

# **Solutions-solutions**

# **SUBJECTIVE PROBLEMS:**

## <u>Sol 1.</u>

(i) Molarity = Moles of solute/Volume of solution in L

(ii)  $N_1V_1 = N_2V_2$ 

A 13% solution (by weight) contains 13 g of solute (i.e H<sub>2</sub>SO<sub>4</sub>) per 100 gm of solution

Moles of solute = Mass of  $H_2SO_4/M$ . wt. of  $H_2SO_4 = 13/98 = 0.1326$ 

Volume of solution in L

= Mass of solution/density of solution \*1000 = 100/1.02 \* 1000 = 0.0980 Litre

: Molarity of solution = 0.1326/0.0980 = 1.35 M

Again, Molality = Moles of solute/Mass of solvent in kg

Mass of solute in 100 ml of solution = 13 g [13% solution]

Mass of solvent = Mass of solution – Mass of solvent

= 100 – 13 = 87 g

∴ Molality = 13/98/87/100 = 1.57 m

Normality = Miolarity \* Mol. wt/Eq. wt. or 1.35 \* 98/49 = 2.70 N

 $N_1 = 2.70$ ,  $V_1 = 100$  ml,  $N_2 = 1.5$ ,  $V_2 = ?$  [: Eq. wt = 98/2 2H<sub>2</sub>SO<sub>4</sub> = 49]

 $N_1V_1 = N_2V_2$ 

2.70 \* 100 = 1.5 \* v<sub>2</sub>

Or  $V_2 = 2.70 \times 100/1.5 = 180$  ml.  $\therefore$  100 ml of this acid should be diluted to 180 ml to prepare 1.5 solution.



# <u>Sol 2.</u>

Molarity = Moles of solute/Volume of solution in L

= Mass of solute/M. wt. of solute/Mass of solution/density of solution \* 1000

*M* = 86/98/100/1.787 \* 1000 = 0.8775/55.5 \* 1000 = 15.81 M

 $M_1V_1 = M_2V_2$ 

 $M_1 = 15.81, V_1 = ?$ 

 $M_2 = 0.2, V_2 = 1 L = 1000 \text{ ml}$ 

 $\therefore$  15.81 \*  $V_1$  = 0.2 \* 1000

Or V<sub>1</sub> = 0.2 \*1000/15.81 = 12.65 ml

 $\therefore$  Amount of acid to be used to make 1 L of 0.2 M H<sub>2</sub>SO<sub>4</sub> – 12.65.

#### <u>Sol 3.</u>

N<sub>1</sub>= I, V<sub>I</sub>=?,N<sub>2</sub>=26.7, V<sub>2</sub>=0.4

 $N_1 V_1 = N_2 V_2$ 

 $1 \times V_1 = 26.7 \times 0.4$ 

 $V_1 = 26.7 * 0.4/1 = 10.68$ 

49g (: eqwt of  $H_2SO_4 = 49$ ) pf  $H_2SO_4$  will be neutralized by = 1N 1000 ml NaOH

 $\therefore$  0.5g of H<sub>2</sub>SO<sub>4</sub> will be neutralized

= 1000/49 \* 0.5 = 10.20 ml 1N NaOH

Volume of 1 N NaOH used by dissolved

SO<sub>3</sub> = 10.68 - 10.20 = 0.48 ml

 $SO_3 + 2NaOH \rightarrow Na_2SO_4 + H_2O$ 

 $\therefore$  Eqwt of SO<sub>3</sub> = Molwt/2 = 80/2 = 40



Wt of  $SO_3$  in 0.48 ml of 1 M solution

= 40/1000 \* 0.48 = 0.0192 g

% of SO<sub>3</sub> = 0.0192/0.5 \* 100 = 3.84 %

# <u>Sol 4.</u>

 $p^{\circ} - p/p^{\circ} = n/N$  [Roults Equation]

Let the molality of the solution = m

Now the solution contain 'm' moles of solute per 1000 gm of benzene

Vapour pressure of benzene,  $p^{\circ}$  = 639.7 mm

Vapour pressure of solution, p = 63.9 mm

Moles of benzene (Mol. wt. 78), N = 1000/78

Moles of solute, n = ?

