Dr. Soumendu Bisoi
Assistant Professor
Department of Chemistry, Narajole Raj College

Calculation of K_p, K_c, and K_x for some reactions:-

a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $\Delta n = 0$

Let 1 mole of H_2 and 1 mole of I_2 are reacting in a vessel of v Lit. capacity. Let a equilibrium x mole of H_2 reacted. So at equilibrium number of moles of different ~~concentrat~~ constituents are.

$n_{H_2} = (1-x)$; $n_{I_2} = (1-x)$ and $n_{HI} = 2x$

Total no of moles $= (1-x) + (1-x) + 2x = 2$.

Let total pressure $= P$.

Conc^n unit	$[H_2]$	$[I_2]$	$[HI]$
moles/Lit	$\frac{1-x}{V}$	$\frac{1-x}{V}$	$\frac{2x}{V}$
mole fraction	$\frac{1-x}{2}$	$\frac{1-x}{2}$	x
partial pr.	$\frac{1-x}{2} \cdot P$	$\frac{1-x}{2} \cdot P$	xP

$$K = \frac{[HI]^2}{[H_2][I_2]}$$

$$K_c = \frac{4x^2}{(1-x)^2}$$

$$K_x = \frac{4x^2}{(1-x)^2}$$

$$K_p = \frac{4x^2}{(1-x)^2}$$

Therefore for the reaction $\Delta n = 0$.

$K_c = K_p = K_x$

If α is the degree of disociation of NH_3, at pressure P, find α in terms of P and equilibrium constant K_p

$\Rightarrow$ Dissociation of NH_3 occurs as

$$NH_3 \rightleftharpoons \frac{1}{2} N_2 + \frac{3}{2} H_2$$

If initially there was 1 mole NH_3 and at equm. α is the degree of dissociation, then at equm.

$n_{NH_3} = 1-\alpha$ $\quad n_{N_2} = \frac{\alpha}{2}$ $\quad n_{H_2} = \frac{3\alpha}{2}$

So, total no of moles $= 1-\alpha + \frac{\alpha}{2} + \frac{3\alpha}{2}$

$= 1+\alpha$

Hence, mole fractions (X) are

$X_{NH_3} = \frac{1-\alpha}{1+\alpha}$ $\quad X_{N_2} = \frac{\alpha}{2(1+\alpha)}$

$X_{H_2} = \frac{3\alpha}{2(1+\alpha)}$

If P is the total pressure, then partial pressure are

$P_{NH_3} = \frac{1-\alpha}{1+\alpha} P$ $\quad P_{N_2} = \frac{\alpha \cdot P}{2(1+\alpha)}$ $\quad P_{H_2} = \frac{3\alpha P}{2(1+\alpha)}$

$$K_P = \frac{P_{N_2}^{1/2} \cdot P_{H_2}^{\frac{3}{2}}}{P_{NH_3}} = \left[\frac{\alpha P}{2(1+\alpha)}\right]^{\frac{1}{2}} \left[\frac{3\alpha P}{2(1+\alpha)}\right]^{\frac{3}{2}} \left[\frac{1+\alpha}{1-\alpha}\right] \cdot \frac{1}{P}$$

$$= 1.3\ P\ \frac{\alpha^2}{(1-\alpha^2)}$$

$$K_P(1-\alpha^2) = 1.3\,P \cdot \alpha^2$$

$$K_P - K_P\alpha^2 = 1.3\,P\alpha^2$$

$$\alpha^2(K_P + 1.3\,P) = K_P$$

$$\alpha^2 = \frac{K_P}{K_P + 1.3\,P}$$

$$\alpha = \left[\frac{K_P}{K_P + 1.3P}\right]^{1/2}$$

It is the expression of α in terms of P and K_P for the above reaction.

Pressure dependence of equilibrium constant :-

For reactions involving ideal gas at a given temp, the values of equilibrium constant K_p and K_c are independent of pressure.

but K_x depend on pressure when $\Delta n \neq 0$

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

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

$$\ln K_x = \ln K_p - \Delta n \ln P$$

$$\left[\frac{d \ln K_x}{dP}\right] = \left[\frac{d \ln K_p}{dP}\right]_T - \Delta n \left[\frac{d \ln P}{dP}\right]_T$$

$$\left[\frac{d \ln K_x}{dP}\right]_T = \frac{-\Delta n}{P}$$

when $\Delta n = 0$ i,e for reaction $H_2 + I_2 \rightleftharpoons 2HI$

K_x independent on pressure.

If $\Delta n = +ve$ i,e. for the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

K_x will decrease with increase in pressure i,e dissociation of PCl_5 decreases.

If $\Delta n = -ve$ i,e for $3H_2 + N_2 \rightleftharpoons 2NH_3$,

K_x will increase with increase in pressure

i,e formation of NH_3 increase.

These are qualitative prediction by Le-Chatelier.

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Narajole Raj College.

Effect of inert gas on equilibrium:-

Let us concider a homogeneous gaseous reaction

$$aA + bB \rightleftharpoons cC + dD$$

If equm. constant $K_p = \frac{P_C^c \times P_D^d}{P_A^a \times P_B^b}$

where P_A, P_B, P_C, P_D are partial pr. of A, B, C, D respectively at equilibrium.

Now, $P_i = x_i P = \frac{n_i}{\Sigma n} P = n_i \left(\frac{P}{\Sigma n}\right)$

$$K_p = \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b} \left(\frac{P}{\Sigma n}\right)^{(c+d)-(a+b)}$$

$$= \frac{n_C^c \times n_D^d}{n_A^a \times n_B^b} \left(\frac{P}{\Sigma n}\right)^{\Delta n}$$

If inert gas is introduced at constant volume then not only Σn but also P increase proportionally. So $\frac{P}{\Sigma n}$ remains constant at constant volume. So n_C, n_D, n_A, n_B will remain unchanged i.e. equm is not affected.

If however inert gas is introduced at constant pressure then as Σn increase $\frac{P}{\Sigma n}$ decrease, depending on the the value of Δn three cases may arise.

1) If $\Delta n = 0$ i.e. for the reaction $H_2 + I_2 \rightleftharpoons 2HI$

$\left(\frac{P}{\Sigma n}\right)^{\Delta n}$ is always unity. So equm is not affected.

ii) If $\Delta n = +ve$, the $\left(\frac{P}{\Sigma n}\right)^{\Delta n}$ decreases i.e ($PCl_5 \rightleftharpoons PCl_3 + Cl_2$). So to keep Kp constant, n_C, n_D should increase i.e ~~equal~~ equilibrium will shift towards right.

iii) If $\Delta n = -ve$, then $\left(\frac{P}{\Sigma n}\right)^{\Delta n}$ increases, so to keep Kp constant, n_C, n_D should ~~increase~~ decrease i.e equilibrium will shift towards left.

$$3H_2 + N_2 \rightleftharpoons 2NH_3$$

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