CHM202

Energetics and dynamics of chemical reactions

Solutions Assignment – V

Q.1 Methane gas is heated from 25 °C until the volume has doubled. The pressure is constant at 1 bar. The variation in molar heat capacity with temperature has been measured and the results of those experiments can be summarized by the equation-

$$C_P = a + bT$$

where a = 22.34 JK⁻¹mol⁻¹ and b = 48.1 × 10⁻³ JK⁻²mol⁻¹ . Calculate ΔH and ΔU per mol. Assume the system follows the ideal gas behaviour.

Sol.

The final volume is twice of the initial volume and pressure is constant,

so, $V_2 = 2V_1$ and $P_2 = P_1$

The initial temperature is $T_1 = 298\ K$, so the final temperature can be found (assuming ideal gas behavior)

$$\frac{T_2}{T_1} = \frac{P_2 V_2}{P_1 V_1} = 2$$

$$T_2 = 2T_1 = 596\ K$$

$$\Delta T = 298\ K$$

$$\Delta H = \left(\frac{\partial H}{\partial T}\right)_P dT = \int_{T_1}^{T_2} C_P(T)dT = \int_{T_1}^{T_2}(a + bT)dT$$

$$= \left[aT + \frac{b}{2}T^2\right]_{T_1}^{T_2}$$

$$= 6.657\ kJ\ mol^{-1} + 6.407\ kJ\ mol^{-1}$$

$$= 13.06\ kJ\ mol^{-1}$$

The change in internal energy

$$\Delta U = \Delta H - p\Delta V = \Delta H - p\Delta T$$

$$= (13.06 - 2.48)kJ\ mol^{-1} = 10.59kJ\ mol^{-1}$$

Q.2 Compute change in Gibbs free energy for the process H_2O (l, -10 °C) = H_2O (s, -10 °C). Specific heat of water and ice over the temperature range is 18 and 9 Cal.mol⁻¹K⁻¹, respectively and $\Delta H_{fus_{273}} = 1440$ Cal. mol⁻¹. Predict whether the change is spontaneous or not.

Sol. For the given transformation, ΔH & ΔS are calculated separately. From these values, ΔG can be calculated as follow:

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

$$\Delta H_{273} - \Delta H_{263} = \int_{273}^{263}\left(C_{P_S} - C_{P_l}\right)dT = (9 - 18)\ Cal.mol^{-1}(263 - 273)$$

$$= 90\ Cal.mol^{-1}$$

$$\Delta H_{263} = \Delta H_{273} - 90\ Cal.mol^{-1} = 1350\ Cal.mol^{-1}$$

To calculate ΔS, the following reversible path is considered:

$$H_2O(l, -10°C) \xrightarrow{\Delta S_1} H_2O(l, 0°C) \overset{\Delta S_2}{\rightleftharpoons} H_2O(s, 0°C) \xrightarrow{\Delta S_3} H_2O(s, -10°C)$$
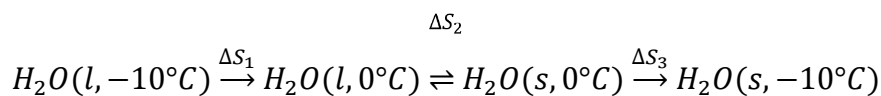
$$\Delta S_1 = nC_{P_l}\ln\frac{T_f}{T_i} = 18 \ Cal.K^{-1}\ln\frac{273}{263} = 0.672 \ Cal.K^{-1}$$

$$\Delta S_2 = \frac{\Delta H}{T} = \frac{1440}{273} \ Cal.K^{-1} = 5.275 \ Cal.K^{-1}$$

$$\Delta S_3 = 9 \times \ln\frac{273}{263} \ Cal.K^{-1} = 0.336 \ Cal.K^{-1}$$

So $\Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 = 6.283 \ Cal.K^{-1}$

$\Delta G = \Delta H_{263} - T\Delta S = 1350 - 263 \times 6.283 \ Cal = -302.43 \ Cal$

As ΔG is negative, the process is a spontaneous process.

Q.3 Calculate entropy change per litre of the solution when pure N_2, H_2, NH_3 gases are mixed to form a solution having the final composition 15% N_2, 55% H_2 and 30% NH_3 (all at STP).

Sol.:

This is a case of free mixing and we know that for free mixing

$\Delta S = -\sum x_i R \ln x_i$ per mole. Here x_i = Mole-fraction.

In the given problem,

$X_{N_2} = 0.15$; $X_{H_2} = 0.55$ and $X_{NH_3} = 0.30$.

So, $\Delta S = -0.15 \times 1.987\ln(0.15) - 0.55 \times 1.987\ln(0.55)$

$\qquad\qquad\qquad\qquad -0.3 \times 1.987\ln(0.30)$

$\qquad = (0.565 + 0.653 + 0.718) \ Cal/mole$

$\qquad = 1.936 \ Cal/mole$

As they are STP, 1 mole = 22.4 litre

So $\Delta S/litre = 0.086 \ Cal \ deg^{-1} litre^{-1}$.