Substitute these values in the Raout's equation

 $p^{\circ} - p/p^{\circ} = n/N \text{ or } 639.7 - 631.9/639.7 = n *78/1000$ 

or 7.8/639.7 = 78 n/1000

∴ n = 1000 \* 7.8/78 \*639.7 = 0.156

Hence, molality of solution = 0.156 m

## <u>Sol 5.</u>

 $P_T = p_1^o + p_2^o x_2$ 

At 300 K, the vapour pressure of the solution containing 1 mole of A & 3 moles of B = 550 mm of Hg and vapour pressure of the solution containing 1 mole of A & 4 moles of B at 300 K = 560 mm Hg.

Let the vapour pressure of pure  $A = p_1^{\circ}$ 

And the vapour pressure of pure  $B = p_2^{o}$ 



Further, let  $x_1$  and  $x_2$  be the mole fractions of A and B in the solutions. Then the total vapour pressure of solution

$$P_{total} = p_1^{0} x_1 + p_2^{0} x_2$$
 ...(i)

In solution 1,  $p_{total} = 550 \text{ mm}$ ,

 $\therefore x_1 = 1/1 - 3, x_2 = 3/1 + 3$  [: moles of A = 1 moles of B = 3]

Substituting these values in (i) we get

$$550 = p_1^{0} * \frac{1}{4} + p_2^{0} * \frac{3}{4}$$

Or 550 = 
$$p_1^0/4 + 3p_2^0/4$$

$$2200 = p_1^{0} + 3p_2^{0}$$
 ...(ii)

In solution 2,  $p_{total} = 560$  mm,

 $X_1 1/1 + 4$ ,  $x_2 = 4/1 + 4$ [: moles of A = 1 moles of B = 4]

Substituting the various values, in equ. (i) we get

$$560 = p_1^0 * 1/5 + p_2^0 * 4/5$$

Or 560  $p_1^0/5 + 4p_2^0/5$ 

 $2800 = p_1^0 + 4p_2^0$  ....(iii)

Solving equation (ii) and (iii), we get

$$P_2^{0} = 6400 \text{ mm of Hg}$$

 $p_1^{0} = 400 \text{ mm of Hg}$ 

 $\therefore$  Vapour pressure of pure A = 400 mm of Hg

And vapour pressure of pure B = 600 mm of Hg



# <u>Sol 6.</u>

The chemical equation for the combustion of organic compound  $C_x H_{2y} O_y$  can be represented as:

 $C_xH_{2y}O_y + 2xO_2 = x CO_2 + y H_2O + x O_2$ 

The gases obtained after cooling = x + x = 2x

 $\therefore$  2x = 2.24 litres [:: H<sub>2</sub>O is in liquid state]

Or x = 2.24/2 = 1.12 litres

Number of moles of  $CO_2 = 1.12$  litres/222.4 litres mole [: 22.4 L at NTP = 1 mole]

= 1/2 mole = 0.05 mole

The empirical formula of the organic compound is C(H<sub>2</sub>O) ...(i

The mole fraction of the solute (A)

= relative decrease in vapour pressure of the solvent (B)

 $P^{o} - p/p^{o} = W_{A}/M_{A}/W_{A}/M_{A}+W_{B}/M_{B}$ 

Or 0.104/17.5 = 50/M<sub>A</sub>/50/M<sub>A</sub>+1000/18 [M<sub>A</sub> = mol. wt. g A]

 $Or 0.104/17.5 = 50/M_A(50 * 18 + 100M_A/18M_A)$ 

Or 104/17500 = 50 \* 18/900 + 1000 M<sub>A</sub>

Or M<sub>A</sub> = 150.6

Molecular wt. of the organic compound

 $(CH_2O)_n = 150$ 

Molecular wt.  $CH_2O = 12 + 2 + 16 = 30$ 

 $:: 30 * n = 150 [:: (CH_2O)_n = mol, formula]$ 

Or n = 150/30 = 5

: Molecular formula of the given organic compound is  $(CH_2O)$  or  $C_5H_{10}O_5$ .



# <u>Sol 7.</u>

If they form an ideal solution which obeys 'Raoult's Law and for which

 $\Delta H_{\text{mixing}} = 0$  and  $\Delta V_{\text{mixing}} = 0$ 

Thus we can separate two volatile and miscible liquids by fractional distillation if, they should not form azeotropic solutions.

