

PHYSICAL CHEMISTRY

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BSc(H) Chem.

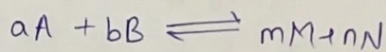
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ASSIGNMENT

Q1. Derive the relationship between K_p° , K_c° and K_x .

solⁿ

for an ideal gas,



acc. to Dalton's law

$$\begin{array}{l} p_i = x_i P \\ \swarrow \quad \searrow \\ \text{partial} \quad \text{total} \\ \text{pressure} \quad \text{pressure} \end{array}, \quad \begin{array}{l} p_A = x_A P \\ p_B = x_B P \\ p_M = x_M P \\ p_N = x_N P \end{array}$$

$$\text{we know that, } K_p = \frac{p_M^m p_N^n}{p_A^a p_B^b} \quad \text{--- (1)}$$

Putting the values in (1)

$$K_p = \frac{(x_M P)^m (x_N P)^n}{(x_A P)^a (x_B P)^b}$$

$$K_p = \frac{x_M^m x_N^n}{x_A^a x_B^b} P^{(m+n)-(a+b)}$$

$$K_p = K_x P^{\Delta n} \quad \text{--- (2)}$$

$$\text{where } \Delta n = (m+n) - (a+b)$$

$$\text{Now, } p_i V = n_i RT \quad (\text{at const. volume } V)$$

eq

$$P_i = \frac{n_i RT}{V} \rightarrow C_i RT = P_i$$

where, V = total volume and C_i = molar conc. of i th component at total volume

$$P_A = [A]RT$$

$$P_B = [B]RT$$

$$P_M = [M]RT$$

$$P_N = [N]RT$$

} Putting these values
in eq ①

$$K_p = \frac{[M]^m (RT)^m [N]^n (RT)^n}{[A]^a (RT)^a [B]^b (RT)^b} = \frac{[M]^m [N]^n}{[A]^a [B]^b} (RT)^{(m+n)-(a+b)}$$

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

where $\Delta n = (m+n) - (a+b)$ — ③

from ② and ③

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

if $\Delta n = 0$

$$K_p = K_c = K_{xc}$$

Q2. Give quantitative treatment for Le-Chatelier's principle.

solⁿ If a system at equilibrium is subjected to a change, then it will react in such a way so as to oppose or reduce the change if this is possible,

ie. the system tends to balance or counter act the effects of any imposed stress.

Quantitative Treatment

$$\Delta G = \left(\frac{\partial G}{\partial \xi} \right)_{T,P}, \quad \Delta G = f(T, P, \xi)$$

$$d(\Delta G) = \underbrace{\left(\frac{\partial \Delta G}{\partial T} \right)_{P,\xi}}_{(-S)} dT + \left(\frac{\partial \Delta G}{\partial P} \right)_{T,\xi} dP + \left(\frac{\partial \Delta G}{\partial \xi} \right)_{T,P} d\xi$$

$$d(\Delta G) = -\Delta S dT + \Delta V dP + G'' d\xi$$

Here,

$$\frac{\partial}{\partial \xi} \Delta G = \left\{ \frac{\partial}{\partial \xi} \left(\frac{\partial G}{\partial \xi} \right)_{T,P} \right\}_{T,P} = G''$$

At equilibrium, $G'' = G''_{eq}$

Here, G'' is having a min. value as G''_{eq} is positive.

$$dP = 0 \text{ (const. } P)$$

$$0 = -\Delta S dT + G''_{eq} d\xi$$

$$\left(\frac{\partial \xi}{\partial T} \right) = \left(\frac{\Delta S}{G''_{eq}} \right)$$

