CHM202

Energetics and dynamics of chemical reactions

Solutions Assignment –VII <u>Updated</u>

Q.1 Given that $p^*(H_2O) = 0.02308$ atm and $p(H_2O) = 0.02239$ atm in a solution in which 0.122 kg of a non-volatile solute ($M = 241$ g mol^{-1}) is dissolved in 0.920 kg water at 20 °C. Evaluate the activity and activity coefficient of water in the solution.

Sol.: The activity of A is given as

$$a_A = \frac{p_A}{p_A^0}$$

Let A = Water and B = Solute

$$a_A = \frac{p_A}{p_A^0}$$
$$= \frac{0.02239\ atm}{0.02308\ atm} = 0.9701$$

$$\gamma_A = \frac{a_A}{x_A}$$

and

$$x_A = \frac{n_A}{n_A + n_B}$$

$$n_A = \frac{0.920\ kg}{0.01802\ kg\ mol^{-1}} = 51.0\overline{5}\ mol \quad and \quad n_B = \frac{0.122\ kg}{0.241\ kg\ mol^{-1}} = 0.506\ mol$$

$$x_A = \frac{51.0\overline{5}}{51.0\overline{5} + 0.506} = 0.990 \quad and \quad \gamma_A = \frac{0.9701}{0.990} = \boxed{0.980}$$

Q.2 The vapour pressure of pure liquid A at 20 °C is 68.8 kPa and that of pure liquid B is 82.1 kPa. These two compounds form ideal liquid and gaseous mixtures. Consider the equilibrium composition of a mixture in which the mole fraction of A in the vapour is 0.612. Calculate the total pressure of the vapour and the composition of the liquid mixture.

Sol.: $p_A = y_A p = 0.612 p = x_A p_A^* = x_A(68.8\ \text{kPa})$ ... (1)

$p_B = y_B p = (1 - y_A)p = 0.388 p = x_B p_B^* = (1 - x_A) \times 82.1\ \text{kPa}$ ... (2)

From eq. (1) and (2):

$$\frac{y_A p}{y_B p} = \frac{x_A p_A^*}{x_B p_B^*} \quad and \quad \frac{0.612}{0.388} = \frac{x_A \times 68.8}{(1 - x_A) \times 82.1}$$

$$1.577 = \frac{x_A}{(1 - x_A)} \times 0.838$$

$$\frac{x_A}{(1-x_A)} = 1.882$$

$$x_A = 1.882 - x_A \times 1.882$$

$$x_A \times 2.882 = 1.882$$

$$x_A = 0.653$$

So, $\qquad x_B = 1 - 0.653 = 0.347$

Total pressure of the vapour

$$p = x_A p_A^* + x_B p_B^* = 0.653 \times 68.8 \text{ kPa} + 0.347 \times 82.1 \text{ kPa} = 73.4 \text{ kPa}$$

Q.3 It is found that the boiling point of a binary solution of A and B with $x_A = 0.4217$ is 96 °C. At this temperature the vapour pressures of pure A and B are 110.1 kPa and 76.5 kPa, respectively. (a) Is this solution ideal? (b) What is the initial composition of the vapour above the solution?

Sol.:

(a) If Raoult's law holds, the solution is ideal.

$$p_A = x_A p_A^* = (0.4217) \times (110.1 \text{ kPa}) = 46.43 \text{ kPa}$$

$$p_B = x_B p_B^* = (1 - 0.4217) \times (94.93 \text{ kPa}) = 54.90 \text{ kPa}$$

$$p = p_A + p_B = (46.43 + 54.90) \text{ kPa} = 101.33 \text{ kPa} = 1.000 \text{ atm}$$

Therefore, Raoult's law correctly predicts the pressure of the boiling liquid and $\boxed{\text{the solution is ideal}}$.

(b) $\qquad y_A = \dfrac{p_A}{p} = \dfrac{46.43 \text{ kPa}}{101.33 \text{ kPa}} = \boxed{0.4582}$

$$y_B = 1 - y_A = 1.000 - 0.4582 = \boxed{0.5418}$$

Q.4 Molecular bromine is 24% dissociated at 1327 °C and 1.00 bar in the equilibrium $Br_2(g) \rightleftharpoons 2$ $Br(g)$. Calculate (a) K at 25 °C, (b) $\Delta_r G^\circ$, (c) K at 2000 °C given that $\Delta_r H^\circ = +112$ kJ mol^{-1} over the temperature range.

