VIVEKANANDA COLLEGE, THAKURPUKUR

NAAC Accredited Grade—A

STUDY MATERIAL

Subject : Physical Chemistry

Course Title : Applications of Thermodynamics II

Topic : Problems & solutions with Question-answers of Collgative Properties.

Paper : Physical Chemistry **– 3** **(CODE: CEMA-CC-4-9-TH)**

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Colligative Properties:

1.The vapour pressure of a solution containing 6.69g of $Ca(NO_3)_2$ in 100 g. of water is 746.9 mm of Hg at 100 ºC. Calculate α ($M_2 = 164$).

We know that $\Delta P / P^o = x_2$ = mole fraction of non -dissociated and non -associated solute. But for the ionic solute which easily dissociates, the above expression of relative lowering of vapour pressure can be represented as

$\Delta P / P^o = i.x_2$ where i = Vant'Hoff factor of the solute

Or, $(760 – 746.9) / 760 = i (w_2/M_2) / (w_1/M_1 + w_2/M_2)$

Or, $0.01724 = i (6.69/164) / (6.69/164 + 100/18) = i. (7.289 \times 10^{-3})$

Or, $i = 2.365$

Again, $\alpha = (i -1)/ (n-1) = (2.365 -1)/ (3-1) = 0.68257$

2.It has been found that minimum temperature recorded in a hill station is – 10 ºC. Calculate the amount of glycerin to be added to 40 dm3 water used in car-radiator, so that it does not freeze. $\Delta H_{fusion} = 6.01$ kJ. $mole^{-1}$ and mol. wt. of glycerin = 82 gm mol^{-1} and freezing. point of water = 0 ºC.

We know that $K_f = (RT_f^2 / 1000 \times L_f) = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times (273K)^2 / [1000 \times (6.01 \times 1000J)/18]$

$= 1.8558$ K/molal

By problem, $\Delta T_f = K_f \times m$

Or, 10 K = 1.8558 K/molal x m

Or, $m = 5.388 = 1000 \times w_2 / w_1 \times M_2$

or, $w_2 = (5.388 \text{ mole /g} \times w_1 \times M_2) / 1000 = 5.388 \text{ mole/g.} \times 40g \times 1000 \times 82g. \text{ mole}^{-1}/ 1000 = 17.674$ kg.

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3. Heavy water boils at 101.42 ºC and it's molal elevation constant (k'_b =10 % than that of pure water. (a) How does the latent heat of heavy water is related with the pure water? (b) What will be the vapour pressure of pure D_2O if its $L_v = 9960$ Cal / mole?

(a) We know that $k_b = R Tb^2 / 1000 \times Lv/M = R Tb^2 / 1000 \times l_v$.
·: k'_b for $D_2O = 1.1 \times k_b$
Or, $k'_b / k_b = 1.1 = (T'^2_b / l'_v) / T_b^2 / l_v$
Or, $l_v / l'_v = 1.1 \times (373K)^2 / (374.42K)^2 = 1.09167$
Or, **$l'_v / l_v = 0.916$**
From Clausius – Clapeyron equation, $\ln (P_1/P_2) = \Delta H'^o (T_2 – T_1) / R. (T_1.T_2)$
$= 9960 \times 1.42/1.987 \times 374.42 \times 373$
$= 0.0509$

Or, $(760/P_2) = (2.72)^{0.0509}$
Or, 760 mm $/P_2 = 1.05225$
Or, $P_2 = 722.433$ mm.

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4. A solution containing 4.13g. LiCl per litre freezes at -0.343 ºC. Calculate Vant' Hoff factor and the degree of dissociation? (M$_{\text{LiCl}}$ = 42.5)

$(\Delta T)_{\text{theo}}$ = - (k_f x m) = -(1.86 ºC/molal) x (1000 x 4.13/1000 x 42.5) = -(1.86 x 4.13/42.5) = - 0.18074

∴ Vant' Hoff factor (i) = ((ΔT)$_{\text{exp}}$ / (ΔT)$_{\text{theo}}$ = -0.343 ºC /- 0.18074 ºC = 0.343/0.18074 = 1.8976.

α = (i -1)/ (n-1) = (1.8976 – 1) / (2 – 1) **= 0.8976**

Therefore, degree of dissociation = 89.76 %

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5. The vapour pressure of water at its boiling point changes by 27.6 mm/degree. Calculate the molal elevation constant (k_b).

We know that k_b = RT_b^2 / 1000 x l_v =

Again, from Clapeyron equation dP /dT = L_v / T (V_g – V_l) = M x l_v / (T x V_g) = P x M x l_v / RT_b^2 /P

= P x M / 1000 x (RT_b^2 /1000 x l_v) = P x M / 1000 x k_b

By problem, L.H.S. = 27.6 mm / degree

∴ 27.6 mm / degree= (760 mm x 18 g mol^{-1}) / 1000g x k_b)

∴ k_b = 0.4956 degree / molal

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6. Heavy water (D_2O) boils at 102 ºC and its k_b value is 10 % higher than that of water. How does its latent heat per mole compare with that of water?

$(k_b)_{H2O}$ = R T_b^2 / 1000 x l_v

$(k'_b)_{D2O}$ = R T'^2_b / 1000 x l'_v

$(k_b)_{H2O}$ / $(k'_b)_{D2O}$ = (T_b^2 / T'^2_b) x (l'_v / l_v) = [(373$^{)2}$ / (375)^2] x (l'_v / l_v) = 1/1.1

Or, (l'_v / l_v) = (375)^2 / [(373)^2 x 1.1] = 0.9188 = 0.92

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7. The molality of dissolved gases in water at 0 ºC and 1 atm. is 1.29 x 10^{-3}. The decrease in volume during melting of ice is 0.907 c.c./g. The latent heat of fusion is 1436.3 cal /mole. The vapour pressure at triple point is 4.58 mm. Calculate the triple point temperature.

