Chemical Equilibrium

↳ Only applicable for reversible reaction

eg:-

$$A \rightleftharpoons B$$

Suppose:-

$$\underbrace{Aa + Bb}_{\text{Reactant}} \underset{\text{backward } rx^n}{\overset{\text{forward } rx^n}{\rightleftharpoons}} \underbrace{Cc + Dd}_{\text{product}}$$

→ Reactant → product (Forward Rx^n)

→ product → reactant (backward rx^n)

→ Reversible reaction lasts for infinite amount of time.

R_f → Rate of forward rx^n.

R_b → Rate of backward rx^n

K → Equilibrium constant

↳ point where forward and backward rx^n meet.

↳ has two types

- K_c (in terms of concentration)
- K_p (in terms of partial pressure)

→ Relation of K_c and K_p:- $K_p = K_c (RT)^{\Delta n}$

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

→ Information obtained from K_c.

We know,

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

→ If $K_c > 1$, K_c 1 भन्दा ठुलो हुनको लागि K_f ko value K_b भन्दा ठुलो हुनुपर्छ, K_f ठुलो हुनु भनेको product side को concentration धेरै हुनु हो, यो condition ma equilibrium will shift in forward direction.

→ $K_c < 1$, K_b K_c भन्दा ठुलो हुनु हो, that means reactant side को concentration धेरै हुनु, so, equilibrium will shift in backward.

K_c and K_p relation

→ $\Delta n = 0$, $K_p = K_c$ (Equal)

→ $\Delta n = +ve$, $K_p > K_c$ (K_p ~~les~~ greater)

→ $\Delta n = -ve$, $K_p < K_c$ (K_c greater)

Le chateliar's principle

Statement (only for understanding)

"If we change concentration, pressure, volume, temperature or add any inert materials to a reversible rxn which is at equilibrium equilibrium gets disturbed and then rx^n try to undo the change made."

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→ Change in concentration

RXn -

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

Suppose:- 12g 4g 18g

→ अहिले हामी सँग 12g N_2 छ भनेर suppose garum, अब हामीलो N_2 को concernbration increase गर्नै हो भने, suppose 12g bata 18g गरौं भने, हाम्रो rx^n equilibrium condition ma आउनको लागि त्यो 18g लाई 12g बनाउने try गर्दछ, 12g बनाउन extra mass product side tira पठाउँछ that means forward rx^n.

Note:-

→ Reactant side को concentration increase भयो भने, equilibrium shift towards forward.

→ Reactant side, concentration decrease भयो भने, equilibrium shift backwards.

→ product side को concentration decrease भयो भने, equilibrium shift forward.

→ product side को concentration increase गर्दा, equilibrium shift backwards.

→ Change in Pressure

Relation:- $P \propto \frac{1}{V}$

(Pressure inversely proportional to volume)

Consider a rx^n:-

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

1 vol. 2 vol.

→ Forward rx^n मा हेर्नेै हो भने 1 volume बाट 2 volume भएको छ, that means volume increase भएको छ and relation ~~मा~~ अनुसार Pressure decrease garnu पर्छ।

→ Backward rx^n को लागि Pressure increase गर्नु पर्छ। (If volume is equal, no change)

→ Change in Temperature

Key point:- If $\Delta H = +ve$, endothermic rx^n

$\Delta H = -ve$, exothermic rx^n

If heat is produced in product side, then it is exothermic rx^n.

→ Temperature increase गर्दा rx^n favour towards endothermic rx^n.

→ Temperature decrease गर्दा rx^n favour towards exothermic rx^n.

Questions:

1. Find the relation between K_p and K_c of the followings:
a. $N_2(g)+3H_2(g)\rightleftharpoons 2NH_3(g)$
b. $H_2(g)+I_2(g)\rightleftharpoons 2HI(g)$
c. $PCl_5(g)\rightleftharpoons PCl_3(g)+Cl_2(g)$

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2. Write down the expression for K_c for the following reactions.
a. $N_2(g)+O_2(g)\rightleftharpoons 2NO(g)$
b. $PCl_5(g)\rightleftharpoons PCl_3(g)+Cl_2(g)$
c. $CaCO_3(s)\rightleftharpoons CaO(s)+CO_2(g)$

Note: Active mass of solid is always 1.

