Assignment - 6 Solutions

1. Van der Waals Equation:

$$\left(P + \frac{a}{V_m^2}\right)(V_m - b) = RT \quad —(1)$$

Case 1: attractive forces between the particles are neglected:
w.k.t Van der Waals coefficient a represents the attraction between the molecules, which can be taken as zero here.

So, Van der waal's equation becomes,

$$P = \frac{RT}{V_m - b} \quad —(2)$$

w.k.t $\ln\phi = \int_0^P \left(\frac{Z-1}{P}\right) dP$ —(*) , ∴ to evaluate the integral, we need expression for compressibility factor Z.

from (2) $\quad PV_m - Pb = RT$

$$\Rightarrow \frac{PV_m}{RT} - \frac{Pb}{RT} = 1$$

$$\Rightarrow Z = 1 + \frac{Pb}{RT} \quad —(3)$$

Put (3) in (*)

$$\ln\phi = \int_0^P \frac{\cancel{1} + \frac{Pb}{RT} - \cancel{1}}{P}\, dP = \int_0^P \frac{b}{RT}\, dP = \frac{bP}{RT}$$

So, $\boxed{\ln\phi = \frac{bP}{RT}}$ → Case 1

Case 2: Attractive forces are dominant, which mean we neglect Vanderwaal coefficient 'b' in this case.

So, equation (1) gets reduced to

$$\left(P + \frac{a}{V_m^2}\right)(V_m) = RT \quad \text{—— (4)}$$

$$P + \frac{a}{V_m^2} = \frac{RT}{V_m}$$

$$PV_m + \frac{a}{V_m} = RT$$

$$\frac{PV_m}{RT} + \frac{a}{V_m RT} = 1$$

$$Z = 1 - \frac{a}{V_m RT} \quad \text{— (5)}$$

Put (5) in (4)

$$\ln\phi = \int_0^P \frac{\left(1 - \frac{a}{V_m RT} - 1\right)}{P} dP = \int_0^P \frac{-a}{V_m PRT} dP \quad \text{— (6)}$$

Now, to integrate the above, we need value of V_m in terms of P

So, re-writting equation (4)

$$PV_m^2 + a = RTV_m$$

$$PV_m^2 - RTV_m + a = 0$$

$$V_m^2 - \frac{RTV_m}{P} + \frac{a}{P} = 0 \quad \text{— (7)}$$

Eq. (7) is a quadratic equation of V_m, so solving for V_m (variable)

$$V_m = \frac{1}{2}\left(\frac{RT}{P} \pm \sqrt{\frac{(RT)^2}{P^2} - 4 \cdot \frac{a}{P}}\right)$$

$$V_m = \frac{1}{2}\left(\frac{RT}{P} \pm \frac{1}{P}\sqrt{(RT)^2 - 4ap}\right)$$

given, $(RT)^2 >> 4ap$ so, we have

$$V_m = \frac{1}{2}\left(\frac{RT}{P} \pm \frac{RT}{P}\right)$$

So, we have two solutions

$$V_m = \frac{\cancel{2}RT}{\cancel{2}P} = \frac{RT}{P} \qquad V_m = 0$$

Choosing + sign, we get $V_m = \frac{RT}{P}$

So, equation (6) becomes

$$\ln\phi = \int_0^P -\frac{a}{\cancel{P}RT} \cdot \frac{\cancel{P}}{RT}\, dP = \frac{-a}{(RT)^2}\int_0^P dP = \frac{-aP}{(RT)^2}$$

$$\boxed{\ln\phi = -\frac{aP}{(RT)^2}} \quad \text{Case 2}$$

2. Let A = water , B = Solute

(1) a_A (activity of Water) $= \frac{P_A}{P_A^*} = \frac{0.02239 \text{ atm}}{0.02308 \text{ atm}} = \underline{0.9701}$

(2) γ_A (activity coefficient of water) $= \frac{a_A}{X_A}$ → we need this

$X_A = \frac{n_A}{n_A + n_B}$ | $n_A = \frac{0.920 \text{ kg}}{0.018 \text{ kg mol}^{-1}} = 51.1$ $n_B = \frac{0.122 \text{ kg}}{0.241 \text{ kg mol}^{-1}} = 0.506$

$$X_A = \frac{51.1}{51.1 + 0.506} = 0.9901 \qquad \gamma_A = \frac{0.9701}{0.9901} = \underline{0.979}$$

3. Given $\ln k = A + \frac{B}{T} + \frac{C}{T^3}$, Temp. range 400 to 500K — (1)

$A = -2.04$, $B = -1176\,K$ & $C = 2.1 \times 10^7\,K^3$

Calculate ΔH° & $\Delta_r S^\circ$

$$\ln k = -2.04 - \frac{1176K}{T} + \frac{2.1 \times 10^7\,K^3}{T^3} \quad —(2)$$

