

Chapter-8

Equilibrium

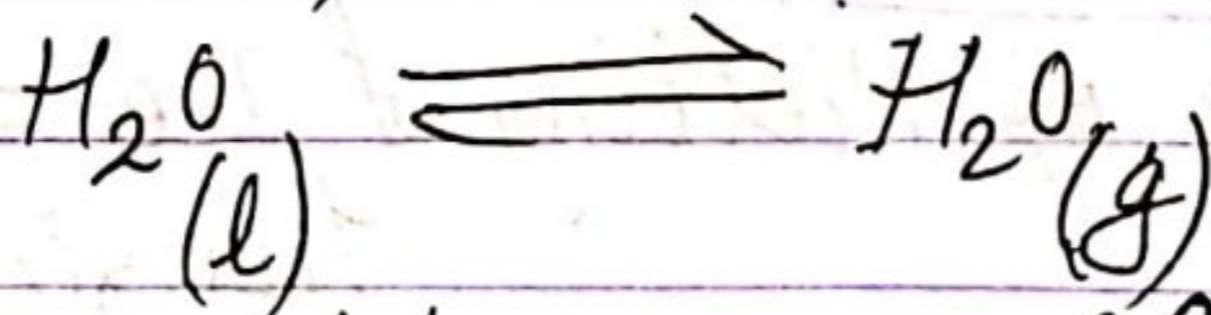
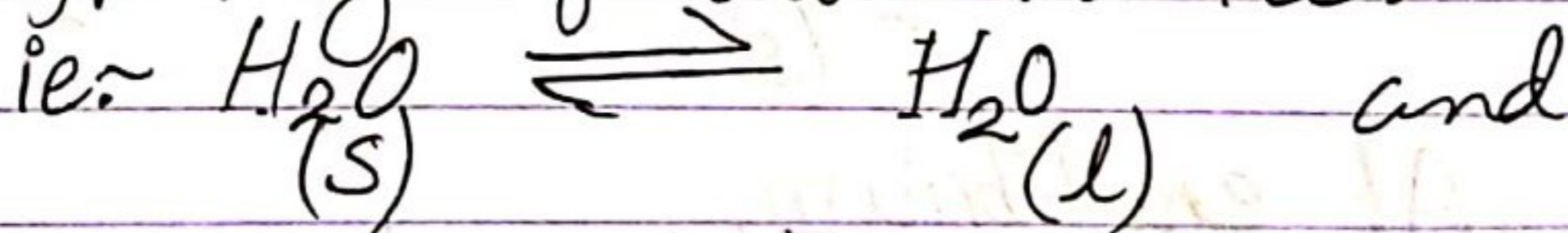
Equilibrium :- Equilibrium represents a state of a system at which measurable properties like - temperature, pressure and concentration of the system are not changed with the time. Equilibrium always involve between two opposing process once they proceed with same speed.

Equilibrium is of 2 types;

- (a) Physical equilibrium and
- (b) Chemical equilibrium

Physical equilibrium :- If opposing process involve only the physical change then, equilibrium is said to be physical equilibrium.

* for eg; Melting of ice into water & freezing of water into ice.



Chemical equilibrium :- If opposing process involve only the chemical changes then, equilibrium is said to be chemical equilibrium.

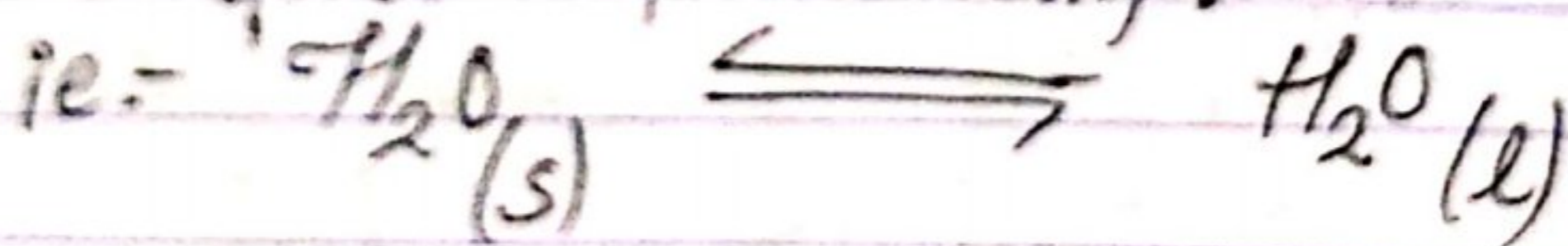


Equilibrium involving the physical changes :-

physical equilibrium exist between physical transformation like:- melting of ice to water, evaporation of water to vapour, etc is physical equilibrium.