At equilibrium,

$$\Delta S = \frac{\Delta H}{T}$$

$$\left(\frac{\partial G}{\partial T}\right) = \frac{\Delta_r H}{T G_{eq}''}$$

$$dT = 0 \text{ (at const } T)$$

$$0 = \Delta_r V dP + G_{eq}'' dG$$

$$\left(\frac{\partial G}{\partial P}\right) = \frac{-\Delta_r V}{G_{eq}''} = \frac{-\Delta_r V R T}{P G_{eq}''}$$

if the gas behaves ideally,

$$\left(\frac{\partial G}{\partial T}\right)_P = \frac{\Delta_r H}{T G_{eq}''}$$

$$\left(\frac{\partial G}{\partial P}\right)_T = \frac{-\Delta_r V}{G_{eq}''} = \frac{-\Delta_r V R T}{P G_{eq}''}$$

Ques. Derive Van't Hoff equation. Draw plots for $\ln K_p^\circ$ vs $\frac{1}{T}$.

Sol.

Acc. to Gibbs-Duhem equation,

$$\frac{d}{dT} \left(\frac{\Delta_r G^\circ}{T} \right) = \frac{-\Delta_r H^\circ}{T^2}$$

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

Put the value above,

$$\frac{d}{dT} \left(\frac{-RT \ln K_p^\circ}{T} \right) = \frac{-\Delta_r H^\circ}{T^2}$$

$$-R \frac{d}{dT} (\ln K_p^\circ) = \frac{-\Delta_r H^\circ}{T^2}$$

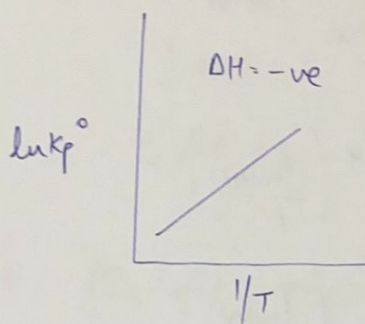
$$nRT = PV$$

$$\frac{d(\ln K_p^\circ)}{dT} = \frac{\Delta_\text{rxn} H^\circ}{RT^2}$$

This equation is known as Van't Hoff Equation.

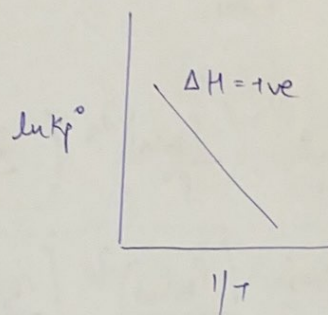
$$\text{Also, } \frac{d \ln K_p^\circ}{d(1/T)} = \frac{\Delta_\text{rxn} H^\circ}{RT^2}$$

$$\ln K_p^\circ = \frac{-\Delta_\text{rxn} H^\circ}{RT} + \text{constant}$$



(exothermic)

$$\text{slope} = \frac{-\Delta_\text{rxn} H^\circ}{R}$$

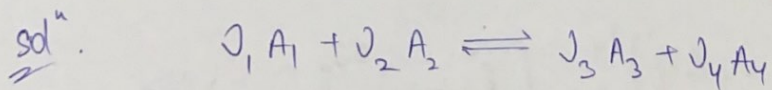


(endothermic)

$$\text{slope} = \frac{-\Delta_\text{rxn} H^\circ}{R}$$

$$\text{and } \frac{\ln K_p^\circ(T_2)}{K_p^\circ(T_1)} = \frac{-\Delta_\text{rxn} H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

Q4. Discuss the effect of addition of inert gas on equilibrium



At $t=0$ ν_1 ν_2

equilibrium $(\nu_1 - \nu_1 \xi_{eq})$ $(\nu_2 - \nu_2 \xi_{eq})$ $\nu_3 \xi_{eq}$ $\nu_4 \xi_{eq}$

total no. of moles, n_{total}

$$= n_1 - \nu_1 \xi_{\text{eq}} + n_2 - \nu_2 \xi_{\text{eq}} + \nu_3 \xi_{\text{eq}} + \nu_4 \xi_{\text{eq}}$$

partial pressure

$$\left(\frac{n_1 - \nu_1 \xi_{\text{eq}}}{n_{\text{total}}} \right) p_{\text{total}} \quad \left(\frac{n_2 - \nu_2 \xi_{\text{eq}}}{n_{\text{total}}} \right) p_{\text{total}}$$