Q.4 Establish the condition for spontaneous vaporization of water, given $\Delta H = 9590$ Cal.mol^{-1} and $\Delta S = 26$ e.u. for the process.

Sol.: For spontaneous vaporization, $\Delta G < 0$

$$\text{or } \Delta H - T\Delta S < 0$$

$$\Delta H < T\Delta S$$

$$T\Delta S > \Delta H$$

$$\Delta S = 26 \ e.u. = 26 \ Cal.mol^{-1}K^{-1}$$
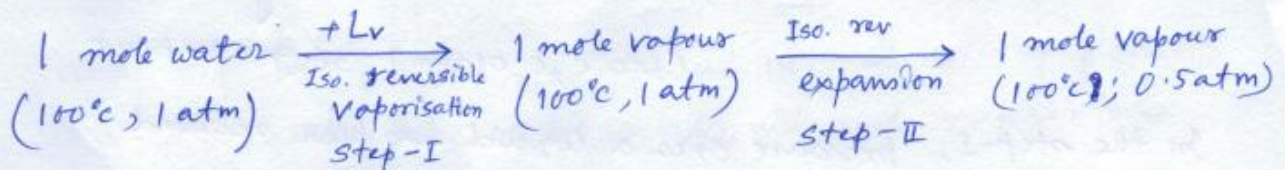
$$T > \frac{\Delta H}{\Delta S} = \frac{9590}{26} \, °K$$
$$T > 368.85 \, °K$$

So, here for spontaneous vaporization T should be greater than 368.85 °K.

Q.5 Describe a reversible process by which one mole of water at 100 °C can be converted to vapour at 0.5 atm and 100 °C. Calculate ΔH and ΔG for the process. How far these quantities would be affected if the operation were performed irreversibly? Assume water vapour behave ideally and latent heat of vaporization of water = 540 Cal.gm⁻¹.

Sol.:

The given change can be brought about reversibly in two steps. In the first stage, water at 100°C and 1 atm is supplied its latent heat so that it is converted to its vapour at 100°C and 1 atm and then it is isothermally reversibly expanded to 0.5 atm i.e.

1 mole water $\xrightarrow[\substack{\text{Iso. reversible} \\ \text{Vaporisation} \\ \text{step-I}}]{+ Lv}$ 1 mole vapour $\xrightarrow[\substack{\text{expansion} \\ \text{step-II}}]{\text{Iso. rev}}$ 1 mole vapour

(100°C, 1 atm)   (100°C, 1 atm)   (100°C; 0.5 atm)

In step-I:

$$\Delta H_1 = 18 \times 540 = 9720 \, Cal$$

and $\Delta G_1 = 0$; as it's reversible equilibrium between liquid and vapour.

In step-II:

$\Delta H_2 = 0$ [Isothermal expansion]

and $\Delta G_2 = RT \ln \frac{P_2}{P_1} = 1.987 \times 373 \ln \frac{0.5}{1} = -513.73 \, Cal.$

So, total $\Delta H = 9720 + 0 = 9720 \, cal.$
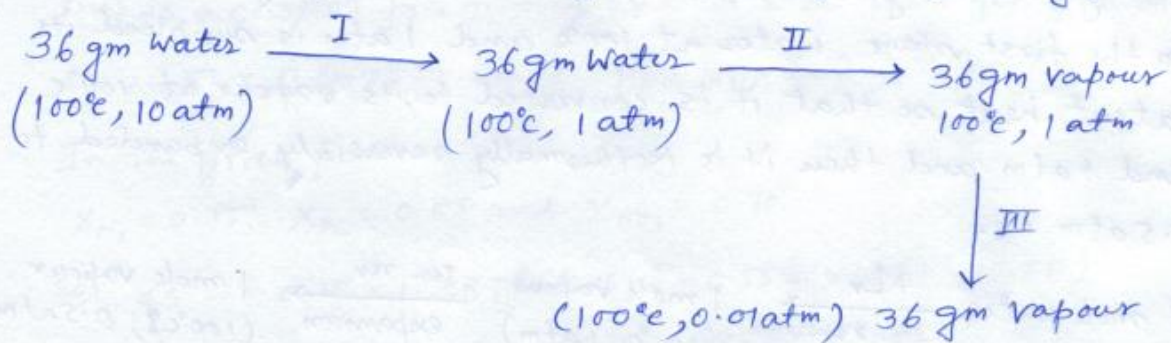
and total $\Delta G = 0 - 513.73 = -513.73 \, Cal.$

As H and G are state functions, their values will remain same in irreversible path.