Equilibrium involving the physical changes are following types :-

(a) Solid-liquid equilibrium :- The equilibrium exists between solid and liquid state of a same substance at normal melting point is said to be solid-liquid equilibrium. The equilibrium exist between solid, liquid and water at $0^\circ C$ is solid-liquid equilibrium.



At equilibrium,

\therefore Rate of Melting of Ice = Rate of Freezing point of water

(b) Liquid-Vapour equilibrium :- If liquid is in equilibrium with vapour, it

is said to be liquid-vapour equilibrium.
* for eg; Heating of water in a closed vessel. i.e.
$$\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}_2\text{O}(\text{g})$$

At equilibrium,

\therefore Rate of evaporation = Rate of condensation

(c) Solid-solution equilibrium :- The equilibrium exist between dissolved solute particles in saturated solution and undissolved solute particles is said to be solid-solution equilibrium.

* for eg;
$$\begin{array}{l} \text{NaCl}(\text{s}) \rightleftharpoons \text{NaCl}(\text{aq}) \\ \text{CuSO}_4(\text{s}) \rightleftharpoons \text{CuSO}_4(\text{aq}) \end{array}$$

(d) Gas-solution equilibrium :- The equilibrium exist between dissolved gas in solution and undissolved gas at constant pressure is said to be gas-solution equilibrium.

* for eg; CO_2 gas in coca-cola beverage
i.e.
$$\text{CO}_2(\text{g}) \rightleftharpoons \text{CO}_2 \text{ in solution}$$

Reversible and Irreversible reaction :-
on observing the nature of direction of chemical reaction, they are

classified into 2 types;

- (i) Reversible reaction and
- (ii) Irreversible reaction.

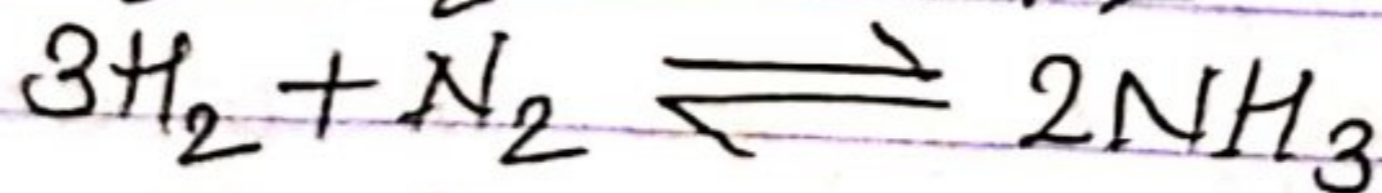
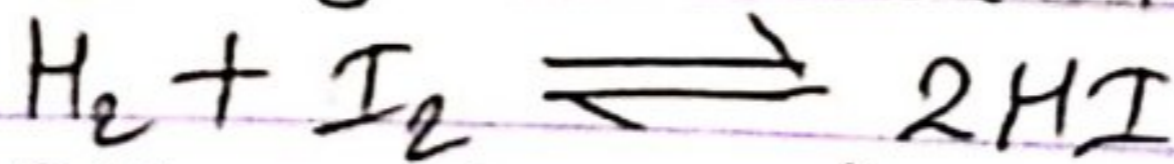
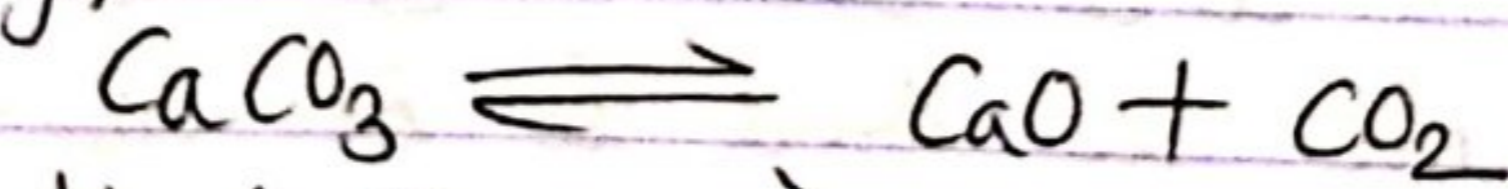
The chemical reaction which can proceed in both the direction, i.e.~ forward direction as well as in back-ward direction is called reversible reaction.

