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

a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

c) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$

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

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

a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ $\Delta n = 2-(1+1) = 0$

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

b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Delta n = -2$

$$\frac{K_p}{K_c} = (RT)^{-2} = (0.082\ dm^3.atm\,K^{-1}.mol^{-1} \times 300K)^{-2}$$

$$= 1.65 \times 10^{-3}\ mol^2.dm^{-6}.atm^{-2}$$

c) $NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g)$ $\Delta n = 2$

$$\frac{K_p}{K_c} = (RT)^2 = (0.0820\ dm^3.atm.K^{-1}.mol^{-1} \times 300K)^2$$

$$= 605.2\ dm^6\ atm^2.mol^{-2}$$

Q. At 2000K the standard free energy change in calories for the reaction $N_2 + O_2 \rightleftharpoons 2NO$ is given by $\Delta G^0 = 22000 - 2.5T$. Calculated K_p at this temperature.

=> $\Delta G^0 = 22000 - 2.5 \times 2000$ cal

$= 17000$ cal

$$\Delta G^0 = -RT \ln K_p$$

$$\ln K_p = -\frac{\Delta G^0}{RT} \qquad K_p = e^{\frac{-\Delta G^0}{RT}} = 1.39 \times 10^{-2}$$

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

$$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$$

$\Delta S^0_{373K} = 30$ cal/deg.

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

b) Calculate ΔH^0_{373K} for the reaction

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

⇒ a) $$COCl_2(g) = CO(g) + Cl_2(g)$$

initially 1 mole $COCl_2(g)$ and the degree of dissociation is α. Thus the number of moles at equilibrium

$$n_{COCl_2} = (1-\alpha) \quad n_{CO} = \alpha \quad n_{Cl_2} = \alpha$$

Total no of moles $= 1+\alpha$

$$P_{COCl_2} = \frac{1-\alpha}{1+\alpha} \quad P_{CO} = \frac{\alpha}{1+\alpha} \quad P_{Cl_2} = \frac{\alpha}{1+\alpha} P$$

$$K_p = \frac{\alpha^2}{1-\alpha^2} P \qquad \alpha = \sqrt{\frac{K_p}{P}} \qquad [1 \gg \alpha]$$

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

b) $$\Delta G^0 = -RT \ln K_p$$

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

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

$$\Delta H^0_{373K} = \Delta G^0 + T\Delta S^0$$

$$= 13820 + 373.15 \times 30$$

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

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

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

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

$$\ln \frac{K_2}{K_1} = \frac{\Delta H^0}{R} \frac{T_2 - T_1}{T_1 T_2}$$

$$\ln \frac{2\times10^{-6}}{8\times10^{-9}} = \frac{25010}{1.987} \frac{T_2 - 373.15}{T_2 \times 373.15}$$

$$T_2 = 446.19\ K.$$

Q. ΔH^0 and ΔG^0 for the reaction ~~$Br_2(g) \rightleftharpoons 2$~~ $Cl_2(g) + Br_2(g) \rightleftharpoons 2\,BrCl(g)$ is -320 cal and -1440 cal respectively at 25°C. Calculate the value of K_p at 500°C assume $\Delta C_p = 0$.

⇒ $$\Delta G^0 = -RT \ln K_p$$

$$K_p = e^{-\frac{\Delta G^0}{RT}}$$

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

$$K_p = 11.3806$$

$\Delta C_p = 0$, ΔH is independent of temp^n

Hence, $$\ln \frac{K_{p\,773\,A}}{K_{p\,298^0\,A}} = \frac{\Delta H}{R} \frac{773 - 298}{773 \times 298}$$

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

$$K_p = 8.164$$

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Q. At high temp^{n} CO_2 dissociates according to the equation $2CO_2 = 2CO + O_2$. At one atm pressure the fraction of CO_2 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^0 and ΔS^0 at 1000K

⇒ For the reaction $2CO_2 \rightleftharpoons 2CO + O_2$. If α is degree of dissociation then if we start with 2 moles of CO_2, then at equm. $n_{CO_2} = 2(1-\alpha)$ $n_{CO} = 2\alpha$ and $n_{O_2} = \alpha$. Total moles $= 2+\alpha$

$$K_P = \frac{n_{CO}^2 \cdot n_{O_2}}{n_{CO}^2}\left(\frac{P}{\Sigma n}\right) = \frac{4\alpha^3}{4(1-\alpha)^2}\cdot\frac{P}{2+\alpha}$$

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

as α is very small so $K_P \simeq \frac{\alpha^3 P}{2}$.

Now, at 1000K $\alpha = 2\times10^{-5}$ So, $K_{P\,1000K} = 4\times10^{-15}$ atm

at 1400K, 1 atm $\alpha = 1.27\times10^{-2}$. $K_{P\,1400K} = 1.02\times10^{-6}$ atm

Vant Hoff's eqn $\ln\frac{1.02\times10^{-6}}{4\times10^{-15}} = \frac{\Delta H}{1.987}\cdot\frac{400}{1400\times1000}$

$\Delta H = 134.643$ K.cal

$\Delta G^0 = -RT\ln K_P$

at 1000K $\Delta G^0 = -1.987\times1000\ln(4\times10^{-15})$ cal $= 65.8$ K cal

$\Delta G^0 = \frac{\Delta H^0 - \Delta G^0}{T} = \frac{134643 - 65886}{1000} = 68.76$ cal.