## <u>Sol 8.</u>

 $P_{total} = p_A + p_B$ 

Molecular weight of  $CH_3OH = 12 + 3 + 16 + 1 = 32$ 

Molecular weight of  $C_2H_5OH = 24 + 5 + 16 + 1 = 46$ 

According to Raoult's law

 $P_{total} = p_1 + p_2$ 

Where P<sub>total</sub> = Total vapour pressure of the solution

 $P_1$  = Partial vapour pressure of one component

P<sub>2</sub> = Partial vapour pressure of other componenet

Again,  $p_1$  = Vapour pressure ( $p_1^{o_1}$ ) \* mole fraction

Similarly,  $p_2 = Vapour pressure (p_2^{\circ})^*$  mole fraction

Mole fraction of  $CH_3OH = 40/32/40/32+60/46 = 0.49$ 

Mole fraction of ethanol = 60/46/60/46+40/32 = 0.51

**NOTE THIS STEP :** Thus now let us first calculate the partial vapour pressures, i.e.,  $p_1$  and  $p_2$  of the two component.

Partial vapour pressure of CH<sub>3</sub>OH(p<sub>1</sub>)

= 44.5 \* 0.51 = 22.69 mm : Total vapour pressure of the solution

= 43.48 + 22.69 mm = 66.17 mm Mole fraction of CH<sub>3</sub>OH in vapour = 43.48/66.17 = 0.65



# <u>Sol 9.</u>

Molality, M = moles of solute/kg of solvent

Mole fraction,  $x_A = n_A/n_A + n_B$ ,  $x_B = n_B/n_A + n_B$ 

 $p_1 = x_1 p_1^{\circ}$ 

 $\therefore x_1 = p_{1/p_1}^{\circ} = 750/760 = 0.9868$ 

 $x_2(solute) = 1 - 0.9868 = 0.0132$ 

molality,  $m = x_2/x_1M_1 * 1000 = 0.0132 * 1000/0.9868 * 18 = 0.7503 mol kg<sup>-1</sup>$ 

#### **ALTERNATIVESOLUTION:**

Given that :

Temperature = 273 K

boiling point of  $H_2O = 373$  K

 $\therefore$  vapour pressure H<sub>2</sub>O = 76 cm

We have,

$$P^{o}-P_{s}/P_{s} = w^{*}M/w^{*}M$$

∴ molality

 $= w/w^*M^* 1000 = P^0 - P_s/P_s^* 1/M^* 1000$ 

= 760 -750/750 \* 1/18 \* 1000

= 0.741 mol/kg of solvent

Also we have,

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= 1000 *1.72 *20/50 *2
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= 344

van't Hoff factor (i) = actual mol. wt./calculate mol. wt = 172/344 = 0.5



 $P^{o}-P_{s}/P_{s} = n/n + N$ 

: mole fraction =  $P^{o} - P_{s}/P^{o} = 760 - 750/760$ 

= 10/760 = 0.013

## <u>Sol 10.</u>

According to Rault's law,

 $P^{o}-P/P^{o} = w/m / w/m + W/M$ 

Here,  $P^{\circ} = 640 \text{ mm}$  p = 600 mm

W = 2.175 g W = 39.0

M = ? M = 78

Substituting the various values in the above equation for Roult'slaw :

640 -600/640 = 2.175/m /2.175/m+39/78

m = 65.25

## Sol 11.

First find moles of  $Ca(NO_3)_2$  and water. Then use the expression

 $P^{o}-P/P^{o} = n/n + N$  to find vapour pressure of solution

Let initially 1 mole of Ca(NO<sub>3</sub>)<sub>2</sub> is taken

Degree of dissociation of  $Ca(NO_3)_2 = 70/100 = 0.7$ 

Ionization of Ca(NO<sub>3</sub>)<sub>2</sub> can be represent as

	$Ca(NO_3)_2$	$\rightleftharpoons$	Ca <sup>2+</sup>	+	2N0 <sup>-</sup> 3
At start	1		0		0
At equilibrium	1 -0.7		0.7		2 * 0.7



 $\div$  Total number of moles in the solution at equilibrium

No. of moles when the solution contains 1 gm of calcium nitrate instead of 1 mole of the salt

= 2.4/164 (164 is the mol. wt. of Cal. nitrate)

 $\therefore$  No. of moles of the solute in the solution containing 7 g of salt, i.e.,

