

2020						
S	M	T	W	T	F	S
1	2	3	4	5	6	7
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29	30	31				

①

6th Week • 034-332

FEBRUARY

03

Dr. Debrunjan Ghosh - Monday

Semester - 4 (H)

CC - 8

Topic - Vapour pressure,

Raoult's law
and

Thermodynamics of ideal
solution

Study Materials.

FEB

February						
S	M	T	W	T	F	S
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04

6th Week • 035-331
FEBRUARY
Tuesday

Lowering of Vapour Pressure

9.00

10.00

11.00

12.00

1.00

2.00

3.00

4.00

5.00

6.00

It is observed that when a nonvolatile solute is dissolved in a volatile solvent, vapour pressure of the later is lowered. The lowering of vapour can be understood as follows.

If a liquid is placed in an evacuated vessel, there occurs migration of solvent molecules from the liquid surface to the empty space above vice versa.

The system attains an equilibrium.

March							2020						
S	M	T	W	T	F	S	S	M	T	W	T	F	S
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(3)

6th Week • 036-330

FEBRUARY

Wednesday

05

when the rates of these two migrations become equal.

At this stage, the pressure recorded at the space above the liquid is known as the vapour pressure of the liquid.

In the presence of a nonvolatile non electrolyte solute, the number of solvent molecules available for migration from surface of solution relative to those present in the pure solvent is decreased.

As a consequence of this, the vapour of the solution is lesser than that of the pure solvent.

NOTES

February							2020
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16	17	18	19	20	21	22	
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06

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FEBRUARY

Thursday

Raoult's Law

Relative lowering of vapour pressure of a solvent by a non-volatile, nonelectrolyte solute is equal to the mole fraction of the solute in solution.

If p° is the original vapour pressure of the pure solvent and p be the vapour of the solution then lowering of vapour pressure is $(p^{\circ} - p)$ and relative lowering of vapour pressure is $\frac{p^{\circ} - p}{p^{\circ}}$.

Relative lowering of vapour pressure is defined as the ratio of the

March							2020						
S	M	T	W	T	F	S	S	M	T	W	T	F	S
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29	30	31											

(5)

6th Week • 038-328

FEBRUARY

Friday

07

Lowering of vapour pressure to the vapour pressure of the pure solvent.

If the solution contains n_2 moles solute dissolved in n_1 moles of solvent then the mole fraction of

the solute is $\frac{n_2}{n_1 + n_2} = X_{\text{solute}} = X_2$

So, Raoult's law becomes

$$\frac{p^{\circ} - p}{p^{\circ}} = \frac{n_2}{n_1 + n_2} = X_{\text{solute}} = X_2 \quad \text{--- (1)}$$

$$\therefore 1 - \frac{p^{\circ} - p}{p^{\circ}} = 1 - \frac{n_2}{n_1 + n_2} = \frac{n_1}{n_1 + n_2} = X_1$$

or $\frac{p}{p^{\circ}} = X_1 = \text{Mole fraction of the solvent.}$

$$\therefore p = p^{\circ} \times X_1 \quad \text{--- (2)}$$

February 2020						
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08

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FEBRUARY

Saturday

⑥

Therefore $p < p^0$ [From eqn. (2)]

Thus Raoult's law can be alternatively

stated as the vapour pressure

of the solvent over a solution

is equal to the vapour pressure

of the pure solvent multiplied

by the mole fraction of the

solvent. ($p = p^0 \cdot X_1$) (2)