OR,

The chemical reaction in which product can give back the reactant under the suitable condition is also known as reversible reaction.

A double headed arrow (\rightleftharpoons) is placed between reactants and products in the reversible reaction.

* For eg;



The chemical reaction having the direction from reactant to product side is called forward reaction and the chemical reaction having the dire-

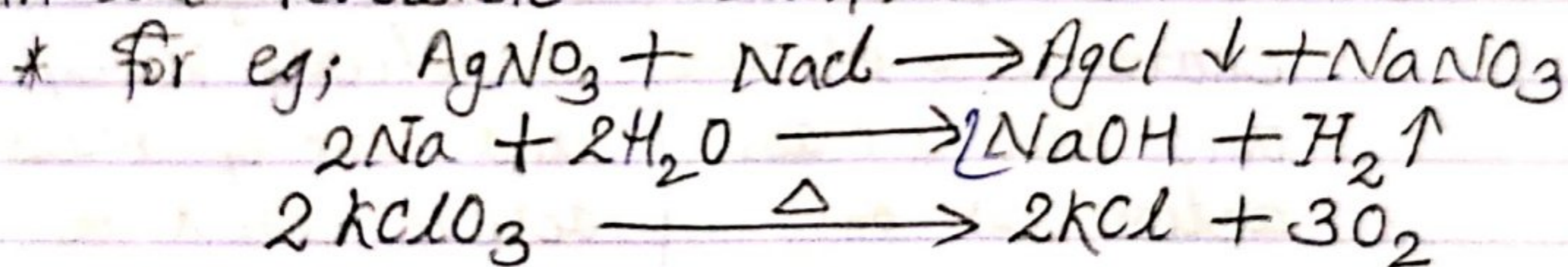
-action from product to reactant side is called backward reaction.

The chemical reaction which can only proceed in one direction, i.e.~ reactants to products is called irreversible reaction.

OR,

The chemical reaction in which product can't give back the reactant under the suitable condition is called irreversible reaction.

A single headed arrow (\longrightarrow) is placed between the reactants and products in the reversible reaction.



> Differences between the reversible and irreversible reaction :-

Reversible reaction	Irreversible reaction
It can proceed in both the direction, i.e.~ both forward and in backward direction.	It is unidirectional; can proceed in only one direction.

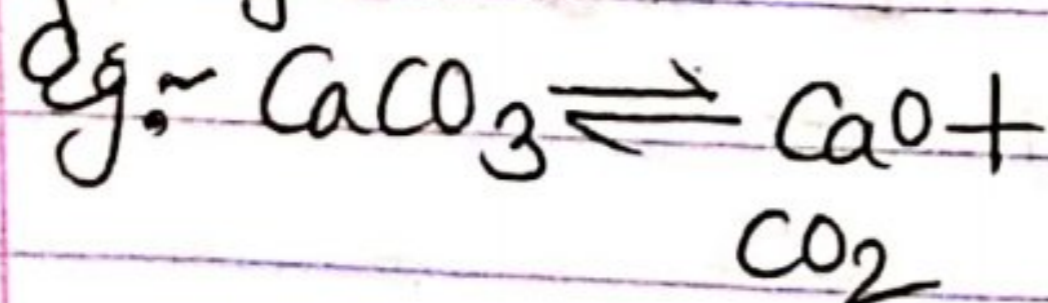
Reversible reaction

(i) A double headed arrow (\rightleftharpoons) is placed between reactants and products in it.

(ii) It follows the condition of equilibrium.

(iii) It can follow Le-Chatelier's principle and law of mass action can be applied on it.