Q.6 Calculate the change in Gibbs potential when 36 gm water initially at 100 °C and 10 atm pressure are converted to vapour at 100 °C and 0.01 atm pressure. Assume water vapor behave ideally.

Sol.:

The given change can be brought about by the following path –

36 gm water $\xrightarrow{\text{I}}$ 36 gm water $\xrightarrow{\text{II}}$ 36 gm vapour
(100°C, 10 atm)   (100°C, 1 atm)   100°C, 1 atm

$\left.\right\downarrow \text{III}$

(100°C, 0·01 atm) 36 gm vapour

In the step-I, pressure over a liquid has been released isothermally, for such change

$$\Delta G_1 = V(P_2 - P_1)$$

Vol. of 36 gm water = 0·036 litre. So,

$$\Delta G_1 = 0·036 (1-10)\text{ litre-atm} = -7·84\text{ Cal.} \quad [1\text{ litre atm} = 24·2\text{ cal}$$

Second step is vaporisation of a liquid at its normal boiling point; during such change, there is a reversible equilibrium, so

$$\Delta G_2 = 0$$

Third step is isothermal expansion of an ideal gas, where

$$\Delta G_3 = nRT \ln \frac{P_2}{P_1}, \quad \text{Here } n = \frac{36}{18} = 2$$

So, $\Delta G_3 = 2 \times 1·987 \times 373 \ln \frac{0·01}{1}$

$$= -6826·25\text{ cal}$$

So, total $\Delta G = (-7·84 + 0 - 6826·25)\text{ cal}$

$$= -6834·09\text{ Cal.}$$

Q.7 One mole of benzene at the normal boiling point of 352.2 K vaporizes into a gaseous state at a pressure of 0.1 atm. Calculate ΔS and ΔG. Given the enthalpy of vaporization is 7364 Cal.mol^{-1}.

Sol: Let first one mole of Benzene be vaporized at its normal boiling point i.e. 352.2 K and 1 atm and then the vapor is isothermally expanded to 0.1 atm.

Then in the first step

$$\Delta S_1 = \frac{\Delta H}{T_b} = \frac{7364}{352.2} \, Cal. K^{-1} = 20.91 \, Cal. K^{-1}$$

And $\Delta G_1 = 0$ as vaporization at normal boiling point is a reversible process where liquid and vapor are in equilibrium.

In the second step,

$$\Delta S_2 = R \ln \frac{P_1}{P_2} = 1.987 \ln \frac{1}{0.1} = 4.58 \, Cal. K^{-1}$$

and

$$\Delta G_2 = RT \ln \frac{P_2}{P_1} = 1.987 \times 352.2 \times \ln \frac{0.1}{1} Cal = -1615.97 \, Cal$$

So $\Delta S = \Delta S_1 + \Delta S_2 = 20.91 + 4.58 \, Cal. K^{-1} = 25.49 \, Cal. K^{-1}$
and $\Delta G = \Delta G_1 + \Delta G_2 = -1615.97 \, Cal$

Q.8 Determine the change in entropy when 1 kg ice at 0 °C and 1 atm is heated to 373 °C and 2 atm pressure. Given $\Delta H_{fus_{273}} = 80$ Cal. g^{-1}; $\Delta H_{Vap_{373}} = 540$ Cal. g^{-1}; $C_{P_L} = 18 \, Cal. K^{-1}mol^{-1}$ and $C_{P_V} = 8 \, Cal. K^{-1}mol^{-1}$.

Sol.:

The change of state can be carried out reversibly as follows,

$$\text{ice} (0°c, 1 \, atm) \xrightarrow{\Delta S_1} \text{water} (0°c, 1 \, atm) \xrightarrow{\Delta S_2} \text{water} (100°c, 1 \, atm)$$

$$\text{vapour} (273°c, 2 \, atm) \xleftarrow{\Delta S_4} \text{vapour} (100°c, 1 \, atm) \xleftarrow{\Delta S_3}$$

$$\Delta S_1 = \frac{\Delta H_f}{T} = \frac{1000 gm \times 80 \, cal \, gm^{-1}}{273 K} = 293.04 \, cal K^{-1}$$

$$\Delta S_2 = n \bar{C_p} \ln \frac{T_2}{T_1}$$

$$= \left(\frac{1000}{18} mol \right) (18 \, cal \, K^{-1} mol^{-1}) \ln \frac{373}{273} = 312.11 \, cal K^{-1}.$$

$$\Delta S_3 = \frac{\Delta H_{vap}}{T} = \frac{1000 \times 540}{373} \, cal K^{-1} = 1447.72 \, cal K^{-1}.$$

$$\Delta S_4 = n \bar{C_p} \ln \frac{T_2}{T_1} - nR \ln \frac{P_2}{P_1}$$

$$= \frac{1000}{18} mol \left[8 \, cal K^{-1} \ln \frac{546}{373} - 1.987 \, cal K^{-1} mol^{-1} \ln \frac{2}{1} \right]$$

$$= 92.84 \, cal K^{-1}.$$

$$\therefore \text{Total } \Delta S = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

$$= (293.04 + 312.11 + 1447.72 + 92.84) \, cal K^{-1}$$

$$= 2145.71 \, cal K^{-1}.$$

Q.9 One mole of O_2 ($C_V = \frac{5}{2}R$) initially at 546K and 10 atm expands adiabatically against a constant pressure of 1 atm until the volume becomes doubled. Calculate ΔU, ΔH and ΔS for the process.