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3. Analyze the following equilibrium conditions:
a. $2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$+Heat (effect of T & P)
b. $PCl_5(g)\rightleftharpoons PCl_3(g)+Cl_2(g)$ (effect of pressure)
c. The favorable conditions for maximum yield of SO3 in the following equilibrium.
$2SO_2(g)+O_2(g)\rightleftharpoons 2SO_3(g)$+Heat

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4. Why does pressure have no effect on $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$? Write Kc for the reaction.
5. Write down the relation between Kp and Kc. What is the condition for a gaseous reaction to have Kp = Kc?
6. How does temperature change affect the equilibrium of the given reaction?
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$, $\Delta H = - 22.4$ kcal/mole
7. What would be the effect on the position of equilibrium of the relation
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ of:
    - (a) adding Cl_2
    - (b) adding PCl_3
    - (c) decreasing the pressure by increasing the volume of the system
    - (d) increasing temperature (the reaction is endothermic in the forward reaction)
    - (e) adding a catalyst.

Answers and Solution on End of Pdf…

Introduction:

In a chemical reaction, chemical equilibrium is the state in which both reactants and products are present in constant concentrations which have no further tendency to change with time, so that there is no observable change in the properties of the system.

Forward Reaction

The reaction having the direction from reactants to products side is called forward reaction.

Backward Reaction

The reaction having the direction from products to reactants side is called backward reaction.

Reversible Reaction

The chemical reaction in which the reactants react to form products while the products also recombine to form the reactants is called reversible reaction. Reversible reaction is denoted by double headed arrow ($\rightleftharpoons$) which is placed between the reactants and products. For examples:

- $3H2+N2\rightleftharpoons 2NH3$
- $H2+I2\rightleftharpoons 2HI$
- $2SO2+O2\rightleftharpoons 2SO3$
- $N2O4\rightleftharpoons 2NO2$

Irreversible Reaction

The chemical reaction in which the reactants react to form products but products do not react to form reactants is called irreversible reaction. Irreversible reaction is denoted by single headed arrow ($\longrightarrow$) which is placed between reactants and products. For examples:

- $2KClO3\longrightarrow 2KCl+3O2$
- $2Mg+O2\longrightarrow 2MgO$
- $Zn+H2SO4\longrightarrow ZnSO4+H2$
- $NaCl+AgNO3\longrightarrow AgCl+NaNO3$

Concept of chemical equilibrium:

In a reversible reaction, the rate of the forward reaction gradually decreases because the concentration of reactants decreases over time. Initially, the concentration of the product is zero, but as the forward reaction proceeds, the concentration of products increases. These products then react to reform the reactants.

As the concentration of products continues to increase, the rate of the backward reaction also increases. Eventually, a state is reached where the rate of the forward reaction equals the rate of the backward reaction, which is defined as equilibrium.

At this equilibrium state:

- The concentrations of reactants and products do not change with time.
- The reaction may appear to have stopped, but it has not; it continues at equal rates in both directions.
- Because of this continuous activity, chemical equilibrium is dynamic in nature rather than static.

Figure Description: The source includes a graph plotting the Rate of reaction (y-axis) against Time (x-axis). It shows the curve for the forward reaction decreasing and the curve for the backward reaction increasing until they meet at a horizontal line labelled Dynamic equilibrium

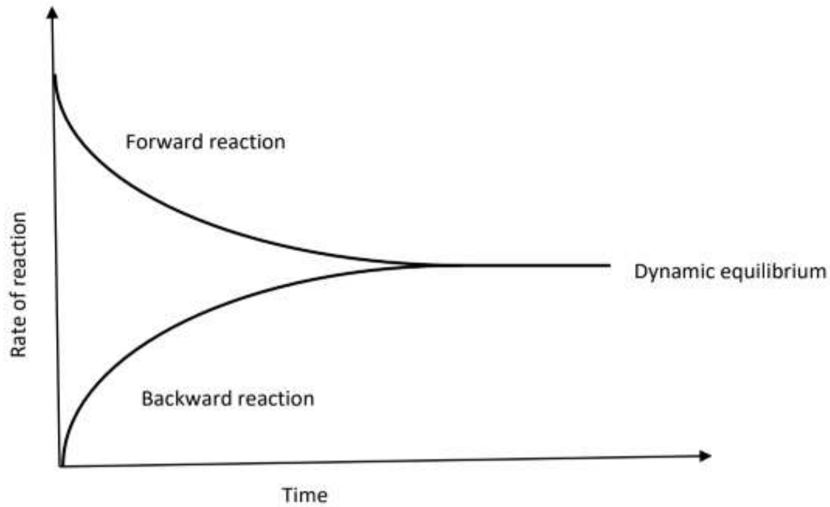

Fig: Reversible reaction and state of equilibrium

Characteristics of chemical equilibrium:

1. Chemical equilibrium is dynamic in nature. At equilibrium, the rate of forward reaction is equal to the rate of backward reaction.
2. The concentration of each of the reactants and products remains constant at the equilibrium condition.
3. The equilibrium condition can be attained from either direction.
4. A catalyst helps to attain equilibrium fast, but it has no effect on the state of equilibrium

Law of mass action:

The law states that:
"The rate at which the substance reacts is directly proportional to its molar concentration (active mass) and the rate of chemical reaction is directly proportional to the products of molar concentrations (active masses) of reacting species where each concentration term is raised to the powers equal to stoichiometric coefficients present in the balanced chemical equation".
Active Mass or Molar Concentration: The term molar concentration or active mass refers to the number of moles of the substance dissolved in per litre of its solution. It is represented by enclosing the symbols or formulae of the substance in square brackets.

Active mass or Molar concentration= $\frac{No.of\ Moles}{\text{Volume of solution in liter}}$

Let us consider a general reversible reaction:

$aA+bB \rightleftharpoons cC+dD$

Where *a*, *b*, *c* and *d* are stoichiometric coefficients of chemical species A, B, C and D, respectively.

According to the law of mass action:

- Rate of forward reaction $\propto [A]^a [B]^b$
- $R_f \propto [A]^a [B]^b$
- $R_f = K_f [A]^a [B]^b$........................ (i)

In this expression, K_f is the rate constant for the forward reaction, while $[A]$ and $[B]$ represent the active mass or molar concentrations of reactants A and B.

Similarly, for the backward reaction:

- Rate of backward reaction $\propto [C]^c[D]^d$
- $R_b \propto [C]^c[D]^d$
- $R_b = K_b [C]^c[D]^d$........................ (ii)

In this expression, K_b is the rate constant for the backward reaction, while $[C]$ and $[D]$ represent the active mass or molar concentrations of products C and D

At equilibrium,

Rate of forward reaction = Rate of backward reaction

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

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

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

Where, Kc is the equilibrium constant and represents the ratio of the rate constant for the forward reaction to the rate constant of the backward reaction.

The equilibrium constant is defined as the ratio of the product of the active masses of the products to the products of active masses of reactants, with each concentration term raised to a power equal to the stoichiometric coefficient of the substance in the balanced chemical equation

Equilibrium constant in terms of partial pressure:

The partial pressure of a gaseous substance is directly proportional to its molar concentration or active mass. This relationship can be derived from the ideal gas equation:

- $PV=nRT$
- $P = \frac{n}{V} RT$

Where:

- P is partial pressure.
- V is volume in litres.
- n is number of moles.
- R is the universal gas constant.
- T is absolute temperature.

P=CRT where, $C=\frac{n}{V}$ (molar concentration or active mass)

For a specific substance A,

i.e. $P_A=C_A RT=[A]RT$

$P_A \propto [A]$

For the reaction

$aA+bB \rightleftharpoons cC+dD$

the equilibrium constant in terms of partial pressure is represented by

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

Where, P_A, P_B, P_C, and P_D represent the partial pressures of the respective substances A, B, C, and D.

Characteristics of Equilibrium Constant:

The characteristics of equilibrium constants are as follows:

1. Equilibrium constant is fixed for a particular reaction at a particular temperature.
2. It does not depend upon the concentration of reactants and products.
3. It is independent of the presence of a catalyst.
4. It depends upon the temperature; for an exothermic reaction, it is inversely proportional to the temperature, and for an endothermic reaction, it is directly proportional to the temperature.

Significance of Equilibrium Constant:

• High Value (Kc>1): This indicates a higher concentration of products than reactants, meaning the rate of the forward reaction is higher than the rate of the backward reaction.

• Low Value (Kc<1): This indicates a higher concentration of reactants than products, meaning the rate of the backward reaction is higher than the rate of the forward reaction.

Equilibrium expression of some reactions:

While writing equilibrium expressions, certain conventions are used:

1. If a solid is involved in the equilibrium, its concentration remains constant. Therefore, by convention, the concentration of active mass of all solids is taken as unity, i.e. [Solid] = 1.
2. If a pure liquid is in equilibrium with some gases, the concentration of the pure liquid is taken as unity, i.e. [Pure liquid] = 1.