$$\left(\frac{\nu_3 \xi_{\text{eq}}}{n_{\text{total}}} \right) p_{\text{total}} \quad \text{and} \quad \left(\frac{\nu_4 \xi_{\text{eq}}}{n_{\text{total}}} \right) p_{\text{total}}$$

$$K_p^\circ = \frac{\left(\frac{\nu_3 \xi_{\text{eq}}}{n_{\text{total}}} \right)^{\nu_3} \left(\frac{p_{\text{total}}}{p^\circ} \right)^{\nu_3} \left(\frac{\nu_4 \xi_{\text{eq}}}{n_{\text{total}}} \right)^{\nu_4} \left(\frac{p_{\text{total}}}{p^\circ} \right)^{\nu_4}}{\left(\frac{n_1 - \nu_1 \xi_{\text{eq}}}{n_{\text{total}}} \right)^{\nu_1} \left(\frac{p_{\text{total}}}{p^\circ} \right)^{\nu_1} \left(\frac{n_2 - \nu_2 \xi_{\text{eq}}}{n_{\text{total}}} \right)^{\nu_2} \left(\frac{p_{\text{total}}}{p^\circ} \right)^{\nu_2}}$$

$$K_p^\circ = \frac{(\nu_3 \xi_{\text{eq}})^{\nu_3} (\nu_4 \xi_{\text{eq}})^{\nu_4}}{(n_1 - \nu_1 \xi_{\text{eq}})^{\nu_1} (n_2 - \nu_2 \xi_{\text{eq}})^{\nu_2}} \left(\frac{p_{\text{total}}}{n_{\text{total}} p^\circ} \right)^{\Delta \nu_g}$$

After adding inert gas,

$$n'_{\text{total}} = n + n_{\text{total}}$$

$$p'_{\text{total}}$$

$$K_p^\circ = \frac{(\nu_3 \xi_{\text{eq}}')^{\nu_3} (\nu_4 \xi_{\text{eq}}')^{\nu_4}}{(n_1 - \nu_1 \xi_{\text{eq}}')^{\nu_1} (n_2 - \nu_2 \xi_{\text{eq}}')^{\nu_2}} \left(\frac{p'_{\text{total}}}{n'_{\text{total}}} \right)^{\Delta \nu_g} \left(\frac{1}{p^\circ} \right)^{\Delta \nu_g}$$

Keeping the value of K_p° same (both cases)

CASE 1:- $\Delta G = 0$

$$E'_{eq} = E_{eq}$$

$$R \quad nRT = PV$$

$$\frac{P}{n} = \frac{RT}{V}$$

$$\left(\frac{P_{total}}{n_{total}} \right) = \frac{RT}{V_{total}}$$

CASE 2:- $\Delta G = +ve / > 0$, $A \rightleftharpoons B + C$

P const

$$E'_{eq} > E_{eq}$$

V const

no change

CASE 3:- $\Delta G = -ve / < 0$

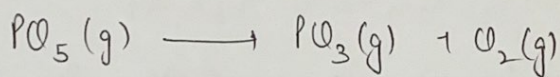
P const

$$E'_{eq} < E_{eq}$$

V const

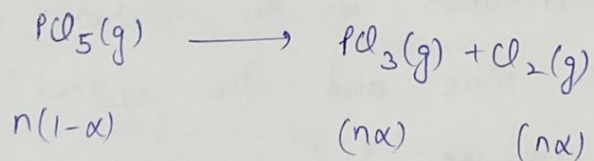
no change

Q5. $PO_5(g)$ dissociates acc. to the equation



At 523K, the equilibrium constant K_p for the reaction is 1.8. Determine the degree of dissociation of PO_5 .