Sol.:

The process is an adiabatic irreversible process. So, T_f is calculated by using the expression,

$$P_{opp}(V_2 - V_1) = -C_V(T_f - T_i)$$

or $P_{opp} V_1 = -\frac{5}{2}R(T_f - 546)$ $[\because V_2 = 2V_1]$

or $1\,atm\,\dfrac{RT_i}{P_i} = -\frac{5}{2}R(T_f - 546)$

or $\dfrac{546\,K}{10} = -\frac{5}{2}(T_f - 546)$

$\therefore$ $T_f = 524.16\,K$

$\Delta U = n\bar{C_V}(T_f - T_i)$

$= (1\,mol)(\frac{5}{2} \times 8.314\,J\,K^{-1}mol^{-1})(524.16 - 546)K$

$= -453.94\,J$

$\Delta H = n\bar{C_p}(T_f - T_i) = \frac{7}{2} \times 8.314(524.16 - 546)J$

$= -635.52\,J$

$\Delta S = n\bar{C_V}\ln\dfrac{T_f}{T_i} + nR\ln\dfrac{V_2}{V_1}$

$= (\frac{5}{2} \times 8.314)\ln\dfrac{524.16}{546} + (\frac{5}{2} \times 8.314)\ln 2\,J\,K^{-1}$

$= 4.914\,J\,K^{-1}$

$= \Delta S_{sur} = 0$ as the process is adiabatic.

$\therefore \Delta S_{universe} = 4.914\,J\,K^{-1}$.

This proves that in an irreversible process $\Delta S_{universe}$ is positive.

Q.10 One mole of an ideal gas ($C_V = \frac{5}{2}R$) is taken reversibly from 400K, 5 atm to 600K, 2 atm. Calculate ΔU, ΔH and ΔG for the process. Given: $\bar{S}^0_{298} = 4J^{-1}K^{-1}mol$).

Sol.:

ΔH is independent of the path of transformation. So, to calculate ΔH let us consider the transformation as follows.

$$gas\,(400K, 5\,atm) \xrightarrow{\Delta H_1} gas\,(600K, 5\,atm) \xrightarrow{\Delta H_2} gas\,(600K, 2\,atm)$$
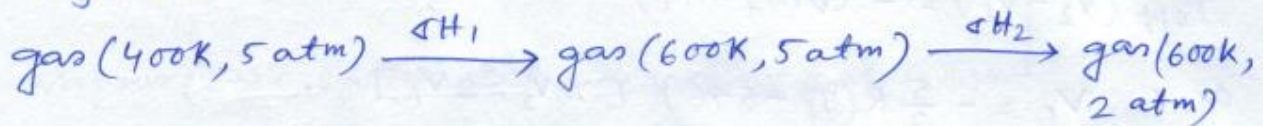
$$\Delta H_1 = nC_p\,(T_2 - T_1)$$

$$= \left(\frac{7}{2} \times 8\cdot314\; J\,\bar{K}^{-1}\,mol^{-1}\right)(600 - 400)\,K$$

$$= 5819\cdot8\; J$$

$\Delta H_2 = 0$ as for an ideal gas at constant temperature $\Delta H = 0$.

$$\Delta H = \Delta H_1 + \Delta H_2$$

$$= 5819\cdot8 J + 0 = 5819\cdot8\; J$$

$$\Delta S = n\bar{C}_p\,\ln\frac{T_2}{T_1} - nR\,\ln\frac{P_2}{P_1}$$

$$= \left\{1\left(\frac{7}{2} \times 8\cdot314\; J\,\bar{K}^{-1}\right)\ln\frac{600}{400} - 1 \times 8\cdot314\; J\bar{K}^{-1}\ln\frac{2}{5}\right\}$$

$$= \left(\frac{7}{2} \times 8\cdot314\,\ln\frac{600}{400} - 8\cdot314\,\ln\frac{2}{5}\right)J\bar{K}^{-1} = 19\cdot42\; J\bar{K}^{-1}$$

$$= \bar{S}_2 - \bar{S}_1$$

Again, for the transformation of state from 298K, 1 atm to 400K, 5 atm.