(iv) Always in closed



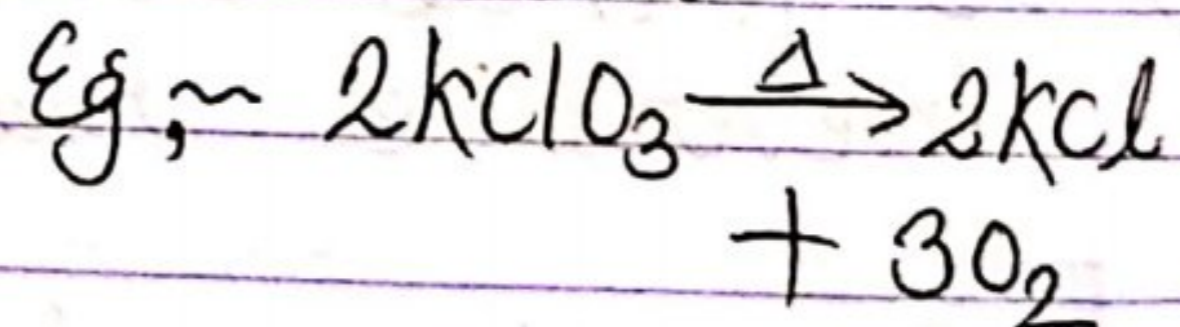
Irreversible reaction

A single headed arrow (\rightarrow) is placed between reactants and products in it.

It does not follow the condition of equilibrium.

It can't follow Le-Chatelier's principle and law of mass action can't be applied on it.

(v) Both in closed and open



Nature of chemical equilibrium :-

Chemical reactions are proceeding by changing reactant into product. But, in reversible reaction, reaction proceed in both direction.