ΔT = k_f x m = 1.862 x 1.29 x 10^{-3} = 0.0024 ºC
By L_f = 1436.3 cal / mole = 1436.3 cal / 18 g = 79.794 cal /g.
ΔP / ΔT = l_f / T ΔV
Or, ΔT = ΔP x T ΔV / l_f = (4.58 – 760) /760 atm x 273 K x (- 0.907 cc/g)/ (82 cc atm/2) x 79.794 = 0.0752K
= 0.0752 ºC
The triple-point temperature = (0.0024 +0.0752) ºC = 0.0776 ºC

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8. A 0.01 molal $K_4[Fe (CN)_6]$ freezes at – 0.06 ºC. Calculate its degree of dissociation. (k_f)

$\Delta T = (k_f) \times (i \times m)$

Or, 0.06 ºC = (k_f) x (i x m) = i (1.86 degree/ molal) x 0.01 molal

Or**, i = 0.06 /1.86 x 0.01 = 3.226**

∴ α = (i-1)/(n-1) = (3.226 - 1) (5- 1) = 0.55645

∴ Degree of dissociation = 55.645 %

Question-Answers:

Q1. What is Vant' Hoff factor (i)?

Vant' Hoff factor (i) is defined as the ratio of colligative properties of a real solution to that of the ideal solution for the same concentration.

$\therefore i = \Pi_{real} / \Pi_{ideal}$

$= (\Delta T_b)_{real} / (\Delta T_b)_{ideal}$

$= (\Delta T_f)_{real} / (\Delta T_f)_{ideal}$

$\Delta P / P^o = (P^o - P') / P^o = i.x_2$

Q2. When Vant' Hoff factor (i) be integer and fractional?

Departure from the ideal can be understood by the value of 'i' which may be integer as well as fractional also. When a solute is completely dissociated into ν number of particles for a concentration 'C' molar solution, then in reality the actual concentration for such type of solutes becomes ν.C. Therefore, for complete dissociation ν becomes integer.

Again 'i' may be fractional for association of solute particles e.g. say complete dimerization i = 1/2 = 0.5 and also for partial dissociation of the solutes.

Q3. When there can be freezing point elevation?

It has been found that $\Delta T_f = K_f \cdot m$ when the solid phase of the solution contains only the pure solvent part but when the separating solid is a solid solution, the above equation can be written as $\Delta T_f = K_f (1 - k)\, m$; where value of k depends upon some restrictions.

(i) When the solid phase of the solution contains only the pure solvent part, then k = 0 and under this condition, $\mathbf{\Delta T_f = K_f \cdot m}$ equation is correctly followed.

(ii) When the solid phase is not pure, however, two conditions may be distinguished:

(a) If the solute is more soluble in the liquid solvent than in the solid, then k is a positive fraction and hence (1-k) is less than unity but positive. The effect will be, therefore, to give a freezing point depression less than that would be anticipated for separation of pure solid solvent.

(b) If, on the other hand, the solute is more soluble in the solid phase than in the liquid, then k>1 and hence, (1-k) is negative. Under this condition a freezing point elevation is observed rather than lowering. Such cases are found in the case of solutions of iodine or thiophene in benzene, where the solid crystallizing out contains solute dissolved in it in the form of solid solutions.

Q4. Why is the vapour pressure lowering in the solution of a non-volatile non-electrolyte solute?

Addition of non-volatile solute reduces the mole fraction of solvent in the liquid phase and correspondingly reduces the chemical potential of solvent in the liquid phase without affecting chemical potential of solvent in vapour phase (μ^o_{vap}). To maintain equilibrium, some solvent molecules revert back from vapour phase to become liquid phase and causing the decrease in vapour pressure of the solution.

If a liquid is kept in a vessel, evaporation takes place as it leads to the increases of the randomness due to presence of more random gas. When a solute is present in the liquid phase, then there is extra randomness in the liquid phase. Consequently, the tendency of escape of solvent molecules to the vapour phase decreases due to solute – solvent interactions. Naturally, in a closed container the vapour phase now contains lesser amount solvent molecules and hence, vapour pressure will decrease.

Q5. Why is it necessary that the solute dissolved in the liquid solvent be non-volatile?

When a solute is dissolved in a solvent, then the chemical potential of the solvent in the liquid phase will decrease in comparison to that in the gaseous phase if the solute is absent in the gaseous phase.

Q6. Addition of $HgI_2$to an aqueous solution of KI results in an increase in vapour pressure of solution. Why?

Addition of HgI_2 to an aqueous solution of KI results in the formation of K_2HgI_4 and number of particles present in the solution decreases.

$$2\,KI + HgI_2 \rightarrow K_2HgI_4 \rightarrow 2K^+ + [HgI_4]^{-2}$$

Q7. Explain why 0.1 (m) NaCl does not have a freezing point equal to (i) – 0.186 ºC (ii) – 0.372 ºC ?

In case of NaCl, freezing point depression is not equal to – 0.186 ºC because NaCl ionizes in solution. It does not equal to – 0.372 ºC because NaCl does not dissociate completely to give two ions per formula unit. Hence the above experimental facts are observed.