$$\Delta S = \left(\frac{7}{2} \times 8\cdot314\,\ln\frac{400}{298} - 8\cdot314\,\ln\frac{5}{1}\right)J\bar{K}^{-1} = -4\cdot81\; J\bar{K}^{-1} = \bar{S}_1 - \bar{S}_{298}^{\circ}$$

$$\therefore \bar{S}_1 = (-4\cdot81 + 4)\,J\bar{K}^{-1} = -0\cdot81\; J\bar{K}^{-1}$$

$$\bar{S}_2 = 19\cdot42 + \bar{S}_1 = (19\cdot42 - 0\cdot81)\,J\bar{K}^{-1} = 18\cdot61\; J\bar{K}^{-1}$$

Now, $\Delta G = \Delta H - \Delta(TS) = \Delta H - (T_2 S_2 - T_1 S_1)$

$$= 5819\cdot8\;J - (600 \times 18\cdot61 + 400 \times 0\cdot81)\,J$$

$$= -5670\cdot2\; J.$$

CHM202

Energetics and dynamics of chemical reactions

Solutions Assignment –VI

Q.1 When a certain liquid freezes at -3.65 °C its density changes from 0.789 g cm^{-3} to 0.801 g cm^{-3}. Its enthalpy of fusion is 8.68 kJ mol^{-1}. Calculate the freezing point of the liquid at 100 MPa.

Sol. The change in molar entropy of the system will be

$$\Delta_{fus}S = \frac{\Delta_{fus}H}{T_f}$$

Fusion is accompanied by a molar enthalpy change $\Delta_{fus}H$ occurs at a temperature T. So, the Clapeyron equation becomes

$$\frac{\Delta P}{\Delta T} = \frac{\Delta_{fus}S}{\Delta_{fus}V}$$

$$\Delta T = \frac{\Delta_{fus}V}{\Delta_{fus}S} \times \Delta P = \frac{T_f \Delta_{fus}V}{\Delta_{fus}H} \times \Delta P$$

$$= \frac{T_f \Delta P}{\Delta_{fus}H} \times M \times \Delta\left(\frac{1}{\rho}\right)$$

Here $T_f = -3.65 + 273.15 = 269.50K$

$$\Delta T = \left(\frac{269.50K \times 100\ MPa}{8.68\ kJ\ mol^{-1}}\right) \times M \times \left(\frac{1}{0.789\ \text{g cm}^{-3}} - \frac{1}{0.801\ \text{g cm}^{-3}}\right)$$

$$= (3.1048 \times 10^6 KPa\ J^{-1}mol) \times M \times (0.018987g^{-1}\ cm^3) \times \left(\frac{m^3}{10^6\ cm^3}\right)$$

$$= (0.058951\ KPa\ J^{-1}m^3g^{-1}mol) \times M$$

$$= (0.058951\ Kg^{-1}mol) \times M$$

(Since 1 Pa = 1 Kg m^{-1} s^{-2} and 1 J = 1 Kg m^2 s^{-2})

Since the initial density is given as 0.789 g cm^{-3}, so M = 46.07g mol^{-1}.

$$\Delta T = (0.058951\ Kg^{-1}mol) \times 46.07\ \text{g mol}^{-1} = 2.716\ K$$

So the freezing point of the liquid 100 MPa is

$$T_f = 269.50\ K + 2.716\ K = 272.22\ K$$

Q.2 The partial molar volumes of two liquids A and B in a mixture in which the mole fraction of A is 0.3713 are 188.2 cm^3 mol^{-1} and 176.14 cm^3 mol^{-1}, respectively. The molar masses of A and B are 241.1 gmol^{-1} and 198.2 gmol^{-1}. What is the volume of a solution of mass 1.000 kg?

Sol. Total volume $V = n_A V_A + n_B V_B = n(x_A V_A + x_B V_B)$

Total Mass $m = n_A M_A + n_B M_B = n(x_A M_A + (1 - x_A)M_B)$

Where $n = n_A + n_B$

$$n = \frac{m}{x_A M_A + (1 - x_A)M_B}$$

$$= \frac{1\ kg(10^3 g/kg)}{0.3713 \times (241.1\ gmol^{-1}) + (1 - 0.3713) \times 198.2\ gmol^{-1}} = \frac{10^3\ g}{214.1287\ gmol^{-1}}$$
$$= 4.67\ mol$$

$$V = n(x_A V_A + x_B V_B)$$
$$= 4.67\ mol \times [(0.3713 \times 188.2\ \text{cm}^3\ \text{mol}^{-1}) + (1 - 0.3713) \times 176.14\ \text{cm}^3\ \text{mol}^{-1}]$$
$$= 4.67 \times 180.6178\ \text{cm}^3 = 843.49\ \text{cm}^3$$

Q.3 Consider a container of volume 250 cm³ that is divided into two compartments of equal size. In the left compartment there is argon at 100 kPa and 0 °C while in the right compartment there is neon at the same temperature and pressure. Determine the entropy and Gibbs energy of mixing when the partition is removed. Assume that the gases are perfect.