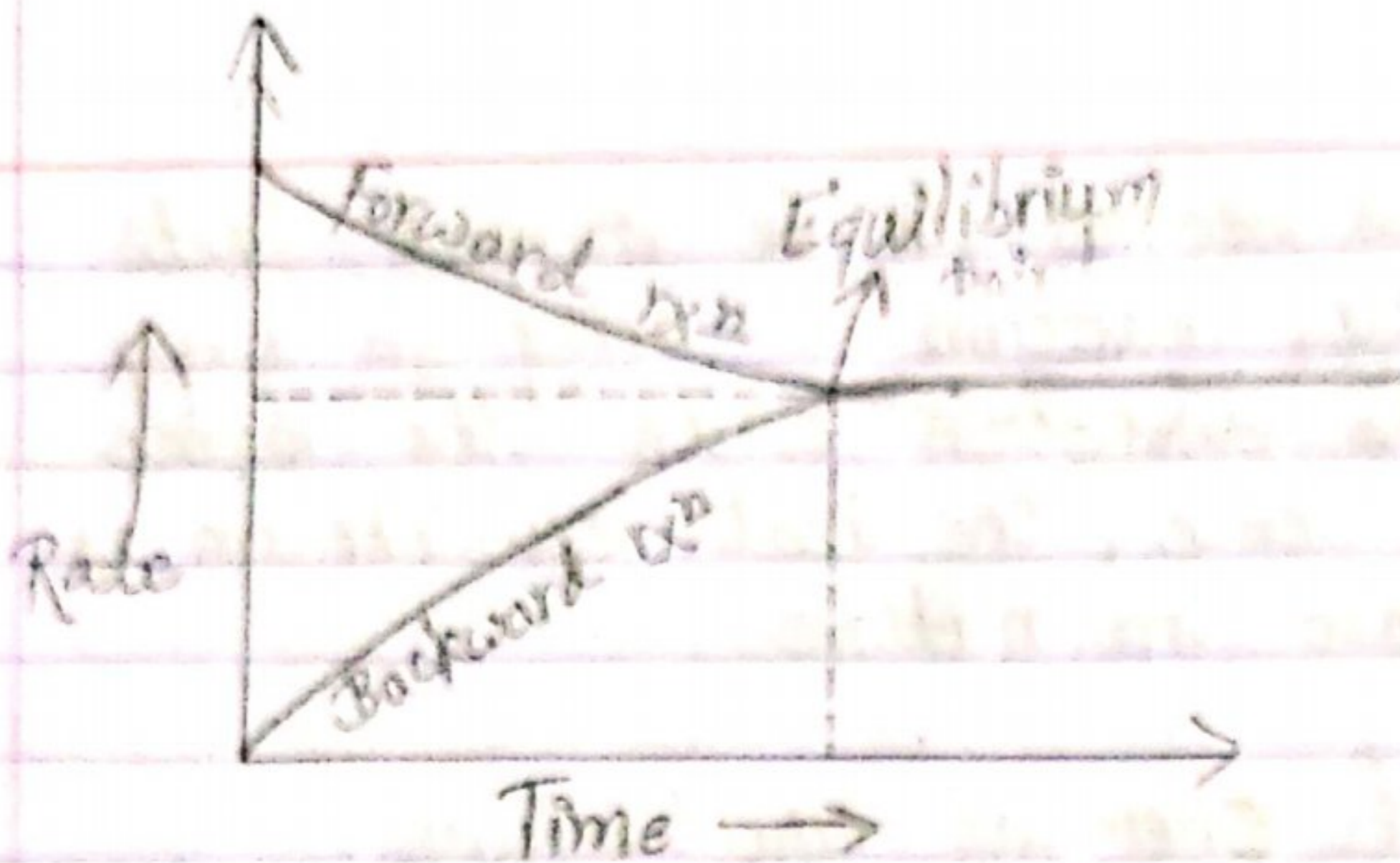


Fig:- Variation of rate vs time.

Initially, concentration of reactant is high. So, that, rate of reaction is also high. After passage of time, products starts to convert back into the reactants. During this process, a state will come at which concentration of reactant becomes equal to the concentration of product is observed and is said to be in equilibrium.

Therefore, equilibrium is a state of a reversible reaction at which concentration of reactant and concentration of product do not change with the time. At equilibrium, rate of forward reaction is equal to the rate of backward reaction.

*In the given figure;

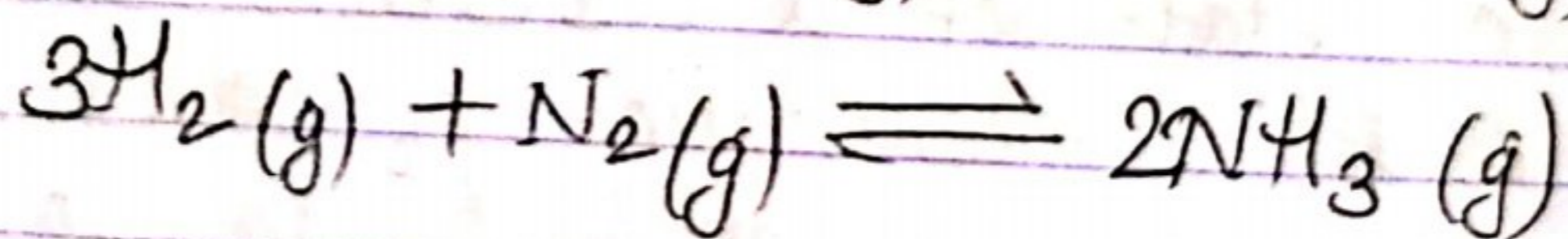
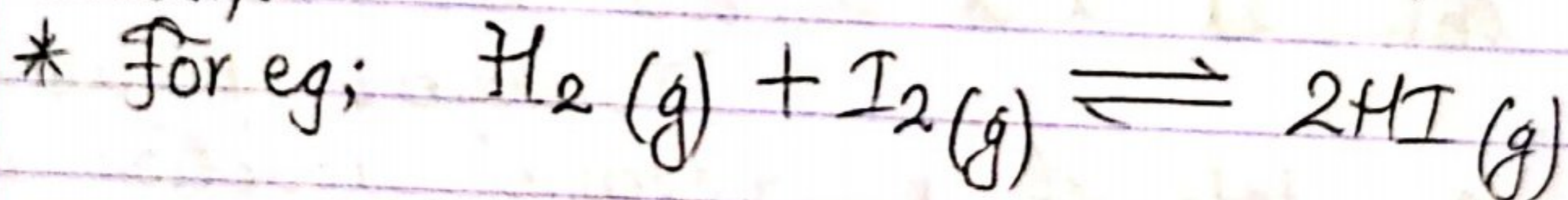
At equilibrium, the

reactions seems to be stopped, but actually, reaction is going on along both the direction with the same speed. Hence, chemical equilibrium is dynamic in nature.

Types of chemical equilibrium :-
(i) Homogeneous and
(ii) Heterogeneous.

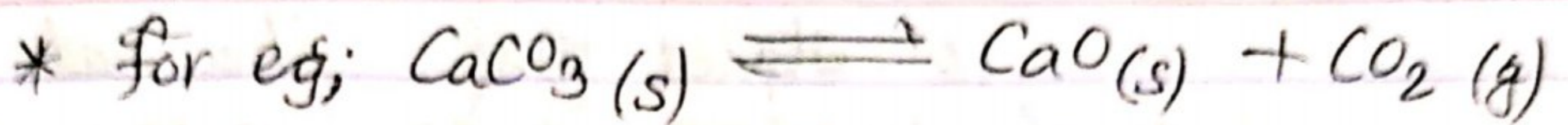
1. Homogeneous chemical equilibrium :-

The chemical equilibrium in which participating all the species, i.e. reactant and product are at the same phase or state is said to be homogeneous chemical equilibrium.



