ g}, M_1 = 78 \text{ g/mole}, \\ P_i^o = 74.66 \text{ mm Hg} \quad P_i = 74.01 \text{ mm Hg}$$

$$\frac{P_i - P_i^o}{P_i^o} = \alpha_2 = \frac{w_2}{M_2} \times \frac{M_1}{w_1}$$

$$M_2 = \frac{w_2 \times M_1}{w_1} \times \frac{P_i^o}{P_i - P_i^o} \\ = \frac{2 \text{ g} \times 78 \text{ g/mole}}{(10 \text{ g})} \times \frac{74.66 \text{ mm Hg}}{(74.66 - 74.01) \text{ mm Hg}}$$

$$M_2 = 179 \text{ g/mole}$$

$$C = 94.4\%, \frac{94.4}{12} = 7.86 = \frac{7.86}{5.86} = 1.4$$

$$H = 5.6\%, \frac{5.6}{1} = 5.6 = \frac{5.6}{5.86} = 1$$

$$\text{Empirical Formula} = C_7H_5$$

$$\text{Empirical Formula wt} = 89$$

$$\frac{\text{Molecular F. W.}}{\text{Empirical F.W.}} = \frac{179}{89} = 2$$

$$\therefore \text{Molecular Formula} = (C_7H_5)_2 = C_{14}H_{10}$$

Elevation of Boiling Pt

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The difference between the boiling pt of a solution (T) containing a non volatile solute and the boiling point of the pure solvent T_b is called the elevation of boiling pt. It is denoted by

$$\Delta T_b = T - T_b$$

A liquid boils at a temp. when its V.P. equals atm. P. If a non volatile solute is added to the liquid its V.P. is decreased and it has to be heated to a higher temp. to equalize the V.P. to atm. P.

The boiling pt of a liquid is elevated by addition of a non volatile solute.

In a pure solvent at a given T & P there exists an equilibrium between the vapour & liquid phase. At equilibrium the chemical potential of solvent (Component 1) in the liquid phase must be equal to that in the vapour phase

$$\mu_1^*(\text{liquid}) = \mu_1^*(\text{vapour})$$

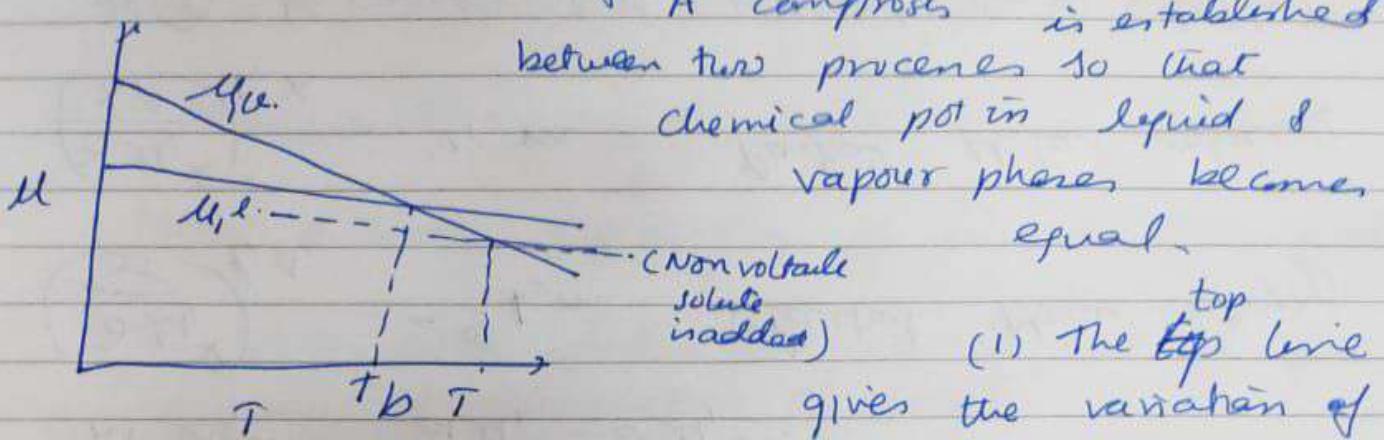
If the system is at 1 atm P, then the chemical potential of pure component μ^* is equal to the std. chemical potential μ°

When a non volatile solute is added, the V.P. of solvent will be lowered, the escaping tendency of the solvent molecules will be diminished. More solvent molecules form vapour phase will pass into liquid phase to restore the equilibrium.

POCO^{figured} is to be heated to a temp

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higher than the boiling pt. of pure liquid T_b
 the escaping tendency of solvent molecules from the
 liquid phase. This increase of temp will decrease
 the chemical pot. of the vapour phase.



chemical pot. of vapour μ_v^u with temp in the above graph

(2) The second line gives the variation of chemical potential of pure liquid μ_l^u with temp.

When these lines meet, $\mu_v^u = \mu_l^u$ & temp is boiling point of pure liquid T_b

(3) The dotted line represents the variation of the chemical potential of the solvent in the solution. The temp. at which vapour & solvent lines meet is boiling pt of solution 'T'.