Sol. The Gibbs energy of mixing

$$\Delta_{mix}G = nRT(x_A\ ln x_A + x_B\ ln x_B)$$

Here $n_{Ar} = n_{Ne}$; $x_{Ar} = x_{Ne} = 0.5$

$$\text{So, } n = n_{Ar} + n_{Ne} = \frac{pV}{RT}$$

$$\Delta_{mix}G = pV\left(\frac{1}{2} ln\frac{1}{2} + \frac{1}{2} ln\frac{1}{2}\right) = -pV\ ln2$$

$$= -(100 \times 10^3 \text{Pa}) \times 250 cm^3 \times \left(\frac{m^3}{10^6\ \text{cm}^3}\right) ln2 = 25\ \text{Pa}\ m^3 \times 0.69314$$

$$= -17.329\ Pa\ m^3 = -17.329\ \text{J}$$

The entropy of mixing

$$\Delta_{mix}S = \frac{-\Delta_{mix}G}{T} = \frac{17.329\ \text{J}}{273\ K} = 0.06348\ JK^{-1} = 6.348 \times 10^{-2}\ JK^{-1}$$

Q.4 At 373.6 K and 372.6 K , the vapor pressure of water is 1.018 and 0.982 atm, respectively. Evaluate the molar entropy of vaporization and ΔV, the change of volume per mole when liquid water vaporises at 373 K. Assume the vapor behaves ideally.

Sol.:

From Clausius- Clapeyron equation

$$ln \frac{P_2}{P_1} = \frac{L_v}{R} \frac{T_2 - T_1}{T_1 T_2}$$

$$T_2 - T_1 = (373 \cdot 6 - 372 \cdot 6)$$
$$= 1\ K$$

$$\text{So, } ln \frac{1 \cdot 018}{0 \cdot 982} = \frac{L_v}{1 \cdot 987} \times \frac{1}{(373 \cdot 6 \times 372 \cdot 6)}$$

or $L_v = 9958 \cdot 57\ Cal$

So, molar entropy of vaporisation $= \frac{L_v}{T_b}$

$$= \frac{9958 \cdot 57}{373 \cdot 6} = 26 \cdot 65\ Cal\ K^{-1}$$

Also, $\dfrac{dP}{dT} = \dfrac{L_v}{T(V_g - V_L)}$

$(V_g - V_L) = \dfrac{L_v}{T(dP/dT)}$

Here $L_v = 9958.57\, Cal \equiv 411.511\, litre\text{-}atm$ [∵ 1 litre atm ≡ 24.2 Cal]

$\dfrac{dP}{dT} = \dfrac{\Delta P}{\Delta T} = \dfrac{1.018 - 0.982}{373.6 - 372.6} = 0.036\, atm\, K^{-1}$

So, $V_g - V_L = \dfrac{411.511}{373.6 \times 0.036} = 30.5965\, litre\, mole^{-1}$.

Q.5 Heavy water boils at 101.42 °C and its molal elevation constant (K_b) is 10% higher than that of pure water. (a) How does its latent heat compare with that of pure water?, (b) What will be vapor pressure of pure D_2O if its $L_v = 9960\,Cal.\,mol^{-1}$?

Sol.:

We know from Gibbs Helmholtz equation;

$$x_B = \dfrac{\Delta_{vap} H}{R}\left(\dfrac{1}{T^*} - \dfrac{1}{T}\right)$$

Now amount of solute present is so small we assume that

$T \approx T^*$

∴ $\dfrac{1}{T^*} - \dfrac{1}{T} = \dfrac{T - T^*}{TT^*} = \dfrac{T - T^*}{T^{*2}} = \dfrac{\Delta T_b}{T^{*2}}$

∴ $x_B = \dfrac{\Delta_{vap} H}{R T^{*2}} \cdot \Delta T_b$

$= \dfrac{\Delta T_b}{K_b}$ $K_b = \dfrac{R T^{*2}}{\Delta_{vap} H}$ = elevation of boiling point constant

∴ $\Delta T_b = K_b \cdot x_B$

x_B is mole fraction of solute α molality (C_m)

∴ $\boxed{\Delta T_b = K_b \cdot C_m}$

$$K_b = \frac{RT^{*2}}{\Delta_{vap}H}$$

$\Delta_{vap}H$ = enthalpy of vaporisation of solvent

$= 1000\ gm$ solvent $\times l_v$ (latent heat of solvent per gm)

$$\boxed{K_b = \frac{RT^{*2}}{1000\ l_v}}$$

$= 1000\ l_v$

Elevation of boiling point : $\Delta T_b = K_b \cdot C_m$

K_b = Ebullioscopic (molal elevation of b. pt.) const.