2. Heterogeneous chemical equilibrium :-

The chemical equilibrium in which reactants and products are not at the same phase (i.e. different phase or state) is said to be heterogeneous chemical equilibrium.



Characteristics of the chemical equilibrium :-

- (i) Chemical equilibrium is dynamic in nature, i.e. - though the reaction seems to be stopped but actually reaction is going on along both the side with same speed.
- (ii) Chemical equilibrium can be approached from both the sides.
- (iii) Chemical equilibrium can be readjust by changing the condition.
- (iv) Chemical equilibrium can't be affected by presence of catalyst.
- (v) Chemical equilibrium can be affected by temperature, pressure and concentration.
- (vi) Chemical equilibrium reached only in closed vessel in reversible reaction.

Law of mass action :-

Two Norwegian Chemist

Guldberg and Waage in 1867, put forwarded a quantitative relationship between rate of chemical reaction and concentration of active mass is known as law of mass action.

It states that, "the rate of chemical reaction is directly proportional to active mass of the reactant and if there are more than one reactants, then rate of chemical reaction is directly proportional to the product of active mass of reactant."

The term 'active mass' refers to molar concentration, i.e. $[\text{mol L}^{-1}]$ and for gaseous reactants, pressure in atmosphere. Active mass of the substance can be expressed inside the square brackets and raise to the power, equal to stoichiometric coefficient in the balanced chemical equation.

* For eg; - Active mass of a substance 'A' can be written as $[A]$, i.e. $A \rightarrow [A]$.

Let us consider a reversible reaction; $aA + bB \rightleftharpoons cC + dD$

According to the law of mass action,

$$\therefore \text{Rate of forward rxn } (R_f) \propto [A]^a [B]^b$$
$$\therefore R_f = k_f [A]^a [B]^b \quad \text{--- (i)}$$

where k_f is proportionality constant and is called rate constant for forward reaction.

Similarly,

Rate of backward reaction (R_b) \propto $[C]^c [D]^d$

$$\therefore R_b = k_b [C]^c [D]^d \quad \text{--- (ii)}$$

where k_b is proportionality constant and is called rate constant for backward reaction.

At equilibrium condition,
Rate of forward reaction = Rate of backward reaction.

$$k_f [A]^a [B]^b = k_b [C]^c [D]^d$$

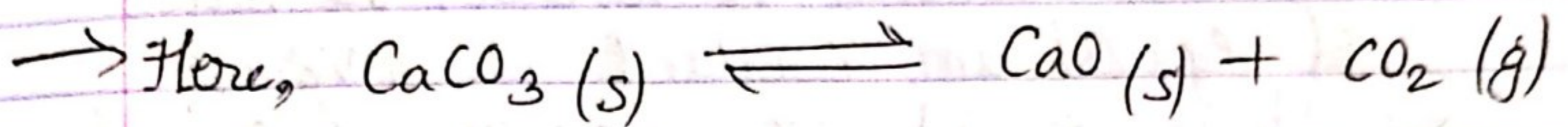
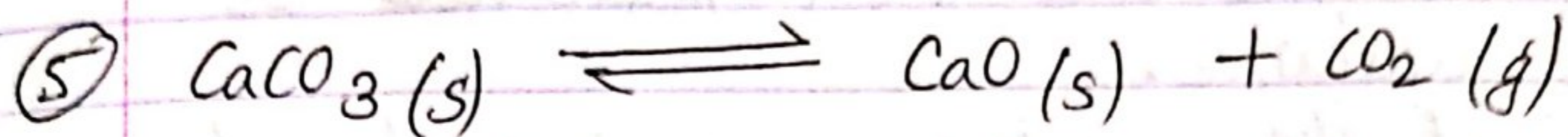
$$\frac{k_f}{k_b} = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

$$\therefore K = \frac{[C]^c [D]^d}{[A]^a [B]^b} \quad \text{--- (iii)}$$

where, $K = \frac{k_f}{k_b}$ is known as equilibrium constant and k_b is defined as the ratio of rate constant for forward rxn, to the rate constant for backward rxn. Larger the value of equilibrium constant, higher will be the rate of reaction.

$$\therefore K_{\text{equil.}} = \frac{[\text{NO}]^2}{[\text{N}_2][\text{O}_2]}$$



$$\therefore K_{\text{equil.}} = \frac{[\text{CaO}(\text{s})][\text{CO}_2(\text{g})]}{[\text{CaCO}_3(\text{s})]}$$

$$= \frac{[1][\text{CO}_2(\text{g})]}{[1]}$$

$$= [\text{CO}_2(\text{g})]$$

[Note:- In case of heterogenous chemical equilibrium, concentration of pure solid and pure liquid are taken as constant (ie.~ unity).]