From Van't Hoff equation:

(1)
$$\frac{d \ln k}{d(1/T)} = \frac{-\Delta_r H^\circ}{R}$$

from equation (2)

$$\frac{d(\ln k)}{d(\frac{1}{T})} = 0 - 1176\,K + (2.1 \times 10^7\,K^3) \times 3\left(\frac{1}{450K}\right)^2 = -864.88\,K$$

$$\cancel{-}\frac{\Delta_r H^\circ}{R} = \cancel{-}\,864.88\,K$$

$$\Delta_r H^\circ = 864.88\,\cancel{K} \times 8.314\,J\,mol^{-1}\,\cancel{K^{-1}} = \underline{7190.6\,J\,mol^{-1}}$$

$$= \underline{7.19\,kJ\,mol^{-1}}$$

(2) $\Delta_r G^\circ = -RT \ln k$

$$= (-8.314\,J\,K^{-1}\,mol^{-1})(450\,K)\left[-2.04 - \frac{1176\cancel{K}}{450\cancel{K}} + \frac{2.1 \times 10^7\,\cancel{K^3}}{(450)^3\,\cancel{K^3}}\right]$$

$$= +16546.27\,J\,mol^{-1} = +16.55\,kJ\,mol^{-1}$$

$$\Delta_r G^\circ = \Delta_r H^\circ - T\Delta S^\circ$$

$$\Delta_r S^\circ = \frac{\Delta_r H^\circ - \Delta_r G^\circ}{T} = \frac{(7.19 - 16.55)\,kJ\,mol^{-1}}{450\,K}$$

$$= \underline{-20.8\,J\,mol^{-1}}$$

4. Given : Two Components A & B

mole fractions in liquid x_A & x_B

$x_A \downarrow$ 0.220

mole fractions in vapour y_A & y_B

$y_A \downarrow$ 0.314

Vapour pressures of pure components $P_A^* = 73.0 kPa$

$P_B^* = 92.1 kPa$

$$y_A = \frac{P_A}{P_A + P_B} = \frac{P_A}{101.3 kPa} = 0.314$$

$$P_A = (101.3 kPa)(0.314) = 31.8 kPa$$

y_B $P_B = 101.3 kPa - 31.8 kPa = 69.5 kPa$

$$a_A = \frac{P_A}{P_A^*} = \frac{31.8 kPa}{73.0 kPa} = 0.436$$

$$a_B = \frac{P_B}{P_B^*} = \frac{69.5 kPa}{92.1 kPa} = 0.755$$

$$\gamma_A = \frac{a_A}{x_A} = \frac{0.436}{0.220} = 1.98$$

$$\gamma_B = \frac{a_B}{x_B} = \frac{0.755}{0.780} = 0.968$$

5. Given: $\Delta_r G^\circ = +22 \times 10^3 \text{ J mol}^{-1}$ at 1120 K

$\Delta_r H^\circ = 125 \times 10^3 \text{ J mol}^{-1}$

Rate constant k at Temp 1120 K is given by

$$k = e^{\frac{-\Delta_r G^\circ}{RT}}$$

now, $$\frac{\Delta_r G^\circ}{RT} = \frac{22 \times 10^3 \cancel{J} \cancel{mol^{-1}}}{8.314 \cancel{J} \cancel{mol^{-1}} \cancel{K^{-1}} \times 1120 \cancel{K}} = 2.362$$

$$k = e^{-2.362} = 0.0942 = 9.42 \times 10^{-2}$$

at $T_1 = 1120$ K , $k_1 = 9.42 \times 10^{-2}$

$T_2 = ?$ $\quad k_2 = 1$

wkT, $$\ln k_2 = \ln k_1 - \frac{\Delta_r H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\underline{\text{zero} = \ln 1} = \ln(9.42 \times 10^{-2}) - \frac{125 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol}^{-1} \text{K}^{-1}}\left(\frac{1}{T_2} - \frac{1}{1120}\right)$$

$$\frac{1}{T_2} = \frac{(8.314 \cancel{J} K^{-1} \cancel{mol^{-1}})[\ln(9.42 \times 10^{-2})]}{125 \times 10^3 \cancel{J} \cancel{mol^{-1}}} + \frac{1}{1120}$$

$$\frac{1}{T_2} = -\frac{8.314 \times 2.362}{125 \times 10^3} \text{K}^{-1} + \frac{1}{1120} \text{K}^{-1} = -0.157 \times 10^{-3} + 0.892 \times 10^{-3} \text{ K}^{-1}$$

$$= 0.735 \times 10^{-3} \text{ K}^{-1}$$

$$\cancel{T_2 = \frac{125 \times 10^3}{8.314 \times 2.362} =}$$

$$T_2 = \frac{1}{0.735 \times 10^{-3}} = \underline{\underline{1360.5 \text{ K}}}$$