$= \frac{RT_b^2}{1000\ l_v}$ T_b = boiling point l_v = latent heat of vaporisation per gm

Similarly,

Depression of freezing point $\Delta T_f = K_f \cdot C_m$

$K_f = \frac{RT_f^2}{1000\ l_f}$ T_f = freezing point l_f = latent heat of fusion /gm

K_f = Cryoscopic (molal depression of fr. point) const.

$$\frac{K_{b1}}{K_{b2}} = \frac{T_{b1}^2}{T_{b2}^2} \cdot \frac{l_{v2}}{l_{v1}}$$ For D_2O $K_{bD_2O} = 1.1\ K_{bH_2O}$

So, $\frac{1}{1.1} = \frac{(373)^2}{(374.42)^2} \cdot \frac{l_{v2}}{l_{v1}}$

or $\frac{l_{v2}}{l_{v1}} = 0.9160$

From Clausius Clapeyron equⁿ

$$\ln \frac{760}{P_1} = \frac{9960}{1.987} \times \frac{374.42 - 373}{373 \times 374.42}$$

or $P_1 = 722.23\ mm$

So, vapour pressure of D_2O at $100°c$ is $722.23\ mm$.

Q.6 An aqueous solution contains 5% by weight of urea and 10% by weight of glucose. What will be its freezing point? [Given: $K_f = 1.86\,°C\ g\ mol^{-1}$].

Sol.:

Moles of urea in 1000 gm water $= \dfrac{50}{60} = 0.833$

[Mol. wt. of urea $= 60$]

Moles of glucose in 1000 gm water $= \dfrac{100}{180} = 0.555$

[Mol. wt. of glucose $= 180$]

$\dfrac{\text{Total moles of solute}}{1000\ gm\ solvent} = (0.833 + 0.555) = 1.388$

This is molal conc. $= C_m = 1.388$

So, $\Delta T_f = K_f \cdot C_m$

or $\Delta T_f = 1.86 \times 1.388 = 2.58\,°C$

So, freezing point of solution will be $-2.58\,°C$.

Q.7 Blood is said to be isotonic with 0.85% NaCl solution at 40 °C. Assuming complete dissociation of *NaCl*; calculate total concentration of various solutes in blood. What is its approximate freezing point? [Given: Cryoscopic constant $K_f = 1.86\,°C\ g\ mol^{-1}$].

Sol.:

As NaCl completely dissociates into two ions its osmotic pressure

$\pi = 2 \times \dfrac{g}{v} \dfrac{RT}{M}$

Here $g = 0.85 g$; $v = 100\ cc. = 0.1\ litre$ $M_{NaCl} = 58.5$

$T = 313\ K$

So, $\pi = 2 \times \dfrac{0.85}{0.1} \times \dfrac{0.082 \times 313}{58.5} = 7.46\ atm$

As it is isotonic with blood at 40°c; blood also has 7.46 atm osmotic pressure. So, if C(M) is conc. of dissolved solutes then

$$c = \frac{\pi}{RT}$$

$$\text{or } c = \frac{7.46}{0.082 \times 313} = 0.29 \, (M)$$

For aqueous solution molar conc. can be approximated taken as molal conc.

So, molal conc. $= 0.29 \, (Cm)$

Now, $\Delta T_f = K_f \cdot Cm = 1.86 \times 0.29 = 0.54\,°C$

So, freezing point of blood will be $- 0.54\,°C$.

Q.8 A mixture which contains 0.550 gm of camphor and 0.045 gm of an organic solute (containing 93.46% *C* and 0.6.54% *H*) freezes at 157 ºC. Find out the molecular formula of the organic compound. [Given freezing point and Cryoscopic constant for camphor are 178.4 and 37.7 ºC g mol⁻¹, respectively].

Sol.:

We know $\Delta T_f = K_f \cdot Cm$ K_f = Cryscopic (Molal depression of free zing point) constant $= 37.7\,°C\,g \cdot mole^{-1}$

$= 37.7 \times \text{1000} \,°C \, gm\,mole^{-1}$.

Cm = Molal conc. $= \dfrac{a \times 1000}{b \times M}$

a gm solute (Mol. wt. M) has been dissolved in b gm solvent.