solⁿ



$$K_p = \frac{[PO_3][O_2]}{[PO_5]}$$

$$K_p = \frac{(n\alpha)(n\alpha)}{n(1-\alpha)} = \frac{n\alpha^2}{1-\alpha}$$

$$1.8(1-\alpha) = n\alpha^2 \quad (n=1)$$

$$1.8 - 1.8\alpha = \alpha^2$$

$$\alpha^2 + 1.8\alpha - 1.8 = 0$$

$$\alpha = \frac{-1.8 \pm \sqrt{(1.8)^2 - 4(1)(-1.8)}}{2}$$

$$\alpha = \frac{-1.8 \pm 3.23}{2}$$

for (+ve)

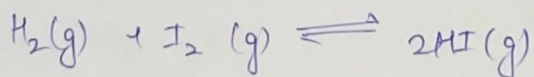
$$\alpha = 0.715$$

for (-ve)

$$\alpha = -2.515$$

Q6. Write a short note on (i) Criteria for equilibrium
(ii) Le-Chatelier's principle

Solⁿ (i) Chemical equilibrium is a state in which the rate of forward reaction is equal to the rate of the backward reaction. It refers to the state of a system in which the concentration of the reactant and product do not change with time. and the system does not display any further change in properties.



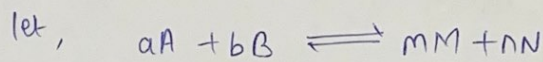
The chemical equilibrium in a reversible reaction is a state in which both forward and backward reactions occur at same speed.

(ii) Le Chatelier's principle states that if a dynamic equilibrium is disturbed by changing the conditions, the position of equilibrium shifts to counteract the change to reestablish an equilibrium. If a chemical reaction at equilibrium and experiences a change in pressure & temperature, the equilibrium shifts in the opposite direction to offset the change.

Q7. Derive thermodynamically using chemical potential concept the relation $\Delta G = -RT \ln K_p$.

solⁿ

$$\mu_i = \left(\frac{\partial \Delta G}{\partial n_i} \right)_{T, P, n_i \neq j} \quad \text{partial molar change}$$



$$G_{\text{product}} = m\mu_M + n\mu_N$$

$$G_{\text{reactant}} = a\mu_A + b\mu_B$$

$$\Delta G = G_{\text{product}} - G_{\text{reactant}}$$

$$= (m\mu_M + n\mu_N) - (a\mu_A + b\mu_B)$$

for ideal gas,

$$\mu_i = \mu_i^\circ + RT \ln p_i$$

$$\Delta G = 0 \quad (\text{at equilibrium})$$

$$\text{so, } m\mu_M + n\mu_N - (a\mu_A + b\mu_B) = 0 \quad \text{--- ①}$$

$$\mu_M = \mu_M^\circ + RT \ln P_M$$

$$\mu_N = \mu_N^\circ + RT \ln P_N$$

$$\mu_A = \mu_A^\circ + RT \ln P_A$$

$$\mu_B = \mu_B^\circ + RT \ln P_B$$

} Put these in ①

$$m(\mu_M^\circ + RT \ln P_M) + n(\mu_N^\circ + RT \ln P_N) - a(\mu_A^\circ + RT \ln P_A) - b(\mu_B^\circ + RT \ln P_B) = 0$$

