

CHM202

Energetics and dynamics of chemical reactions

Solutions Assignment –VII Updated

Q.1 Given that $p^*(\text{H}_2\text{O}) = 0.02308 \text{ atm}$ and $p(\text{H}_2\text{O}) = 0.02239 \text{ atm}$ in a solution in which 0.122 kg of a non-volatile solute ($M = 241 \text{ g mol}^{-1}$) 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

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

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

and

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

$$n_A = \frac{0.920 \text{ kg}}{0.01802 \text{ kg mol}^{-1}} = 51.05 \text{ mol} \quad \text{and} \quad n_B = \frac{0.122 \text{ kg}}{0.241 \text{ kg mol}^{-1}} = 0.506 \text{ mol}$$

$$x_A = \frac{51.05}{51.05 + 0.506} = 0.990 \quad \text{and} \quad \gamma_A = \frac{0.9701}{0.990} = \boxed{0.980}$$

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

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

From eq. (1) and (2):

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

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

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

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

$$x_A \times 2.882 = 1.882$$

$$x_A = 0.653$$

$$\text{So, } x_B = 1 - 0.653 = 0.347$$

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.

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

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

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

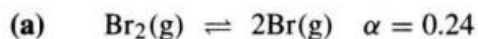
Therefore, Raoult's law correctly predicts the pressure of the boiling liquid and the solution is ideal.

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

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

Q.4 Molecular bromine is 24% dissociated at 1327°C and 1.00 bar in the equilibrium $\text{Br}_2(\text{g}) \rightleftharpoons 2\text{Br}(\text{g})$. Calculate (a) K at 25°C , (b) $\Delta_r G^0$, (c) K at 2000°C given that $\Delta_r H^0 = +112 \text{ kJ mol}^{-1}$ over the temperature range.

Sol.:



Amount at equilibrium	$(1 - \alpha)n$	$2\alpha n$
Mole fraction	$\frac{1 - \alpha}{1 + \alpha}$	$\frac{2\alpha}{1 + \alpha}$
Partial pressure	$\frac{(1 - \alpha)P}{1 + \alpha}$	$\frac{2\alpha P}{1 + \alpha}$

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

$$K = \frac{(p_{\text{Br}}/p^\ominus)^2}{p_{\text{Br}_2}/p^\ominus} = \frac{4\alpha^2 p}{(1-\alpha^2)p^\ominus} = \frac{4\alpha}{1-\alpha} \quad [p = p^\ominus]$$

$$= \frac{4(0.24)^2}{1 - (0.24)^2} = 0.2445 = \boxed{0.24}$$

(b) $\Delta_r G^\ominus = -RT \ln K = -(8.314 \text{ J K}^{-1} \text{ mol}^{-1}) \times (1600 \text{ K}) \times \ln(0.2445)$

$$= 19 \text{ kJ mol}^{-1}$$

(c) $\ln K(2273 \text{ K}) = \ln K(1600 \text{ K}) - \frac{\Delta_r H^\ominus}{R} \left(\frac{1}{2273 \text{ K}} - \frac{1}{1600 \text{ K}} \right)$

$$= \ln(0.2445) - \left(\frac{112 \times 10^3 \text{ mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \right) \times (-1.851 \times 10^{-4})$$

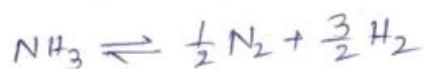
$$= 1.084$$

$$K(2273 \text{ K}) = e^{1.084} = \boxed{2.96}$$

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



If initially there was 1 mole NH_3 and α is the degree of dissociation, then at equilibrium,

$$n_{\text{NH}_3} = (1-\alpha); \quad n_{\text{N}_2} = \frac{\alpha}{2} \quad \text{and} \quad n_{\text{H}_2} = \frac{3\alpha}{2}$$

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

Hence the mole fractions (x) are

$$x_{\text{NH}_3} = \frac{1-\alpha}{1+\alpha}, \quad x_{\text{N}_2} = \frac{\alpha}{2(1+\alpha)} \quad \text{and} \quad x_{\text{H}_2} = \frac{3\alpha}{2(1+\alpha)}$$

$$\text{Now, } K_p = \frac{(p_{N_2})^{1/2} (p_{H_2})^{3/2}}{p_{NH_3}}$$

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

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

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

$$\text{or } K_p - \alpha^2 K_p = 1.3 \alpha^2 P$$

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

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

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

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

$\mu_A = \mu_A^* + RT \ln \frac{p_A}{p_A^*}$ (I) 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

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

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 eqnⁿ (III) is true for both real and ideal solutions.

We can conclude it by comparing with equation (I)

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

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

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 $x_A \rightarrow 1$:

$$a_A \rightarrow x_A \text{ as } x_A \rightarrow 1$$

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

$$\therefore a_A = \gamma_A x_A \quad \gamma_A \rightarrow 1 \text{ as } x_A \rightarrow 1$$

\therefore 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 $A \rightarrow B + 3H^+ \text{ aq.}$.

Sol.:

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

\therefore 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 $\mu_{H^+} = \mu_{H^+}^{\ominus} - 7RT \ln 10$

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

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

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

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

$$A \rightarrow B + 3H^+$$

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

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

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

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

$$G_m = G_m^\theta + RT \ln(f/p^\theta)$$

$f = \phi p$ 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 eqn

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

when $f/p = 1$ i.e. $\phi = 1$ that means $Z \rightarrow 1$

✓
At $\sim 760\text{ K}$, 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.