Assignment 1

(1) for each of the following systems, determine the # of components

(a) $NH_4Cl(s)$, $NH_4^+(aq)$, $Cl^-(aq)$, $H_2O(liq)$, $H_3O^+(aq)$, $H_2O(g)$, $NH_3(g)$, $OH^-(aq)$, $NH_4OH(aq)$

(b) $NH_4Cl(s)$, $NH_3(g)$, $HCl(g)$ where $p_{NH_3} = p_{HCl}$.

(c) $NH_4Cl(s)$, $NH_3(g)$, $HCl(g)$ where $p_{NH_3} \neq p_{HCl}$

(d) $CH_3COONH_4(s)$, $CH_3COO^-(aq)$, $NH_4^+(aq)$, $H_3O^+(aq)$, $NH_3(g)$, $OH^-(aq)$, $CH_3COOH(aq)$, $H_2O(l)$, $H_2O(g)$, assuming hydrolysis to take place.

(e) $NaCl(s)$, $KBr(s)$, $K^+(aq)$, $Na^+(aq)$, $Cl^-(aq)$, $Br^-(aq)$, $H_2O(l)$, $H_2O(g)$.

Assignment 2

① Determine the # of degree of freedom in:

ⓐ liquid water and water vapour in equilibrium

ⓑ liquid water and water vapour in equilibrium at a pressure of 1 atm.

② Calculate the number of components and the number of degree of freedom in:

(a) an aqueous solution of glucose

(b) an aqueous solution of acetic acid

(c) $2KClO_3(s) \rightleftharpoons 2KCl(s) + 3O_2(g)$

Assignment 3

(1) At 100°C, the specific volumes of water and steam are 1 cc and 1673 cc. Calculate the change in vapour pressure of the system by 1°C change in temperature. $\Delta H_v = 40584.8$ J/mol.

(2) The vapor pressure of water at 95°C = 634 mm. What would be the vapour pressure at a temperature of 100°C. $\Delta H_{vap} = 40593$ J/mol.

(3) The specific volume of ice and water at 0°C are 1.0907 cm^3 and 1.0001 cm^3. What would be the change in melting point of ice per atm increase in pressure. $\Delta H_{fus} = 6009.9$ J/mol.

(4) A lady weighing 50 kg is standing on ice wearing shoes with sole area of 60 cm^2 per shoe. Calculate the temperature at which the ice will melt under her feet.

(5) The following equations give the vapour pressure of ice and water:

$$\ln P_{vapour\ (ice)} = -\left(\frac{6140.1}{T}\right) + 24 \quad \text{—(I)}$$

$$\ln P_{vapour\ (water)} = -\left(\frac{5432.8}{T}\right) + 21.41 \quad \text{—(II)}$$

where P is in mm Hg. Calculate (a) the temperature and pressure at the triple point of the water. (b) the molar enthalpies of sublimation, vaporization and fusion at the triple point.

Solution to Assignment 1

① (a) $N = 8$

$E = 5$

(i) electroneutrality of the system

(ii) $NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

(iii) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

(iv) $NH_3 + H_2O \rightleftharpoons NH_4OH$

(v) $2H_2O \rightleftharpoons H_3O^+ + OH^-$

$C = 8 - 5 = 3$

(b) $N = 3$

(i) $NH_4Cl \rightleftharpoons NH_3 + HCl$

(ii) $P_{NH_3} = P_{HCl}$

$C = 3 - 2 = 1$

(c) $N = 3$

(i) $NH_4Cl \rightleftharpoons NH_3 + HCl$

$C = 3 - 1 = 2$

(d) $N = 8$

$E = 4$

(i) electroneutrality of the solution

(ii) $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$

(iii) $CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

(iv) $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$C = N - E = 8 - 4 = 4$

We have not counted $2H_2O \rightleftharpoons H_3O^+ + OH^-$ eq because it can be derived by adding eq (ii) and (iii)

