Law of Mass action

(C.M. Guldberg and P. Waage 1864)

" The rate at which a substance reacts is directly proportional to its active mass and the rate at which the reaction proceeds is directly proportional to the product of the active masses of the reactants."

What is active mass: The concentration of reactants and products in $mol.dm^{-3}$ for a dilute solution. It is expressed with [ ].

Mathematical derivation: Consider a general reaction.

$$\underset{(g)}{aA} + \underset{(g)}{bB} \rightleftharpoons \underset{(g)}{cC} + \underset{(g)}{dD}$$

According to the Law of mass action.

Rate of forward reaction $\propto [A]^a[B]^b$

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

Rate of reverse reaction $\propto [C]^c[D]^d$

$= K_r[C]^c[D]^d$

At equilibrium

Rate of forward reaction = Rate of reverse reaction

$K_f[A]^a[B]^b = K_r[C]^c[D]^d$

$$\frac{K_f}{K_r} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

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

K_c = Equilibrium Constant

$$K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

What is equilibrium constant: The ratio of the product of concentration of products to the product of concentration of reactants each raised to the power equal to the co-efficient in the balanced chemical equation. K_c depends upon temperature.

How to write Equilibrium constant Expression?

1. Write products in the numerator and reactants in the denominator in square brackets.
2. Raise each concentration to the power that corresponds to the co-efficient of each species in the balanced chemical equation.

Example:

$$CO_{(g)} + 3H_{2(g)} \rightleftharpoons CH_{4(g)} + H_2O_{(g)}$$

$$K_c = \frac{[CH_4][H_2O]}{[CO][H_2]^3}$$

Conditions for Equilibrium

1. Concentration of none of the reactant or product is changed.
2. Temperature of the system is kept constant.
3. Pressure or volume of the system is kept constant.

Units of Equilibrium Constant

Equilibrium constant may or may not have units. The units of K_c therefore depend on the form of equilibrium expression. We have two examples to prove it

1. When K_c have unit:

$$N_2O_4 \underset{(g)}{} \rightleftharpoons 2NO_2 \underset{(g)}{}$$

$$K_c = \frac{[NO_2]}{[N_2O_4]}$$

$$K_c = \frac{[mol\,dm^{-3}]^2}{[mol\,dm^{-3}]} \quad mol.dm^{-3}$$

$$K_c = mol\,dm^{-3}$$

2. When K_c have no unit:

$$H_2 \underset{(g)}{} + I_2 \underset{(g)}{} \rightleftharpoons 2HI \underset{(g)}{}$$

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

$$K_c = \frac{[mol\,dm^{-3}]^2}{[mol\,dm^{-3}][mol\,dm^{-3}]}$$

K_c = No unit

Importance of equilibrium constant

Equilibrium constant can be used to:

a. determine the equilibrium concentration of equilibrium mixture knowing the initial concentration of reactants.
b. predict the direction of a chemical reaction.
c. predict the extent of a chemical reaction.
d. predict the effect of change in conditions of the chemical reaction on the equilibrium state.

Explanation: (1) Ammonia gas is produced by the reaction of (N_2) and (H_2) at 450C°, 200 atm pressure and with the help of catalyst.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \quad \text{(Haber Process)}$$

This is a reversible reaction. 33% NH_3 is produced at equilibrium. High pressure also favors NH_3 formation. Cooling equilibrium mixture gives 98% NH_3.

(2) Sulphur dioxide (SO_2) is oxidized at 450C° and 200 atm pressure with the help of catalyst (Pt) or (V_2O_5).

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

This is a reversible reaction. Maximum amount of SO_2 is converted into SO_3 at equilibrium.

CH# 9 (Chemical Equilibrium)

What is reversible reaction? Examples?

A reaction in which products can react together to form the original reactants is reversible reaction.

OR

A reaction which proceeds in both directions (forward as well as reverse) under the same conditions

i. $2SO_2(g) + O_2(g) \underset{450C^\circ,\ 200\ atm}{\overset{V_2O_5}{\rightleftharpoons}} 2SO_3(g)$

ii. $N_2(g) + 3H_2(g) \underset{450C^\circ,\ 200\ atm}{\overset{Fe}{\rightleftharpoons}} 2NH_3(g)$

iii. $2NO(g) + O_2(g) \underset{Spark}{\overset{Electric}{\rightleftharpoons}} 2NO_2(g)$

What is chemical equilibrium and dynamic equilibrium.

A State of a chemical reaction in which forward and reverse reactions take place at the same rate is called chemical equilibrium

Chemical equilibrium is a Dynamic equilibrium. This is because reactions do not stop when they come to equilibrium state. The individual molecules keep on reacting continuously. But there is no change in the actual amounts of reactants and products. This means concentration of reactants and products become constant at equilibrium stage.

Differentiate b/w forward and reverse reaction

Forward reaction	Reverse reaction
• It is written from left to right	• It is written from right to left.
• Reactants produce products.	• Products produce reactants.
• Rate is fastest in the begining and gradually slows down	• Its rate is zero in the begining and gradually speeds up.