Relationship between *Kc* and *Kp*:

Consider a general reversible reaction:

$aA+bB \rightleftharpoons cC+dD$

The equilibrium constant in terms of concentration or active mass is:

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

(Where [A], [B], [C], and [D] are the active masses of A, B, C, and D respectively).

The equilibrium constant in terms of partial pressure is:

$$K_p = \frac{[P_C]^c\ [P_D]^d}{[P_A]^a\ [P_B]^b} \text{..........(ii)}$$

(Where P_A, P_B, P_C, and P_D are the partial pressures of A, B, C, and D respectively).

From the ideal gas equation:

• $PV=nRT$
• $P = \frac{n}{V} RT$
• $P=CRT$ (Where $C=\frac{n}{V}$, representing molar concentration or active mass).

By applying this to each substance:
• $P_A = C_ART = [A]RT$
Similarly, $P_B=[B]RT$, $P_C=[C]RT$, and $P_D=[D]RT$

Substituting these values into equation (ii):

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

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

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

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

Where:
• $\Delta n=(c+d)-(a+b)$
• Δn represents the difference between the total number of moles of the products and the total number of moles of reactants.

Special Condition:
• When $\Delta n=0$, then $Kp=Kc$.

Le-Chatelier's Principle

The principle states that if a system already in equilibrium is subjected to a change in these factors, the equilibrium shifts in a way that nullifies the effect of the change.

Important Conclusions of the Principle

• **Effect of change in concentration**: Increasing concentration causes the equilibrium to shift toward the direction where the added concentration is consumed.

• **Effect of change in pressure**: Increasing pressure shifts the equilibrium toward the side where the volume or number of moles is decreased.

• **Effect of change in temperature**: Increasing temperature causes the equilibrium to shift in the direction where heat is absorbed.

Application of Le-Chatelier's Principle:
Formation of Ammonia
The sources apply these rules to the chemical reaction:
$3H2(g)+N2(g) \rightleftharpoons 2NH3(g), \Delta H=-92.5kJ$.

• Effect of Concentration: Increasing the concentration of the reactants ($H2$ and $N2$) shifts the equilibrium in the forward direction to consume them. Conversely, the opposite occurs if concentrations are decreased.
• Effect of Pressure: In this specific reaction, 4 moles of reactants (3 moles of hydrogen and 1 mole of nitrogen) combine to produce 2 moles of ammonia. Because the number of moles decreases from the reactant side to the product side, increasing pressure shifts the equilibrium in the forward direction.
• Effect of Temperature: The forward reaction is exothermic (releasing heat), while the backward reaction is endothermic (absorbing heat). Therefore, increasing the temperature causes the equilibrium to shift toward the backward side, while decreasing it shifts the reaction forward

Answers:- **Relation of kp and kc**

(a) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

→ no. of mole in product = 2

→ no. of mole in reactant = 3+1 = 4

$\Delta n = 2 - 4$

$= -2$

$Kp = Kc\, RT^{\Delta n}$

$Kp = Kc\, RT^{-2}$

$\boxed{Kp = \frac{Kc}{(RT)^2}}$

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

→ In product = 2

→ In reactant = 1+1 = 2

$\Delta n = 2 - 2$

$= 0$

$Kp = Kc\, RT^{0}$

$\boxed{Kp = Kc}$

Expression for K_c:

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

$K_c = \frac{\text{concentration of } \cancel{\text{...}} \text{ product}}{\text{concentration of reactant}}$

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

Note:- Take only gaseous reactant & product

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(c) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$K_c = [CO_2]$

Analyze equilibrium

(a) $2SO_2(g) + O_2(g) \underset{endo}{\overset{exo}{\rightleftharpoons}} 2SO_3(g) + Heat$

2 1 3 2 2

For Temperature,

→ ~~On~~ The reaction is exothermic, so on increasing temperature it favours to endothermic i.e. backwards.

→ Likewise on decreasing, equilibrium shift to forward rxn.

For pressure,

→ On increasing pressure, equilibrium shift to forward rxn as reactant mole is greater than product mole.

→ on decreasing pressure, equilibrium shift to backward.

Ans key :-

1 (c) → $K_p = K_c(RT)$

2 (b) → $K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]}$

4 → No effect