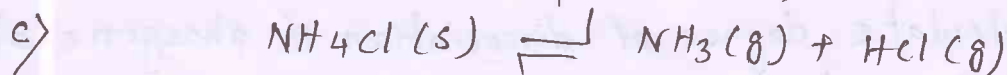
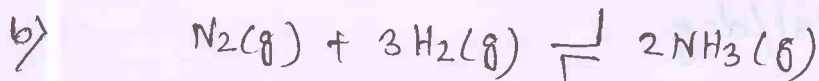
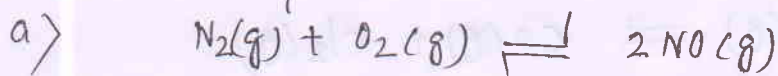
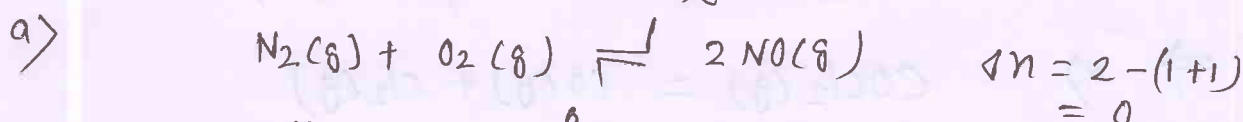


Q. Calculate K_p/K_c and K_c for the reaction at 27°C

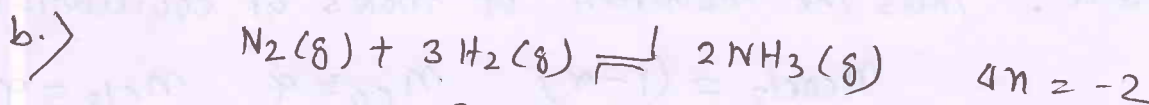


$\Rightarrow$ The units of $\frac{K_p}{K_c}$ depend upon the type of reaction involved, as well as since,

$$K_p = K_c (RT)^{\Delta n} \quad \frac{K_p}{K_c} = (RT)^{\Delta n}$$



$$\frac{K_p}{K_c} = (RT)^0 = 1$$



$$\begin{aligned} \frac{K_p}{K_c} &= (RT)^{-2} = (0.082 \text{ dm}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 300\text{K})^{-2} \\ &= 1.65 \times 10^{-3} \text{ mol}^2 \cdot \text{dm}^{-6} \cdot \text{atm}^2 \end{aligned}$$



$$\begin{aligned} \frac{K_p}{K_c} &= (RT)^2 = (0.0820 \text{ dm}^3 \cdot \text{atm} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 300\text{K})^2 \\ &= 605.2 \text{ dm}^6 \cdot \text{atm}^2 \cdot \text{mol}^{-2} \end{aligned}$$

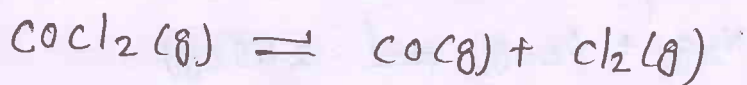
Q. At 2000K the standard free energy change in calories for the reaction $\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO}$ is given by $\Delta G^\circ = 22000 - 2.5T$. Calculate K_p at this temperature.

$$\begin{aligned} \Rightarrow \Delta G^\circ &= 22000 - 2.5 \times 2000 \text{ cal} \\ &= 17000 \text{ cal} \end{aligned}$$

$$\Delta G^\circ = -RT \ln K_p$$

$$\ln K_p = -\frac{\Delta G^\circ}{RT} \quad K_p = e^{-\frac{\Delta G^\circ}{RT}} = 1.39 \times 10^{-2}$$

Q. K_p is 8×10^{-9} atm at 100°C for the equilibrium

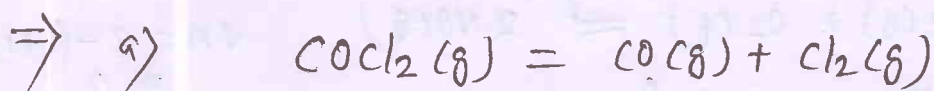


$$\Delta S_{373\text{K}}^\circ = 80 \text{ cal/deg.}$$

a) Calculate degree of dissociation of phosgene at 100°C and 2 atm pressure.

b) Calculate $\Delta H_{373\text{K}}^\circ$ for the reaction

c) at what temperature phosgene will be 0.1% dissociated at 2 atm pressure.