$a = 0.045 \, gm$ $b = 0.55 \, gm$ of Camphor

$\Delta T_f = (178.4 - 157)\,°c = 21.4\,°c$

$\therefore \Delta T_f = K_f \cdot \dfrac{a \times 1000}{b \times M}$

$21.4 = \dfrac{37.7 \times 1000 \times 0.045 \times 10^{3}}{0.55 \times M}$

or $M = \dfrac{1.696 \times 10^{3}}{11.77} = 144.14$

Now % of C $= 93.46$ and % of H $= 6.54$

$\therefore$ Atomic ratio of C : H is $\dfrac{93.46}{12} : \dfrac{6.54}{1}$

$= 7.78 : 6.54$

So, empirical formula is $\left(C_{7.78} H_{6.54}\right)_n = 144 \cdot 14$

$\therefore \quad 100n = 144 \cdot 14 \quad$ or $\quad n = 1 \cdot 44$

So, no. of C atoms per molecule $= 7 \cdot 78 \times 1 \cdot 44 \approx 11 \cdot 20 \approx 11$

no. of H atoms " $= 6 \cdot 54 \times 1 \cdot 44 = 9 \cdot 41 \approx 9$

Hence the formula is $= C_{11} H_9$ (1-methylnaphthalene)

Q.9 If boiling point of an aqueous solution is 100.1 °C, what is its freezing point? Given l_f and l_v for water are 80 Cal.gm^{-1} and 540 Cal.gm^{-1}, respectively.

Sol.:

Elevation of boiling point $\Delta T_b = K_b \cdot C_m$ and for the same

sol^n depression of freezing point $\Delta T_f = K_f \cdot C_m$. So,

$$\frac{\Delta T_b}{\Delta T_f} = \frac{K_b}{K_f} = \frac{R T_b^2}{1000 \, l_v} \cdot \frac{1000 \, l_f}{R T_f^2}$$

or $\quad \dfrac{\Delta T_b}{\Delta T_f} = \dfrac{T_b^2}{T_f^2} \cdot \dfrac{l_f}{l_v}$

In the given case $\Delta T_b = 0 \cdot 1 \,°c; \; T_b = 373 \, K, \; T_f = 273 \, K$

$l_f = 80 \, cal \, gm^{-1}, \quad l_v = 540 \, cal \, gm^{-1}$.

So, $\dfrac{0 \cdot 1}{\Delta T_f} = \left(\dfrac{373}{273}\right)^2 \dfrac{80}{540} \quad$ or $\quad \Delta T_f = 0 \cdot 36 \,°c$

So, freezing point is $-0 \cdot 36 \,°c$.

Q.10 Chemical potential of O_2 at 300 K is supposed to be 10 kCal. mol^{-1} at 1 atm. A 1:4 (mole ratio) mixture of O_2 and N_2 is prepared at 1 atm and 300 K. The pressure of the mixture is increased to 5 atm. Calculate the chemical potential of oxygen in the mixture and in the pure state at 5 atm and 300 K.

Sol.:

For pure oxygen, $d\mu_i^* = \bar{V}_i \, dP$

$$\int_{\mu_i^*(1atm)}^{\mu_i^*(5atm)} d\mu_i^* = \int_{1atm}^{5atm} \frac{RT}{P} dP = RT \ln \frac{5}{1}$$

$\therefore \mu_i^*(5\text{atm}) - \mu_i^*(1\text{atm}) = RT\ln 5$

chemical potential of O_2 in the pure state at 5 atm, 300K is

$\mu_{O_2}^*(5\text{atm}) = \mu_{O_2}^*(1\text{atm}) + RT\ln 5$

$\Rightarrow 10\,K\,cal\,mol^{-1} + (1.987\,cal\,K^{-1}\,mol^{-1})(300K)\ln 5$

$= 10.96\,K^{-1}\,cal^{-1}\,mol^{-1}$

In the mixture,

$\mu_{O_2}(5\text{atm}) = \mu_{O_2}^*(5\text{atm}) + RT\ln x_{O_2}$

$= 10.96\,Kcal\,mol^{-1} + (1.987\,cal\,K^{-1}\,mol^{-1})(300K)\ln\frac{1}{5}$

$= 10\,Kcal\,mol^{-1}.$

Q.11 Calculate the change in free energy when 2 moles of H_2, 3 moles of O_2 and 5 moles of N_2 are mixed at 1 atm, 300 K. Also determine ΔG when the pressure of the mixture is increased to 5 atm. Calculate ΔS_{mix} and ΔH_{mix}.

Sol.:

1.

Here $x_{H_2} = \frac{1}{5}$, $x_{O_2} = \frac{3}{10}$, $x_{N_2} = \frac{1}{2}$

$\Delta G_{mixture} = RT\sum n_i \ln x_i$

$= (1.987\,cal\,K^{-1}\,mol^{-1})(300K)\left[2\ln\frac{1}{5} + 3\ln\frac{3}{10} + 5\ln\frac{1}{2}\right]\,mole$

$= -6.138\,Kcal$

$\Delta G_{mixture}$ is independent of pressure.

$\Delta S_{mix} = -\left[\frac{\partial(\Delta G_{mix})}{\partial T}\right] = -R\sum n_i \ln x_i = 20.46\,cal\,K^{-1}$

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

$$= 6.138 \, Kcal - \frac{20.46 \times 300}{1000} \, Kcal$$

$$= 0.$$