No. of moles of water (N) = Wt. of water/Mol. wt. of water = 100/18 = 5.55

Applying Raoult's law,  $P^{o}-P/P^{o} = n/n + N$ 

760 -p/760 = 0.102/0.102 + 5.55

760 – p/760 = 0.0180

⇒ p = 760 – (760 \* 0.0180) = 746.3 mm Hg

#### **ALTERNATIVESOLUTION :**

 $\begin{array}{rcl} Ca(NO_3)_2 & \rightleftharpoons & Ca^{2+} & + & 2NO^{-}_3 \\ 1 & 0 & 0 & \text{before dissociation} \\ 1 - \propto & \propto & 2 \propto & \text{After dissociation} \end{array}$ 

: Total moles at equilibrium =  $(1 + 2 \propto)$ 

= 1 + 2 \* 0.7 (: a = 0.7)

= 2.4

For  $Ca(NO_3)_2$ :  $m_{ob}/m_{exp} = 1 + 2 \propto$ 

 $\therefore m_{exp} = m_{ob}/1 + 2 * 0.7 = 164/2.4 = 68.33$ 

Also at 100°  $P^{o}_{H \text{ base } 2}$ O = 760 mm, w = 7g

W = 100 g



Now,  $P^{o}-P_{s}/P_{s} = 7 * 18/68.33 * 100 = 0.0184$ 

Or  $P^{o}/P^{s} - 1 = 0.0184$ 

 $\therefore P_s = 760/1.0184 = 74.26 \text{ mm}$ 

## <u>Sol 12.</u>

Give Wt. of benzene (solvent),

W = Volume \* density = 50 \* 0.789 = 43.95 g

Wt. of compound (solute), w = 0.643 g

Mol. wt of benzene, M = 78

Mol. wt. of solute, m = ?

Depression in freezing point,  $\Delta T_f = 5.51 - 5.03 = 0.48$ 

Molal freezing constant, K<sub>f</sub> = 5.12

Now we know that,

 $M - 1000 * K_f * w/W * \Delta T_f = 1000 * 5.12 * 0.643/43.95 * 0.48 = 156.056$ 

## <u>Sol 13.</u>

 $P^{o} - P/P^{o} = w/3 / w/m + W/M$ 

Here, w and m are wt. and molecular wt. of solute, W and M are wt. and molecular weight of solvent

p = pressure of solution;

p<sup>o</sup> = Normal vapour pressure

Let the initial (normal) pressure  $(p^{\circ}) = p$ 

 $\therefore$  Pressure of solution = 75/100 \* p = 3/4 p

M = 60, M = 118, W = 100 gm

∴ p-3/4 p/p = w/60 /w/60 + 100/18



1/4 = w/60 / (w/60) + 5.55Or 4w/60 = w/60 + 5.553w/60 = w/20 = 5.55Or w = 111 g Molality = No. of moles of solute/Wt. of solvent \* 1000 = 111 \*1000/60 \*100 = **18.52 m** 

## <u>Sol 14.</u>

(i)Volume = No. of moles \* molar mass/density

(ii) PV = nRT or P = nRT/V

Volume of 1 mole of liq. Benzene = 78/0.877

Volume of 1 mole of toluene. 92/0.867

In vapour phase,

At 20°C, for 1 mole of benzene,

Volume = 1 \*\*78 \*2750/0.877 = 244583.80 mL

= 244.58 L

Similarly for 1 mole of toluene,

Volume = 1 \*92/0.867 \* 7720

= 819192.61 mL = 819.199 L

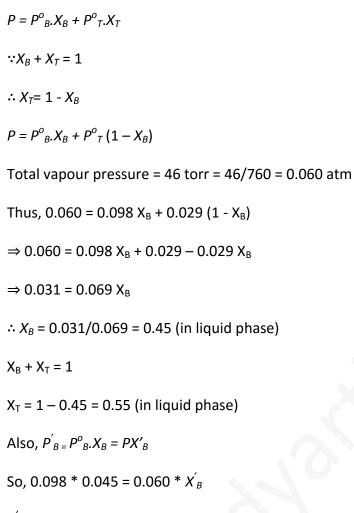
As we know that, PV = nrt

For benzene,  $P_B^o = nRT/V = 1 * 0.0821 * 293/244.58$  atm

= 0.098 atm

For toluene,  $P_{T}^{o} = nRT/V = 1 * 0.0825 * 293/819.19$  atm = 0.029 atm





 $\dot{X_B} = 0.098 * 0.45/0.060 = 0.735$  (in gas phase)