initially 1 mole $\text{COCl}_2(\text{g})$ and the degree of dissociation is α . Thus the number of moles at equilibrium

$$n_{\text{COCl}_2} = (1 - \alpha) \quad n_{\text{CO}} = \alpha \quad n_{\text{Cl}_2} = \alpha$$

$$\text{Total no of moles} = 1 + \alpha$$

$$P_{\text{COCl}_2} = \frac{1 - \alpha}{1 + \alpha} P$$

$$P_{\text{CO}} = \frac{\alpha}{1 + \alpha} P$$

$$P_{\text{Cl}_2} = \frac{\alpha}{1 + \alpha} P$$

$$K_p = \frac{\alpha^2}{1 - \alpha^2} P$$

$$\alpha = \sqrt{\frac{K_p}{P}} \quad [1 \gg \alpha]$$

$$\alpha = 6.3 \times 10^{-5}$$

b)

$$\Delta G^\circ = -RT \ln K_p$$

$$= -1.987 \text{ cal} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \times 373.15 \text{ K} \ln (8 \times 10^{-9})$$

$$= 13.82 \text{ kcal} \cdot \text{mol}^{-1}$$

$$\Delta H_{373\text{K}}^\circ = \Delta G^\circ + T \Delta S^\circ$$

$$= 13820 + 373.15 \times 30$$

$$= 25.01 \text{ kcal/mol}$$

c) $\alpha = 0.1\%$ $\alpha = 10^{-3}$

$$K_p = \frac{\alpha^2 P}{1 - \alpha^2}$$

$$\alpha^2 P = 2 \times 10^{-6}$$

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^\circ}{R} \frac{T_2 - T_1}{T_1 T_2}$$

$$\ln \frac{2 \times 10^{-6}}{8 \times 10^{-9}} = \frac{25010}{1.987} \frac{T_2 - 373.15}{T_2 \times 373.15}$$

$$T_2 = 446.19 \text{ K.}$$

Q. ΔH° and ΔG° for the reaction ~~$\text{Cl}_2(\text{g}) + \text{Br}_2(\text{g}) \rightleftharpoons 2 \text{BrCl}(\text{g})$~~ is -320 cal and -1440 cal respectively at 25°C . Calculate the value of K_p at 500°C assume $\Delta C_p = 0$.

$$\Rightarrow \Delta G^\circ = -RT \ln K_p$$

$$K_p = e^{-\frac{\Delta G^\circ}{RT}}$$

at 25°C i.e. 298 K $K_p = e^{+\frac{1440}{1.987 \times 298}}$

$$K_p = 11.3806$$

$\Delta C_p = 0$, ΔH is independent of tempⁿ

Hence, $\ln \frac{K_{p773 \text{ K}}}{K_{p298 \text{ K}}} = \frac{\Delta H}{R} \frac{773 - 298}{773 \times 298}$

$$\ln \frac{K_{p773}}{11.38} = \frac{-320}{1.987} \frac{475}{773 \times 298}$$

$$K_p = 8.164$$

Q. At high tempⁿ CO₂ dissociates according to the equation
 $2\text{CO}_2 = 2\text{CO} + \text{O}_2$. At one atm pressure the fraction of CO₂ dissociated is 2×10^{-5} at 1000K at 1400K it is 1.27×10^{-2} . Assuming that the enthalpy change ΔH of the reaction is independent of temperature, calculate ΔG° and ΔS° at 1000K

⇒ For the reaction $2\text{CO}_2 \rightleftharpoons 2\text{CO} + \text{O}_2$. If α is degree of dissociation then if we start with 2 moles of CO₂, then at equm. $n_{\text{CO}_2} = 2(1-\alpha)$ $n_{\text{CO}} = 2\alpha$ and $n_{\text{O}_2} = \alpha$. Total moles = $2 + \alpha$

$$K_p = \frac{n_{\text{CO}}^2 \cdot n_{\text{O}_2}}{n_{\text{CO}_2}^2} \left(\frac{P}{\sum n} \right) = \frac{4\alpha^3}{4(1-\alpha)^2} \cdot \frac{P}{2+\alpha}$$

$$K_p = \frac{\alpha^3 P}{(1-\alpha)^2 (2+\alpha)}$$

as α is very small so $K_p \approx \frac{\alpha^3 P}{2}$

Now, at 1000K $\alpha = 2 \times 10^{-5}$ so, $K_{p, 1000\text{K}} = 4 \times 10^{-15} \text{ atm}$

at 1400K, 1 atm $\alpha = 1.27 \times 10^{-2}$. $K_{p, 1400\text{K}} = 1.02 \times 10^{-6} \text{ atm}$

Vant Hoff's eqn $\ln \frac{1.02 \times 10^{-6}}{4 \times 10^{-15}} = \frac{\Delta H}{1.987} \cdot \frac{400}{1400 \times 1000}$

$$\Delta H = 134.643 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta G^\circ = -RT \ln K_p$$

at 1000K $\Delta G^\circ = -1.987 \times 1000 \ln(4 \times 10^{-15}) \text{ cal} = 65.8 \text{ kJ cal}$

$$\Delta G^\circ = \frac{\Delta H^\circ - T \Delta G^\circ}{T} = \frac{134643 - 65886}{1000} = 68.76 \text{ cal}^\circ$$