$$\Delta G^\circ + \frac{RT \ln P_M^m P_N^n}{P_A^a P_B^b} = 0$$

$$\Delta G^\circ = \frac{-RT \ln P_M^m P_N^n}{P_A^a P_B^b}$$

OR

$$\frac{P_M^m P_N^n}{P_A^a P_B^b} = e^{-\Delta G^\circ / RT}$$

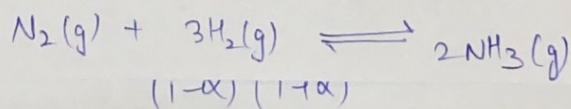
$$K_p = e^{-\Delta G^\circ / RT}$$

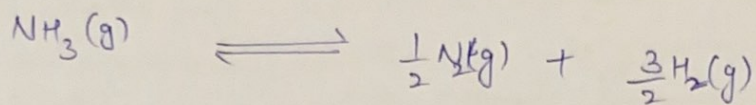
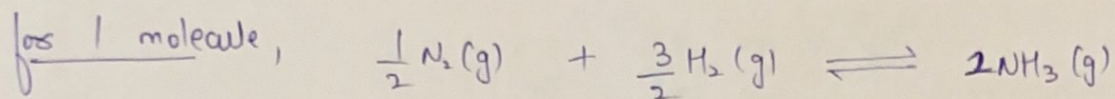
Q8. show that $\frac{1}{2} \text{N}_2(\text{g}) + \frac{3}{2} \text{H}_2(\text{g}) \rightleftharpoons \text{NH}_3(\text{g})$

$$K_p^\circ = \frac{4(1-\alpha^2)}{3\sqrt{3}\alpha^2} \left(\frac{P^\circ}{P} \right)$$

Solⁿ

we know that





$$\text{as } K_p^{\circ'} = \frac{1}{K_p^{\circ}}$$

At $t=0$	n	0	0	total amount n
At equilibrium	$n(1-\alpha)$	$\frac{1}{2}(n\alpha)$	$\frac{3}{2}(n\alpha)$	$n(1-\alpha)$
Mole fraction	$\left(\frac{1-\alpha}{1+\alpha}\right)$	$\frac{\alpha/2}{1+\alpha}$	$\frac{3\alpha/2}{1+\alpha}$	
Partial pressure	$\left(\frac{1-\alpha}{1+\alpha}\right)p$	$\left[\frac{\alpha/2}{1+\alpha}\right]p$	$\left[\frac{3\alpha/2}{1+\alpha}\right]p$	

$$K_p^{\circ'} = \frac{(P_{\text{N}_2}/P^{\circ})^{1/2} (P_{\text{H}_2}/P^{\circ})^{3/2}}{(P_{\text{NH}_3}/P^{\circ})}$$

$$K_p^{\circ'} = \frac{\left(\frac{\alpha/2}{1+\alpha}\right)^{1/2} \left(\frac{p}{P^{\circ}}\right)^{1/2} \left(\frac{3\alpha/2}{1+\alpha}\right)^{3/2} \left(\frac{p}{P^{\circ}}\right)^{3/2}}{\left(\frac{1-\alpha}{1+\alpha}\right) \left(\frac{p}{P^{\circ}}\right)}$$

$$K_p^{\circ'} = \frac{\left(\frac{\alpha}{2}\right)^{1/2} \left(\frac{3\alpha}{2}\right)^{3/2} \left(\frac{p}{P^{\circ}}\right)}{(1-\alpha)(1+\alpha)}$$

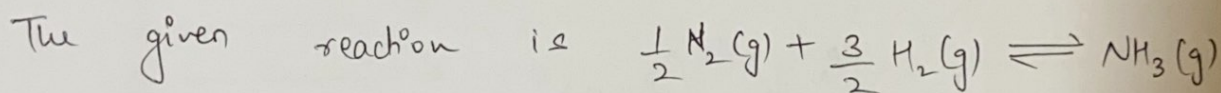
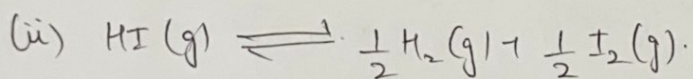
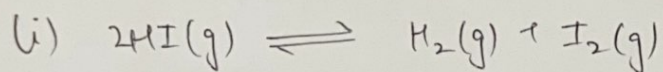
$$K_p^{\circ'} = \frac{\alpha^2 3\sqrt{3}}{4(1-\alpha^2)} \left(\frac{P}{P^\circ} \right)$$

Now, $K_p^{\circ'} = \frac{1}{K_p^\circ}$

$$K_p^\circ = \frac{4(1-\alpha^2)}{3\sqrt{3}\alpha^2} \left(\frac{P^\circ}{P} \right)$$

Hence proved

Q9. The value of K_p° for the reaction is 8.32 at 873 K and 1 bar pressure. Calculate K_p° , K_c° and K_{xx} for



solⁿ