# <u>Sol 15.</u>

According to Roult's law

 $P^{o} - p/p^{o} = w/m * M/W ; \Delta T_{f} = K_{f} * m$ 

Substituting the given values;

1000 - 98.88/98.88 = w \*78 \*1000/m \*W \* 1000

w/m \* 1000/W = 1.12 \*1000/78.98.88 = 0.1452

: Molality = **0.1452** (: w/m \* 1000/W = Molality) Further  $\Delta T = K_f$  molality

 $0.73 = K_f * 0.1452 K_f = 5.027 K molality^{-1}$ 



# <u>Sol 16.</u>

 $\Delta T_f = K_f.m$   $P^o - p/p^o = \text{moles of solute/moles of solvent}$ Depression in freezing point,  $\Delta T_f = K_f m$   $\therefore m \Delta T_f/K_f = 0.30/1.86 = 0.161$ According to Raoult's law  $P^o - p/p^o = \text{No. of moles of solute/No. of moles of solvent}$  23.51 - p/23.51 = 0.161/1000/18 = 0.161 \* 18/1000(:: No. of moles of H<sub>2</sub>O = 1000/18)
On usual calculations, 23.51 - p/23.51 = 0020898 P = 23.51 - 23.51 \* 0.0020898 = 23.51 - 068 p = 23.44 mm Hg

## <u>Sol 17.</u>

 $\Delta T_b = k_b * m$ 

Element	%	Relative no. of atoms	Simplest ratio
С	42.86	42.86/12 = 3.57	3.57/1.19 = 3
н	2.40	2.40/1 = 2.40	2.40/1.19 = 2
Ν	16.67	16.67/14 = 1.19	1.19/1.19 = 1
0	38.07	38.07/16 = 2.38	2.38/1.19 = 2

: Empirical formula of the minor product is  $C_3H_2NO_2$  Molar empirical formula mass of the minor product = 3 \* 12 + 2 \* 1 \* 14 + 2 \* 16 = 84 g mol<sup>-2</sup>



Let M be the molar mass of the minor product. For 5.5 g of the minor product dissolved in 45 g benzene, the molality

(m) of the solution = 5.5 g/M/0.045 kg

Substituting this in the expression of elevation of boiling point,

 $\Delta T_{b} = k_{b}m \Rightarrow 1.84 \text{ K} = (2.53 \text{ K kg mol}^{-1}) (5.5 \text{ g/M}/0.045 \text{ kg})$ 