$\mu_v^u = \mu_l^u$ is at new boiling pt, the change in the chemical pot. of liquid & vapour phase are equal at equilibrium

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$d\mu_i^l = d\mu_i^u$ (12)
 μ_i^l of liquid (solvent) in solution depends on T, P
& composition of solution

μ_i^u is chemical potential of solvent in vapour phase & depends on T & P because in vapour phase there is only solvent molecule, solute being non volatile will remain in solution.

$$\mu_i^l = f(T, P, x_i) \quad ; \quad \mu_i^u = f(T, P)$$

$$d\mu_i^l = \left(\frac{\partial \mu_i^l}{\partial T}\right)_{P, x_i} dT + \left(\frac{\partial \mu_i^l}{\partial P}\right)_{T, x_i} dP + \left(\frac{\partial \mu_i^l}{\partial x_i}\right) d\chi_i \quad (1)$$

$$d\mu_i^u = \left(\frac{\partial \mu_i^u}{\partial T}\right)_P dT + \left(\frac{\partial \mu_i^u}{\partial P}\right)_T dP \quad (2)$$

$$\text{At eqn. } d\mu_i^l = d\mu_i^u.$$

$$\left(\frac{\partial \mu_i^l}{\partial T}\right)_{P, x_i} = -S_{f, m} \quad (\text{Partial Molar Entropy})$$

$$\left(\frac{\mu_i^l}{P}\right)_{T, x_i} = V_{i, m} \quad \text{Partial Molar volume}$$

(1) becomes due to above 2 substitut

$$S_{i, m}^l dT + V_{i, m}^l dP + \left(\frac{\partial \mu_i^l}{\partial x_i}\right) d\chi_i = S_{i, m}^u dT + V_{i, m}^u dP$$

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$$(S_{1,m}^u - S_{1,m}^l) dT + (V_{1,m}^e - V_{1,m}^u) dP + \left(\frac{\partial \mu_1^l}{\partial x_1}\right) dx_1 = 0 \quad (13)$$

Since most of expt are carried at const P , $dP = 0$

$$(S_{1,m}^u - S_{1,m}^l) dT = -\left(\frac{\partial \mu_1^l}{\partial x_1}\right) dx_1$$

$$\Delta S_{\text{vap},m} dT = -\left(\frac{\partial \mu_1^l}{\partial x_1}\right) dx_1 \quad \rightarrow \quad (3)$$

Molar entropy vaporization of solvent from solution

For very dilute solution $\Delta S_{\text{vap},m} \approx$ Entropy of vaporization of solvent

The chemical potential of component 1 in ideal sol.

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

$$\left(\frac{\partial \mu_1}{\partial x_1}\right)_{T,P} = \frac{RT}{x_1} \quad (4)$$

$$\text{eq. (3)} \rightarrow (4) \text{ gives } \Delta S_{\text{vap},m} dT = -RT \frac{dx_1}{x_1} \quad (5)$$

$$\text{At eqn } \Delta G = 0 \quad \Delta H - T\Delta S = 0 \text{ or } \Delta S = \frac{\Delta H}{T} \quad (6)$$

Sub (6) in (5)

$$\frac{\Delta H_{\text{vap}} dT}{T} = -RT \frac{dx_1}{x_1} \Rightarrow \frac{dx_1}{x_1} = -\frac{\Delta H_{\text{vap}}}{RT^2} dT$$

$$d \ln x_1 = -\frac{\Delta H_{\text{vap}}}{RT^2} dT$$

$$\therefore \int_1^T d \ln x_1 = - \int_{T_b}^T \frac{\Delta H_{\text{vap}}}{RT^2} dT \quad (7)$$

$$\ln n_1 = \frac{\Delta H_{\text{vap}}}{R} \left(\frac{1}{T} - \frac{1}{T_b} \right) \quad (14)$$

$$\ln(1-x_2) = \frac{\Delta H_{\text{vap},m}}{R} \left[\frac{\Delta T_b}{TT_b} \right] \quad (8)$$

For a dilute solution ΔT_b is very small $T \approx T_b$

$$\ln(1-x_2) \approx -x_2$$

$$x_2 = \frac{\Delta H_{\text{vap},m}}{RT_b^2} \Delta T_b \quad (9)$$

Eq. (9) gives the variation of the elevation in bp with the mole fraction of the molal solutes. ΔT_b depends only on the amt x_2 of the solute added to a given solvent. hence it is a colligative property

$$x_2 = \frac{n_2}{n_1+n_2} \approx \frac{n_2}{n_1} = \frac{n_2}{w_1/M_1} = \frac{m_2 M_1}{1000} \quad (10)$$

$$\frac{m_2 M_1}{1000} = \frac{\Delta H_{\text{vap},m}}{R T_b^2} \frac{\Delta T_b}{}$$

$$\Delta T_b = \frac{R T_b^2}{\Delta H_{\text{vap}}} \frac{m_2 M_1}{1000}$$

$$\Delta T_b = K_b m_2 \quad \text{where } K_b = \frac{RT_b^2 M_1}{1000 \Delta H_{\text{vap}}}$$

~~Value of~~ The elevation in the boiling pt of
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the solvent caused by 1 mole of non volatile solute
dissolved per kg of solvent is called molal boiling
point elevation or ebullioscopic constant

Molar Mass of solute

$$\Delta T_b = K_b \frac{n_2}{n_1} = K_b \frac{w_2 \times 1000}{M_2 \times w_1}$$

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

w_2 = Mass of solute

w_1 = Mass of solvent

M_2 = Molar Mass of solute

ΔT_b = Elevation in Δbpt

Conditions for M.WT determination

- (1) Substance must be non volatile
- (2) Solution must obey Raoult's law
- (3) ΔH_{vap} must be independent of temp ie elevation of bpt must not be very large
- (4) The solution must be dilute