Sol.:

(a) $\qquad Br_2(g) \rightleftharpoons 2Br(g) \quad \alpha = 0.24$
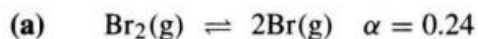
Amount at equilibrium	$(1-\alpha)n$	$2\alpha n$
Mole fraction	$\dfrac{1-\alpha}{1+\alpha}$	$\dfrac{2\alpha}{1+\alpha}$
Partial pressure	$\dfrac{(1-\alpha)P}{1+\alpha}$	$\dfrac{2\alpha P}{1+\alpha}$

Assuming both gases are perfect $a_J = \dfrac{p_J}{p^\ominus}$

$$K = \frac{(p_{Br}/p^\ominus)^2}{p_{Br_2}/p^\ominus} = \frac{4\alpha^2 p}{(1-\alpha^2)p^\ominus} = \frac{4\alpha}{1-\alpha} \quad [p = p^\ominus]$$

$$= \frac{4(0.24)^2}{1-(0.24)^2} = 0.24\overline{45} = \boxed{0.24}$$

(b) $\quad \Delta_r G^\ominus = -RT \ln K = -(8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}) \times (1600\,\mathrm{K}) \times \ln(0.24\overline{45})$

$$\boxed{= 19\,\mathrm{kJ\,mol^{-1}}}$$

(c) $\quad \ln K(2273\,\mathrm{K}) = \ln K(1600\,\mathrm{K}) - \dfrac{\Delta_r H^\ominus}{R}\left(\dfrac{1}{2273\,\mathrm{K}} - \dfrac{1}{1600\,\mathrm{K}}\right)$

$$= \ln(0.24\overline{45}) - \left(\frac{112 \times 10^3\,\mathrm{mol^{-1}}}{8.314\,\mathrm{J\,K^{-1}\,mol^{-1}}}\right) \times (-1.851 \times 10^{-4})$$

$$= 1.08\overline{4}$$

$$K(2273\,\mathrm{K}) = e^{1.08\overline{4}} = \boxed{2.96}$$

Q.5 If α is the degree of dissociation of NH_3 at pressure P, find α in terms of P and equilibrium constant K_p.

Sol.:

Dissociation of NH_3 occurs as

$$NH_3 \rightleftharpoons \tfrac{1}{2}N_2 + \tfrac{3}{2}H_2$$
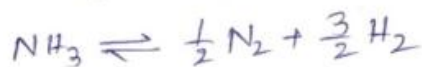
If initially there was 1 mole NH_3 and α is the degree of dissociation, then at equilibrium,

$$n_{NH_3} = (1-\alpha); \quad n_{N_2} = \frac{\alpha}{2} \quad \text{and} \quad n_{H_2} = \frac{3\alpha}{2}$$

So, total moles $= 1 + \alpha$.

Hence the mole fractions (x) are

$$x_{NH_3} = \frac{1-\alpha}{1+\alpha}, \quad x_{N_2} = \frac{\alpha}{2(1+\alpha)} \quad \text{and} \quad x_{H_2} = \frac{3\alpha}{2(1+\alpha)}$$

Now, $K_p = \dfrac{(P_{N_2})^{1/2} (P_{H_2})^{3/2}}{P_{NH_3}}$

$K_p = \left[\dfrac{\alpha}{2(1+\alpha)}\right]^{1/2} \cdot \left[\dfrac{3\alpha}{2(1+\alpha)}\right]^{3/2} \left[\dfrac{1+\alpha}{1-\alpha}\right] \cdot P$

$= \dfrac{3^{3/2}}{2^2} \cdot \dfrac{\alpha^2}{(1+\alpha)^2} \cdot \dfrac{1+\alpha}{1-\alpha} \cdot P$

or $K_p = 1.3 P \dfrac{\alpha^2}{(1-\alpha^2)}$

$\propto$ $K_p - \alpha^2 K_p = 1.3 \alpha^2 P$

or $\alpha^2 (K_p + 1.3 P) = K_p$

or $\alpha^2 = \dfrac{K_p}{K_p + 1.3 P}$

or $\alpha = \left[\dfrac{K_p}{K_p + 1.3 P}\right]^{1/2}$.

Q.6 What are the contributions that account for the difference between activity and concentration?