## $Or M = 168 g mol^{-1}$

No. of unit of empirical formula in molecular formula

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= 168 \text{g mol}^{-1}/84 \text{g F} = 2
```

Hence the molecular formula of the minor product is

2 (C<sub>3</sub>H<sub>2</sub>NO<sub>2</sub>), i.e., C<sub>6</sub>H<sub>4</sub>(NO<sub>2</sub>)<sub>2</sub>.

The product is m – dinitrobenzene

$$\left\langle \bigcirc_{NO_2}^{I} \right\rangle$$

## <u>Sol 18.</u>

 $\Delta T_f = i * k_f * m$ 

Weight of water = 500 \* 0.997 = 498.5 g (weight = volume \* denisty)

No. of moles of acetic acid

= Wt. of CH<sub>3</sub> COOH in g/Mol. wt. of CH<sub>3</sub> COOH =  $3 \times 10^{-3} \times 10^{3}/60 = 0.05$ 

Since 498.5 g of water has 0.05 moles of CH<sub>3</sub>COOH

1000 g of water has = 0.05 \*1000/498.5 = 0.1

Therefore molality of the solution = 0.1

Determination of van't Hoff factor, i

 $CH_3COOH \rightarrow CH_3COO^- + H^+$ 



No. of moles at start 1 0 0

No. of moles at equb. 1 – 0.23 0.23 0.23

Therefore vant Hoff factor

= No. of particles before dissociation/No. of particles after dissociation

= 1 - 0.23 + 0.23 + 0.23/1 = 1.23

Now we know that

 $\Delta T_f = i * k_f * m = 1.23 = 1.86 * 0.1 = 0.2228K$ 

#### **ALTERNATIVE SOLUTION:**

Density of water =  $0.997 \text{ g/cm}^3$ 

Weight of water (W) = 500 \* 0.997 = 498.5 g

Weight of acetic acid (w) =  $3.0 \times 10^{-3}$  kg = 33.0 kg

 $\Delta T_f = 1000 * K_f * w/m * W$ 

Given that  $K_f$  for water = 1.86 K kg<sup>-1</sup> mol<sup>-1</sup>

mol. wt. of  $CH_3COOH_{(m)} = 60$ 

 $(\Delta T_f)_{cal} = 1000 * 1.86 * 3.0/60 * 498.5 = 0.186$ 

(Because CH<sub>3</sub>COOH is an electrolyte and 23% dissociated)

 $CH_{3}COOH \rightleftharpoons CH_{3}COO^{-} + H^{+}$ At t = 0 1 mole 0 0

At equilibrium  $(1 - \alpha)$  mole  $\alpha$  gm-ion  $\alpha$  gm-ion

No. of particles after dissociation =  $1 - \alpha + \alpha + \alpha = 1 + \alpha$ 

 $\propto$  for CH<sub>3</sub>COOH = 23/100 = 0.23 (on 23% dissociation)

So, no. of particles after dissociation = 1 + 0.23 = 1.23

By van't Hoff factor



 $(\Delta T_f)_{obs}/(\Delta T_f)_{cal}$  = No. of particles after dissociation/No. of particles before dissociation

 $(\Delta T_f)_{obs}/(\Delta T_f)_{cal} = 1.23/1$ 

 $(\Delta T_f)_{obs} = 1.23 * 0.186 = 0.228 \text{ K}$ 

Hence depression in freezing point ( $\Delta T_f$ ) = 0.228K

## <u>Sol 19.</u>

 $\Delta T_b = K_b * M$ 

In first case,

 $\Delta T_b = K_b * m = K_b^* Wt.$ of solute/Mol. wt. of solute

 $Or 0.17 = 1.7 * 1.22/M * 1000 * 10^{-3}$ 

#### Or **M = 122**

Thus the benzoic acid exists as a monomer in acetone

(ii)  $\Delta T_b = K_b * Wt.$  of solute/Mol. wt. of solute

Or 0.13 = 2.6 \* 1.22/M' \* 100 \* 10<sup>-3</sup>

#### *M'* = 224

**NOTE** :Double the expected molecular weight of benzoic acid (244) in acetone solution indicates that benzoic acid exists as a dimer in acetone.

## <u>Sol 20.</u>

$$2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$$

Initial no. of moles 1 0

No. of moles at equilibrium  $1 - \propto \alpha/2$ 

Total number of moles at equilibrium =  $1 - \propto + \propto/2 = 1 - \propto/2$ 

 $\Delta T_f = iK_f^* \text{ (molality)}$ 

 $\Rightarrow$  7 = 14 \* 75.2/94 \* (1 -  $\propto$ /2) [weight of phenol = 75.2g mol. wt of phenol = 94]

∴ ∝ = 0.75

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So the percentage of phenol that dimerises = **75%**.

#### ALTERNATIVESOLUTION :

Phenol dimerises in the solvent (organic) as :

 $2C_6H_5OH \rightleftharpoons (C_6H_5OH)_2$ 

1 mol 0 mol (Initial)

 $1 - \propto \text{mol}$   $\propto/2 \text{ mol}$  (Equilibrium)

Van't Hoff factor,  $i = 1 - \alpha + \alpha/2 = 1 - \alpha/2$ 

Where  $\propto$  is the degree of dimerization.

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\Delta T_{f(obs)} = K_f * molality * i
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Or 7 = 14 \* m \*  $(1 - \alpha/2)$ 

**NOTE :** In the given problem, amount of the solvent used to dissolved 75.2 g of phenol is not mentioned. Hence molality m, can not be calculated and so also the value of  $\propto$ .

If amount of solution is presumed to be 1 kg (= 100g) then,

M = 75.2/94 = 0.8 (mol. mass of phenol = 9.4)

And 7 = 14 \* 75.2/94 \* (1 - ∝/2)

Or ∝ = 0.75 = 75%

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