Now, $X_2 + X_1 = \frac{n_2}{n_1 + n_2} + \frac{n_1}{n_1 + n_2} = 1$

$\therefore X_1 = (1 - X_2)$

Now equation (2) becomes

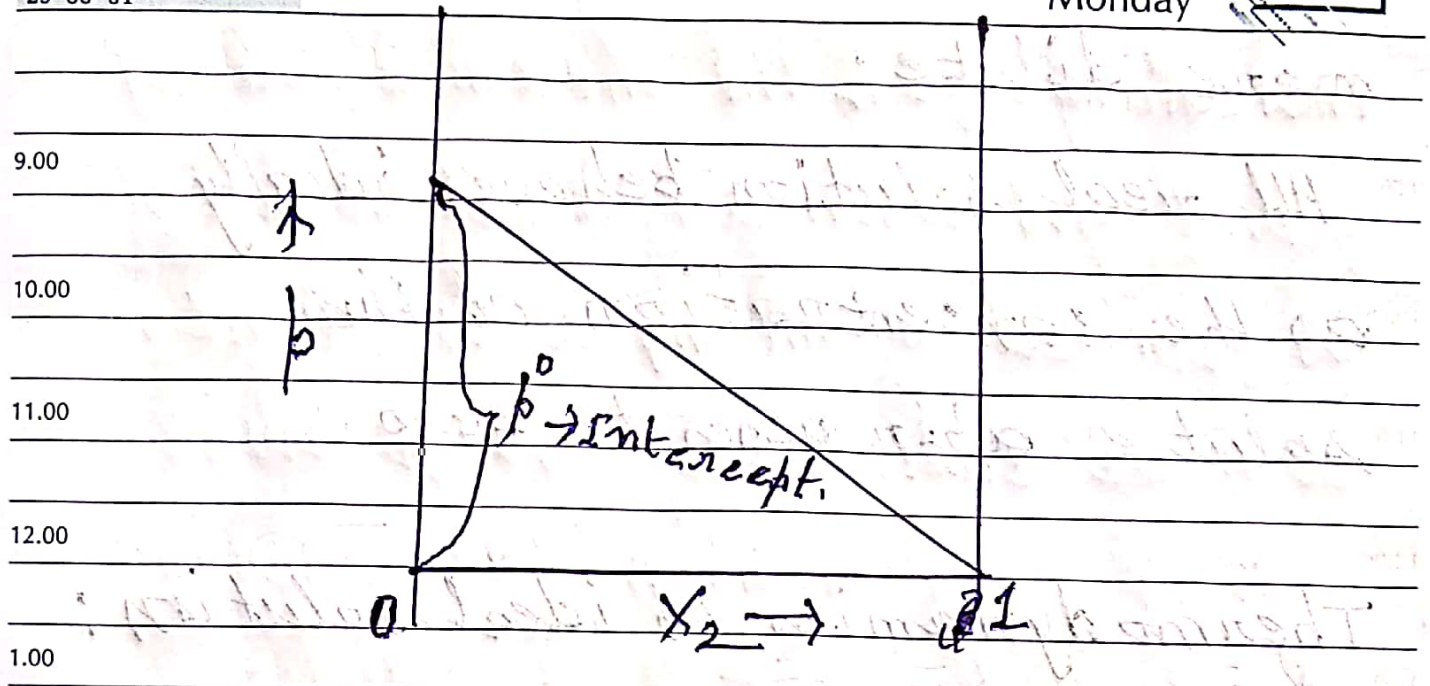
09 - Sunday

$$\begin{aligned}
 p &= p^0 \cdot X_1 \\
 &= p^0 (1 - X_2) \\
 &= p^0 - p^0 \cdot X_2
 \end{aligned}$$

NOTES

$$Y = -mx + c \text{ (type)}$$

March							2020						
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Ideal solution :-

The ideal solution is defined

as one that follows the Raoult's

law over the entire range of

concentration. Raoult's law is an example of limiting law.

Real solution follows this law

more closely as the solution becomes



7th Week • 042-324

FEBRUARY

Tuesday

(8)

February							2023
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more dilute.

9.00 All real solution behaves ideally
10.00 as the concentration of the
11.00 solute approaches to zero.

12.00

Thermodynamics of ideal solution:

1.00

2.00 The ideal solution has the following
3.00 properties also.

4.00

$$(i) \Delta V_{mix} = 0$$

5.00

$$(ii) \Delta H_{mix} = 0$$

6.00

$$(iii) \Delta G_{mix} = nRT \sum x_i \ln x_i$$

$$(iv) \Delta S_{mix} = -nR \sum x_i \ln x_i$$

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(9)

7th Week • 043-323
 FEBRUARY
 Wednesday

12

Thermodynamics of an ideal solution

9.00

The various constituents of an ideal solution follows the relation

10.00

11.00

$$\mu_{i(\text{soln})} = \mu_i^{\circ}(l) + RT \ln x_i \quad \dots (3)$$

12.00

1.00

$\mu_i(\text{solution}) = \mu_i(\text{soln}) =$ chemical

2.00

potential of the i^{th} constituent of the

3.00

solution.

4.00

$\mu_i^{\circ}(l) =$ chemical potential of pure

5.00

liquid constituent.

6.00

$x_i =$ mole fraction of the constituent in solution.

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13

7th Week • 044-322

FEBRUARY

Thursday

The changes in the thermodynamic functions, when an ideal solution is formed by mixing constituents can be calculated as follows:

A] (i) Change in Gibb's free energy

$$\Delta G_{mix} = G_{final} - G_{initial}$$

$$= \sum n_i \mu_i - \sum n_i \mu_i^0$$

$$= \sum n_i [\mu_i(\text{soln}) - \mu_i^0(l)]$$

$$= \sum n_i RT \ln x_i \quad \text{--- (4)}$$

$$[x_i = \frac{n_i}{n_1 + n_2 + \dots} = \frac{n_i}{n_{total}}, \text{ by definition}]$$

$$\therefore n_i = n_{total} \cdot x_i$$

Putting this value in eqn (4)

$$\Delta G_{mix} = n_{total} \sum x_i RT \ln x_i$$

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(11)

7th Week • 045-321

FEBRUARY

Friday

14

$$\therefore \Delta G_{mix} = nRT \sum x_i \ln x_i \quad \dots (5)$$

9.00

(Proved.)

B Change in ~~enthalpy~~ entropy on mixing

$$\left[\frac{\delta}{\delta T} (\Delta G)_{mix} \right]_{P, n_i} = -\Delta S_{mix}$$

11.00

12.00

$$\therefore \Delta S_{mix} = - \frac{\delta}{\delta T} [nRT \sum x_i \ln x_i]$$

1.00

$$= -nR \sum x_i \ln x_i \quad \dots (6)$$

4.00

5.00

6.00

C Change of enthalpy on mixing

$$\Delta G_{mix} = \Delta H_{mix} - T \Delta S_{mix}$$

$$\therefore \Delta H_{mix} = \Delta G_{mix} + T \Delta S_{mix}$$

$$= nRT \sum x_i \ln x_i - nRT \sum x_i \ln x_i$$

$$= 0$$

Thus in the formation of an ideal solution neither heating nor cooling is observed.

NOTES

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(12)

15
7th Week • 046-320
FEBRUARY
Saturday

D] change of volume of mixing

$$\Delta V_{mix} = \left[\frac{\partial (\Delta G_{mix})}{\partial P} \right]_{T, n_i, s} = 0$$

as ΔG_{mix} is independent of pressure.

Total volume of ideal solution will be equal to the sum of the individual volume of its constituents.