

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 $\text{mol} \cdot \text{dm}^{-3}$ for a dilute solution. It is expressed with $[\]$.

Mathematical derivation: Consider a general reaction.



According to the Law of mass action.

$$\begin{aligned} \text{Rate of forward reaction} &\propto [A]^a [B]^b \\ &= K_f [A]^a [B]^b \end{aligned}$$

$$\begin{aligned} \text{Rate of reverse reaction} &\propto [C]^c [D]^d \\ &= K_r [C]^c [D]^d \end{aligned}$$

At equilibrium

$$\begin{aligned} \text{Rate of forward reaction} &= \text{Rate of reverse reaction} \\ K_f [A]^a [B]^b &= K_r [C]^c [D]^d \end{aligned}$$

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

$K_c =$ Equilibrium Constant

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

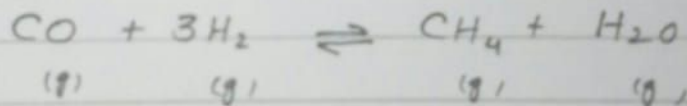
$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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 coefficient 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 coefficient of each species in the balanced chemical equation.

Example:



$$K_c = \frac{[\text{CH}_4][\text{H}_2\text{O}]}{[\text{CO}][\text{H}_2]^3}$$

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.

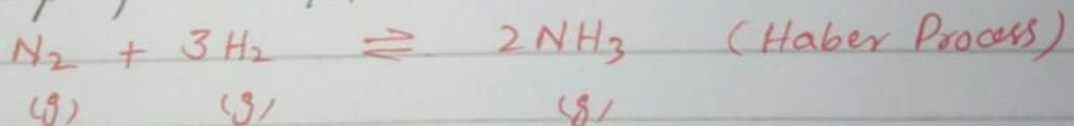
Importance of equilibrium constant

Equilibrium constant can be used to:

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

Explanation: (1) Ammonia gas is produced by the

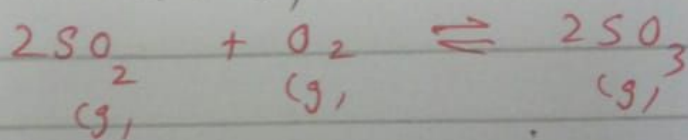
reaction of (N_2) and (H_2) at $450^\circ C$, 200 atm pressure and with the help of catalyst.



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 $450^\circ C$ and 200 atm pressure with the help of catalyst (Pt) or (V_2O_5) .



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

