Law of Mass Action

On the basis of observation of many equilibrium reaction two Norwegian chemist Cato Maximillian Guldberg and Peter Waage suggested a relationship between rate of reaction and concentration of relation

It states that the rate of chemical reaction is directly proportional to the product of the molar concent ration of the reaction at constant temperature

A + B → Product

$r \propto [A][B]$

[Molar concentration no. of moles per litre)

$\Rightarrow r = K[A][B]$

K = rate constant
= velocity constant

Ex

$2A + 3B \rightarrow$ product

↳ stoichiometric coefficent

$r = K[A]^2[B]^3$

↳ rate of reaction

Law of Chemical Equilibrium

Let us consider a simple reversible reaction

$$A + B \rightleftharpoons C + D$$

The Forward Reaction

$$A + B \rightarrow C + D$$

Rate of forward Reaction

$$r = K_f [A][B]$$

K_f = rate constant for forward reaction

[A] & [B] are molar concentration of A and B

The Backward Reaction

(Product → Reaction)

Reactant

$r \propto$ mole

$$C + D \rightarrow A + B$$

Rate of backward reaction

$$r = K_b [C] [D]$$

K_b = rate constant of backward reaction

At equilibrium

Rate of backward reaction = Rate of forward reaction

$$\Rightarrow K_b [C] [D] = K_f [A] [B]$$

$$\Rightarrow \frac{[C][D]}{[A][B]} = \frac{K_f}{K_b}$$

$$\Rightarrow K_c = \frac{[C][D]}{[A][B]}$$

K_c = equlibrium constant

$K_c = \frac{K_f}{K_b}$

K_f → Rate constant for forward

K_b → Rate constant for backward

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

$$K_c = \frac{[C]^c [D]^d}{}$$

$$[A]^a [B]^b$$

The equilibrium constant is ratio between the product of molar concentration of the reaction with each raise to power with each its stoichiometric coefficient

Ex

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$$

$$K_c = \frac{[NO]^4 [H_2O]^6}{[NH_3]^4 [O_2]^5}$$

Equilibrium Constant in Gaseous System

$aA(g) + bB(g) \rightleftharpoons cC(g) + dD(g)$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b}$$

P_A, P_B, P_C, P_D are partial pressure of A, B, C, D

<u>Note</u> :- K_p is not always equal to K_c

VVI

Relationship between Kp & Kc

For the Reaction

$aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{—— (I)}$$

$$K_p = \frac{(P_C)^c (P_D)^d}{(P_A)^a (P_B)^b} \quad \text{—— (II)}$$

According Ideal Gas

$$PV = nRT$$

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

$$\frac{n}{V} = \frac{\text{no of moles}}{\text{volume}} = C$$

$$P = CRT$$

$$\Rightarrow P = [\text{gas}] RT$$

$$P_A = [A] RT$$

$$P_B = [B]RT$$

$$P_C = [C]RT$$

$$P_D = [D]RT$$

$$K_p = \frac{P_C^{\,c}\; P_D^{\,d}}{P_A^{\,a}\; P_B^{\,b}}$$

$$K_p = \frac{([C]RT)^c\,([D]RT)^d}{([A]RT)^a\,([B]RT)^b}$$

$$K_p = \frac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b}$$

$$K_p = \frac{[C]^c [D]^d}{[A]^a [B]^b} \frac{(RT)^{c+d}}{(RT)^{a+b}}$$

$$K_p = K_c (RT)^{(c+d)-(a+b)}$$

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

$\Delta n = (c+d) - (a+b)$

Unit of Equilibrium Constant

1) When the total number of moles of product is equal to mole of reactant

$$1N_2(g) + 1O_2(g) \rightleftharpoons 2NO(g)$$

$1 + 1 = 2$; 2

K = no unit

$$K = \frac{[NO]^2}{[N_2][O_2]}$$

molar concentration

SI unit mol/L = mol L^{-1}

$$K = \frac{(mol\,L^{-1})^2}{(mol\,L^{-1})(mol\,L^{-1})} \qquad \frac{mol}{L}$$

$$= \frac{mol^2\,L^{-2}}{mol^2\,L^{-2}} = 1$$

K = no unit

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

K = ?

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

$$= \frac{mol\,L^{-1} \times mol\,L^{-1}}{(mol\,L^{-1})^2}$$

$$= \frac{mol^2\,L^{-2}}{mol^2\,L^{-2}}$$

$$= 1 = \text{no unit}$$

$$\underbrace{N_2(g) + 3H_2(g)}_{R} \rightleftharpoons \underbrace{2NH_3(g)}_{P}$$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3}$$

$$= \frac{(mol\ L^{-1})^2}{(mol\ L^{-1})(mol\ L^{-1})^3}$$

$$= \frac{mol^2\ L^{-2}}{mol^1 L^{-1} \times mol^3 L^{-3}}$$

$$= \frac{mol^2\ L^{-2}}{mol^4\ L^{-4}}$$

$$= mol^{2-4} \; L^{-2-(-4)}$$

$$= mol^{-2} \; L^{-2+4}$$

$$= mol^{-2} \; L^{2}$$