Sol.:

The general form of the chemical potential of a real or ideal solution solvent is given by

$\mu_A = \mu_A^* + RT \ln \dfrac{P_A}{P_A^*}$ —(1) where P_A^* is the vapour pressure of pure A and P_A is the vapour pressure of A when it is a component of a solution.

The solvent in an ideal solution obeys Raoult's law i.e.

$P_A = x_A P_A^*$ at all concentrations and we can express the chemical potential as

$\mu_A = \mu_A^* + RT \ln x_A$ —(11)

However, when the solution does not obey Raoult's law, the

form of this equation can be

$$\mu_A = \mu_A^* + RT \ln a_A \quad - \text{(III)}$$

The quantity a_A is the activity of A, a kind of effective mole fraction.

Therefore equ^n (III) is true for both real and ideal solutions.

We can conclude it by comparing with equation (I)

$$\mu_A = \mu_A^* + RT \ln(P_A/p_A^*)$$

$$\therefore \quad a_A = \frac{P_A}{p_A^*}$$

Now, because all solvents obey Raoult's law more closely as the concentration of solute approaches zero, the activity of the solvent approaches the mole fraction as $x_A \to 1$:

$$a_A \to x_A \quad \text{as} \quad x_A \to 1$$

A convenient way of expressing this equation by introducing activity coefficient (γ).

$$\therefore \quad a_A = \gamma_A \, x_A \qquad \gamma_A \to 1 \quad \text{as} \quad x_A \to 1$$

∴ The chemical potential of solvent is then

$$\mu_A = \mu_A^* + RT \ln x_A + RT \ln \gamma_A$$

The standard state of solvent is established when $x_A = 1$ and the pressure is 1 bar.

Q.7 Find the relation between the standard and biological standard Gibbs energies of a reaction of the form A $\to$ B+3H$^+$ aq.).

Sol.:

Biological standard state means at $pH = 7$ (an activity of 10^{-7}, neutral solution).

∴ To find the relation between the thermodynamic and biological standard values of the chemical potential of hydrogen ions, we write

$$\mu_{H^+}^{\oplus} = \mu_{H^+}^{\ominus} + RT \ln a_{H^+}$$

$$= \mu_H^{\ominus} - (RT \ln 10) pH$$

It follows that $\mu_{H^+}^{\oplus} = \mu_{H^+}^{\ominus} - 7 RT \ln 10$

Now, from the reaction $A \longrightarrow B + 3H^+(aq)$, Gibbs energies are related as,

$$\Delta_r G^{\oplus} = \left(\mu_B^{\ominus} - \left\{ \mu_A^{\ominus} \right\} + 3\mu_{H^+}^{\oplus} \right\}$$

$$= \left(\mu_B^{\ominus} - \left\{ \mu_A^{\ominus} \right\} + 3 \left(\mu_{H^+}^{\ominus} - 7 RT \ln 10 \right) \right.$$

$$= \underbrace{\left\{ \left(\mu_B^{\ominus} - \mu_A^{\ominus} \right) + 3\mu_{H^+}^{\ominus} \right\}}_{\Delta_r G^{\ominus} \text{ standard Gibbs energy}} - 21 RT \ln 10$$

$A \longrightarrow B + 3H^+$
$\Delta_r G^{\ominus} = \mu_B^{\ominus} + 3\mu_{H^+}^{\oplus} - \mu_A^{\ominus}$
$\mu_{H^+}^{\oplus} = \mu_H^{\ominus} - 7RT\ln 10$

$$\boxed{\Delta_r G^{\oplus} = \Delta_r G^{\ominus} - 21 RT \ln 10}$$

Q.8 At what temperature would CO$_2$ have a fugacity of 400 atm when its pressure is 400 atm?.

Sol.:

Fugacity is the function of the pressure and temperature. We replace the true pressure p by fugacity and write

$$G_{zm} = G_{zm}^{\ominus} + RT \ln(f/p^{\ominus})$$

$f = \phi p$ where ϕ is the fugacity coefficient which depends on temperature, and pressure and identity of gas.

Fugacity is related to compression factor z of a gas by the equⁿ

$$\ln \phi = \int_0^p \frac{z-1}{p} dp$$

when $f/p = 1$ ie. $\phi = 1$ that means $z \to 1$

At ~760 K, fugacity of CO_2 is equal to pressure (400 atm). (above critical or Boyle temp) [From Atkins' book]

i.e. At higher temperature and pressure when ~~gas~~ real gas behaves as perfect gas, fugacity is equal to pressure.