

## Assignment 1

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

- (a)  $\text{NH}_4\text{Cl (s)}$ ,  $\text{NH}_4^+ \text{ (aq)}$ ,  $\text{Cl}^- \text{ (aq)}$ ,  $\text{H}_2\text{O (liq)}$ ,  $\text{H}_3\text{O}^+ \text{ (aq)}$ ,  $\text{H}_2\text{O (g)}$ ,  $\text{NH}_3 \text{ (g)}$ ,  $\text{OH}^- \text{ (aq)}$ ,  $\text{NH}_4\text{OH (aq)}$
- (b)  $\text{NH}_4\text{Cl (s)}$ ,  $\text{NH}_3 \text{ (g)}$ ,  $\text{HCl (g)}$  where  $p_{\text{NH}_3} = p_{\text{HCl}}$ .
- (c)  $\text{NH}_4\text{Cl (s)}$ ,  $\text{NH}_3 \text{ (g)}$ ,  $\text{HCl (g)}$  where  $p_{\text{NH}_3} \neq p_{\text{HCl}}$
- (d)  $\text{CH}_3\text{COONH}_4 \text{ (s)}$ ,  $\text{CH}_3\text{COO}^- \text{ (aq)}$ ,  $\text{NH}_4^+ \text{ (aq)}$ ,  $\text{H}_3\text{O}^+ \text{ (aq)}$ ,  $\text{NH}_3 \text{ (g)}$ ,  $\text{OH}^- \text{ (aq)}$ ,  $\text{CH}_3\text{COOH (aq)}$ ,  $\text{H}_2\text{O (l)}$ ,  $\text{H}_2\text{O (g)}$ , assuming hydrolysis to take place.
- (e)  $\text{NaCl (s)}$ ,  $\text{KBr (s)}$ ,  $\text{K}^+ \text{ (aq)}$ ,  $\text{Na}^+ \text{ (aq)}$ ,  $\text{Cl}^- \text{ (aq)}$ ,  $\text{Br}^- \text{ (aq)}$ ,  $\text{H}_2\text{O (l)}$ ,  $\text{H}_2\text{O (g)}$ .

## Assignment 2

① Determine the # of degree of freedom in:

(a) liquid water and water vapour in equilibrium

(b) 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)  $2 \text{KClO}_3 (\text{s}) \rightleftharpoons 2 \text{KCl} (\text{s}) + 3 \text{O}_2 (\text{g})$

### Assignment 3

- ① At  $100^{\circ}\text{C}$ , the specific volumes of water and steam are  $1\text{ cc}$  and  $1673\text{ cc}$ . Calculate the change in vapour pressure of the system by  $1^{\circ}\text{C}$  change in temperature.  $\Delta H_v = 40584.8\text{ J/mol}$ .
- ② The vapor pressure of water at  $95^{\circ}\text{C} = 634\text{ mm}$ . What would be the vapour pressure at a temperature of  $100^{\circ}\text{C}$ .  $\Delta H_{\text{vap}} = 40593\text{ J/mol}$ .
- ③ The specific volume of ice and water at  $0^{\circ}\text{C}$  are  $1.0907\text{ cm}^3$  and  $1.0001\text{ cm}^3$ . What would be the change in melting point of ice per atm increase in pressure.  $\Delta H_{\text{fus}} = 6009.9\text{ J/mol}$ .
- ④ A lady weighing  $50\text{ kg}$  is standing on ice wearing shoes with sole area of  $60\text{ cm}^2$  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:
- $$\ln P_{\text{vapour}}(\text{ice}) = -\left(\frac{6140.1}{T}\right) + 24 \quad \text{--- (I)}$$
- $$\ln P_{\text{vapour}}(\text{water}) = -\left(\frac{5432.8}{T}\right) + 21.41 \quad \text{--- (II)}$$
- 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.

