

**CU-2014**

2)a) the value of  $K_P$  for the  $rea^n NH_3(g) \rightleftharpoons \frac{3}{2}H_2(g) + \frac{1}{2}N_2(g)$  IS  $1.36 \times 10^{-3}$  at 298 k. Determine the corresponding value of  $K_c$ .

→ we know,  $K_P = K_C (RT)^{\Delta n}$

Here,  $\Delta n = \left( \frac{3}{2} + \frac{1}{2} \right) - 1 = 1$

$\therefore 1.36 \times 10^{-3} = K_C (8.314 J k^{-1} mol^{-1} \times 298 k)$

$= K_C = \frac{1.36 \times 10^{-3}}{8.314 \times 298} = 5.48 \times 10^{-7}$

5)a) show that  $\frac{dmk_c}{dT} = \frac{\Delta U^\circ}{RT^2}$ , for a  $rea^n$  involving ideal gases.

- we know, Gibb's Helmholtz  $equ^n$ ,

$$\Delta G^\circ = \Delta H^\circ + T \left[ \frac{\partial(\Delta G^\circ)}{\partial T} \right]_P$$

$$\begin{aligned} \frac{\Delta G^\circ}{T^2} &= \frac{\Delta H^\circ}{T^2} + \frac{1}{T} \left[ \frac{\partial(\Delta G^\circ)}{\partial T} \right]_P \\ &= \frac{1}{T} \left[ \frac{\partial(\Delta G^\circ)}{\partial T} \right] - \frac{\Delta G^\circ}{T^2} = -\frac{\Delta H^\circ}{T^2} \end{aligned}$$

$$\frac{\partial}{\partial T} \left( \frac{\Delta G^\circ}{T} \right) = -\frac{\Delta H^\circ}{T^2}$$

NOW AS,  $\Delta G^\circ = -RTmk_p$

$$= \frac{\Delta G^\circ}{T} = -Rmk_p$$

$$= \frac{\partial}{\partial T} (-Rmk_p) = -\frac{\Delta H^\circ}{T^2}$$

$$= \frac{\partial}{\partial T} mk_p = -\frac{\Delta H^\circ}{RT^2} \text{----- (1)}$$

Now, we have,  $K_P = K_C(RT)^{\Delta n}$

Taking logarithm on both side,  $mk_p = mk_c + \Delta n mR + \Delta n mT$

$$= mk_c = mk_p + \Delta n mR + \Delta n mT$$

Differentiating both side w.r.t.T,

$$\frac{d}{dT} mk_c = \frac{d}{dT} mk_p - \frac{\Delta n}{T}$$

$$\frac{dmk_p}{dT} = \frac{\Delta H^\circ}{RT^2} - \frac{\Delta n}{T} \text{ [ } \therefore \text{ FROM (1) ]}$$

$$= \frac{dmk_p}{dT} = \frac{\Delta H^\circ - \Delta nRT}{RT^2}$$

$$= \frac{dmk_p}{dT} = \frac{\Delta U^\circ}{RT^2} \text{ [ } \therefore \Delta H^\circ = \Delta U^\circ + \Delta nRT \text{ ] (proved)}$$

a) The fugacity coefficient of a certain gas at 200k and 50 bar is 0.72  
 calculate the difference of its chemical potential from that of a perfect  
 gas in the same state.

- Temperature, T=200k pressure, p= 50 bar fugacity coefficient,  $\gamma=0.72$

$$\text{Now, } \gamma = \frac{f}{p} = 0.72$$

$$= \frac{f}{50 \text{ bar}} = 0.72 = f = 36 \text{ bar}$$

Now, the chemical potential of the gas when fugacity is 36 bar is ,

$$\mu_{real} = \mu^{\circ}_{real} + RT \ln f \quad \text{--- (1)}$$

the chemical potential of the perfect gas at pressure 50 bar is,

$$\mu_{ideal} = \mu^{\circ}_{ideal} + RT \ln p \quad \text{--- (1)}$$

the chemical potential of the perfect gas at pressure 50 bar is,

$$\mu_{real} = \mu^{\circ}_{real} + RT \ln p \quad \text{--- (2)}$$

$$\text{now, } \mu_{ideal} - \mu_{real} = \mu^{\circ}_{real} + RT \ln p - \mu^{\circ}_{real} + RT \ln f$$

$$= RT \ln \frac{p}{f} \quad [\because \mu^{\circ}_{ideal} = \mu^{\circ}_{real}]$$

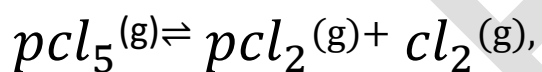
$$\mu_{ideal} - \mu_{real} = 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 200 \text{ K} \times m \frac{1}{0.72}$$

$$= 546.23 \text{ J mol}^{-1}$$

∴ the difference is  $546.23 \text{ J mol}^{-1}$

4) For the ideal gas reaction  $\text{PCl}_5(\text{g}) \rightleftharpoons \text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g})$ , state with reasons, how the equilibrium is affected when each of the following changes is made in the above equilibrium mixture at  $25^\circ\text{C}$ .

- He (g) is added at constant T and V
- He (g) is added at const. T and P



Let  $a$  = initial no. of moles of  $\text{PCl}_5$  and  $x$  = no. of moles of  $\text{Cl}_2$  produced at equilibrium then  $(a-x)$  = no. of  $\text{PCl}_5$  remains unreacted at equilibrium.

Let  $V$  be the total volume,  $P$  is total pressure at  $T$  is temp then,  $k_c = \frac{\frac{x}{v} \cdot \frac{x}{v}}{\frac{a-x}{v}}$

Let  $y$  moles of He gas is added.

- We have,  $pV = nRT = p \propto n$  at const. T and V
- SO, On adding He gas at const. T and V at equilibrium, there is no shift of equilibrium although pressure increases. This is because the conc. Of

reactants and products i.c. no of moles per unit volume will not change .

Hence , equilibrium will not be affected.

c) We have,  $pv=nRT =v=\frac{nRT}{P} =v \propto n$  at const. P and T

So, when He gas is added to the system at equilibrium keeping pressure

constant, volume of the system increases. This results in decrease in no. of moles per unit volume . Hence the equilibrium will shift in a direction where there is increase in no. Of moles of gases .here , the eq will shift on RHS having higher no. Of moles than reactant side.

1)b) show that  $\left(\frac{\partial \mu_i}{\partial T}\right)_{P,n_j} = \left(\frac{\partial S}{\partial n_i}\right)_{T,P,n_j}$

- We have,  $\mu_i = \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}$  ----- (1)

Differentiating both side w.r.t . T at const P and N (N=Total no. Of moles of different constituents

$\therefore \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = \left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}\right]_{P,N}$  ----- (2)

Since, G is a state func. Hence it is a perfect differential and can be written as-

$\left[\frac{\partial}{\partial p} \left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_{j \neq i}}\right]_{P,N} = \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial T}\right)_{P,N}\right]_{T,P,n_{j \neq i}}$

SO, from(2),

$$\left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = \left[\frac{\partial}{\partial n_i} \left(\frac{\partial G}{\partial T}\right)_{P,N}\right]_{T,P,n_{j \neq i}} \text{-----(3)}$$

For constant composition and const. Temp,

$$\left(\frac{\partial G}{\partial T}\right)_{P,N} = -S$$

$$\therefore \text{From (3), } \left(\frac{\partial \mu_i}{\partial T}\right)_{P,N} = -\left(\frac{\partial S}{\partial n_i}\right)_{P,T,n_{j \neq i}} = -S_i$$