(e) $N = 9$

$E = 5$

(i) electroneutrality of the sol^n

(ii) $NaCl \rightleftharpoons Na^+ + Cl^-$

(iii) $KBr \rightleftharpoons K^+ + Br^-$

(iv) $NaBr \rightleftharpoons Na^+ + Br^-$

(v) $NaCl + KBr \rightleftharpoons NaBr + KCl$

$C = 9 - 5 = 4$

Solution of Assignment 2

① a) $C = 1$

$P = 2$

$F = 1 - 2 + 2 = 1$

b) Since the pressure is held constant, F reduces by one

$\Rightarrow F = C - P + 1$

$= 1 - 2 + 1 = 0$

② a) $C = 2$

$P = 1$

$F = 3$

(b) $C = 2$

$P = 1$

$F = 3$

(c) If given mixture of 3 components $C = 3$

$P = 3$

$F = 2$

if the mixture is produced by decomposition of $KClO_3$, only two components need to be specified since third can be calculated from stoichiometry of the reaction.

$C = 2$

$P = 3$

$F = 1$

Solution of Assignment 3

(1) Molar volume of liquid water, $V_l = 18\ cm^3/mol = 18 \times 10^{-6}\ m^3/mol$

Molar volume of steam, $V_g = 18 \times 1673 = 30114 \times 10^{-6}\ m^3/mol$

according to Clapeyron equation,

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(V_g - V_l)}$$

$dT = 1\ K$

$T = 100 + 273 = 373\ K$

$$dP = \frac{40584.8 \times 1}{373 \times (30114 - 18) \times 10^{-6}} = 0.00361 \times 10^{-6}\ N/m^2$$

$= 0.03561$ ~~$\times 10^{-5}$~~ atm

$= 27.08$ mm of Hg

(1 atm = 101,325 N/m^2)

(2) $T_1 = 273 + 95 = 368\ K$

$P_1 = 634$ mm

$T_2 = 273 + 100 = 373\ K$

for liquid $\rightleftharpoons$ vapour

Clapeyron - Clausius equation, $\ln \frac{P_2}{P_1} = \frac{\Delta H_{vap}}{R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}$

$P_2 = 759.8$ mm.

(3) Molar volume of ice $V_s = 18 \times 1.0907 \times 10^{-6}\ m^3$

Molar volume of water $V_l = 18 \times 1.0001 \times 10^{-6}\ m^3$

$T = 273\ K$

$\Delta H_{fus} = 6009.9\ J/mol$

(66) $\Rightarrow$ $P = 4.55$ mm Hg.

(b) Clapeyron - Classius equation →

$$\ln P = -\left(\frac{\Delta H}{RT}\right) + \text{Constant (C)}$$

Comparing this equation with (I) and (II)

$$-\frac{\Delta H_{sub}}{R} = -6140.1$$

$$-\frac{\Delta H_{vap}}{R} = -5432.8$$

$$\Delta H_{sub} = 51.05 \text{ kJ/mol}$$

$$\Delta H_{vap} = 45.17 \text{ kJ/mol}$$

At triple point $\Delta H_{sub} = \Delta H_{fusion} + \Delta H_{vap}$

$$\Delta H_{fusion} = 5.88 \text{ kJ/mol.}$$

$dP = 1\ atm = 101325\ N/m^2$

$$\frac{dT}{dP} = \frac{T(V_l - V_s)}{\Delta H_{fus}}$$

$dT = -0.0075\ K.$

④ $m = 50\ kg$

Weight of lady $= mg = 50 \times 9.8$

pressure on ice under the lady's feet $= \frac{mg}{area} = \frac{50 \times 9.8}{2 \times 60 \times 10^{-4}}$

$$= \frac{4.083 \times 10^4\ N/m^2}{1.01325 \times 10^5\ N/m^2}\ atm$$

$= 0.403\ atm$

$\Delta H_{fus} = 6009.9$
$dP = 0.403\ atm$
$V_s = 18 \times 1.0907 \times 10^{-6}$
$V_l = 18 \times 1.0001 \times 10^{-6}$
} See ✱ question ③

$T = 273\ K$

$$\frac{dT}{dP} = \frac{T(V_l - V_s)}{\Delta H_{fus}}$$

$dT = -0.003^\circ C$

$\Rightarrow$ ice will melt at $-0.003^\circ C$ under the lady's feet.

⑤ (a) at triple point, $P_{vapour} = P_{ice}$.

$$\Rightarrow -\frac{6140.1}{T} + 24 = -\frac{5482.8}{T} + 21.41$$

$T = 273.089\ K$