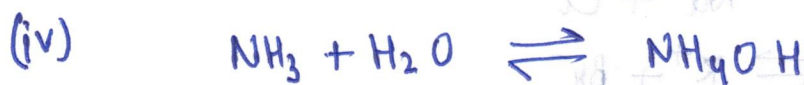
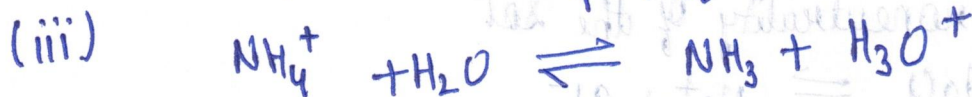
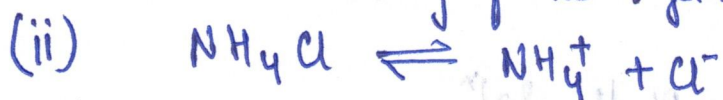


## Solution to Assignment 1

① (a)  $N = 8$

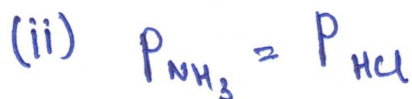
$$E = 5$$

(i) electroneutrality of the system



$$C = 8 - 5 = 3$$

(b)  $N = 3$



$$C = 3 - 2 = 1$$

(c)  $N = 3$

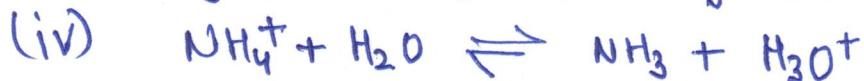
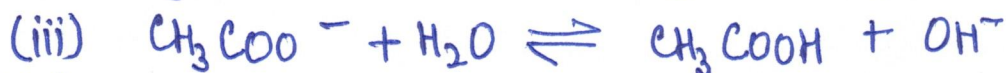
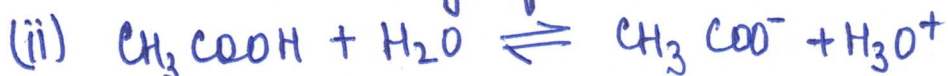


$$C = 3 - 1 = 2$$

(d)  $N = 8$

$$E = 4$$

(i) electroneutrality of the solution



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

④

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

(e)  $N = 9$   
 $E = 5$

- (i) electroneutrality of the sol<sup>n</sup>
- (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  $\text{KClO}_3$ ,

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,  $V_l = 18 \text{ cm}^3/\text{mol} = 18 \times 10^{-6} \text{ m}^3/\text{mol}$

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

according to Clapeyron equation,

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

$$dT = 1 \text{ K}$$

$$T = 100 + 273 = 373 \text{ K}$$

$$dp = \frac{40584.8 \times 1}{373 \times (30114 - 18) \times 10^{-6}}$$

$$= 0.00361 \times 10^{-6} \text{ N/m}^2$$

$$= 0.03561 \text{ atm}$$

$$= 27.08 \text{ mm of Hg}$$

$$(1 \text{ atm} = 101,325 \text{ N/m}^2)$$

②  $T_1 = 273 + 95 = 368 \text{ K}$

$$P_1 = 684 \text{ mm}$$

$$T_2 = 273 + 100 = 373 \text{ K}$$

for liquid  $\rightleftharpoons$  vapour

Clapeyron - Clausius equation,

$$\ln \frac{P_2}{P_1} = \frac{\Delta H_{\text{vap}}}{R} \left\{ \frac{T_2 - T_1}{T_1 T_2} \right\}$$

$$P_2 = 759.8 \text{ mm.}$$

③ Molar volume of ice  $V_g = 18 \times 1.0907 \times 10^{-6} \text{ m}^3$

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

$$T = 273 \text{ K}$$

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

(6a)  $\Rightarrow P = 4.55 \text{ mm Hg.}$

(b) Clapeyron - Clausius equation  $\rightarrow$

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

Comparing this equation with (i) and (ii)

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

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

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

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

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

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



$$dP = 1 \text{ atm} = 1.01325 \text{ N/m}^2$$

(12)

$$\frac{dT}{dP} = \frac{T(V_L - V_S)}{\Delta H_{\text{fus}}}$$

$$dT = -0.0075 \text{ K}$$

④  $m = 50 \text{ kg}$

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

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

$$= 4.083 \times 10^4 \text{ N/m}^2 \text{ atm}$$

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

$$= 0.403 \text{ atm}$$

$$\Delta H_{\text{fus}} = 6009.9$$

$$dP = 0.403 \text{ atm}$$

$$V_S = 18 \times 1.0907 \times 10^{-6}$$

$$V_L = 18 \times 1.0001 \times 10^{-6}$$

$$T = 273 \text{ K}$$

$$\frac{dT}{dP} = \frac{T(V_L - V_S)}{\Delta H_{\text{fus}}}$$

$$dT = -0.003^\circ \text{C}$$

See Question ③

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

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

$$\Rightarrow \frac{-6140.1}{T} + 24 = \frac{-54232.8}{T} + 21.41$$

$$T = 273.089 \text{ K}$$