Characteristics of the equilibrium constant :-

① Equilibrium constant has constant value under the given condition of temperature and pressure.

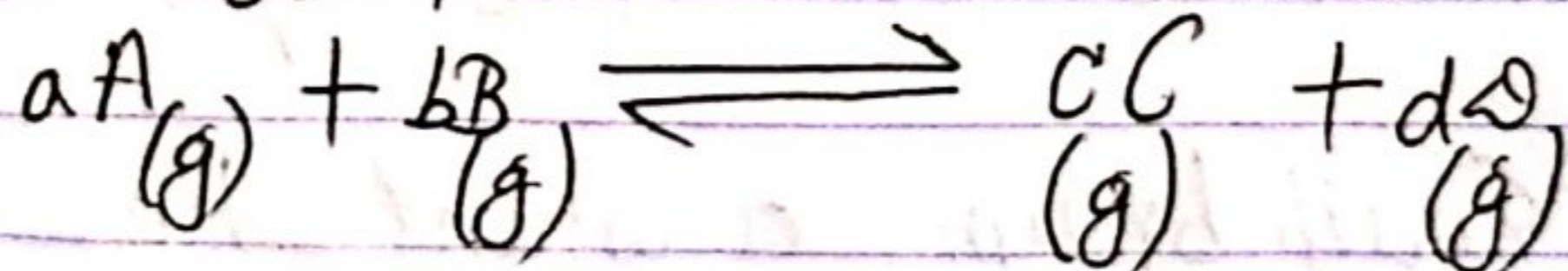
② Equilibrium constant have different value for different reaction.

- ③ It is independent of initial concentration of reactant and product, presence of catalyst and inert materials or substance.
- ④ If the reaction is reverse, the value of equilibrium constant is inverted.
- ⑤ It is significant measure of extent to which direction, reaction proceed.

VI # Relationship between K_p and K_c :-
 For a gaseous reversible reaction; equilibrium constant can be expressed in terms of molar concentration as well as in terms of partial pressure.

Equilibrium constant in terms of molar concentration can be written as ' K_c ' and equilibrium constant in terms of partial pressure can be written as ' K_p '.

Let us consider a reversible gaseous reaction.



Equilibrium constant in terms of molar concentration can be written as;

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

and, Equilibrium constant in terms of partial pressure can be written as;

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

where P_A , P_B and P_C and P_D are partial pressure for A, B, C and D respectively.
Now,

We have, an ideal gas equation, i.e.

$$\therefore PV = nRT$$

$$\text{or, } P = \frac{n}{V} RT$$

$$\text{or, } P = CRT \quad \left[\because C = \frac{n}{V} \right]$$

$$\therefore P_A = \frac{n_A}{V} RT = C_A RT = [A] RT$$

Similarly,

$$\therefore P_B = \frac{n_B}{V} RT = C_B RT = [B] RT$$

$$\therefore P_C = \frac{n_C}{V} RT = C_C RT = [C] RT$$

$$\therefore P_D = \frac{n_D}{V} RT = C_D RT = [D] RT$$

Now,

Substituting the value of P_A , P_B , P_C and P_D in eq. (ii); we get,

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

$$\boxed{\therefore K_p = K_c (RT)^{\Delta n}} \text{----- (iii)} ; \text{ where}$$

$$\begin{aligned}
 \Delta n &= (c+d) - (a+b) \\
 &= \text{no. of moles of gaseous} \\
 &\quad \text{product} - \text{no. of moles of} \\
 &\quad \text{gaseous reactant.}
 \end{aligned}$$

Hence,

Equation (iii) is the required relationship between K_p and K_c .

Note :-

① When $K_c > 1$, molar concentration of product is higher than molar concentration of reactant.

② When $K_c < 1$, molar concentration of product is less than that of reactant.

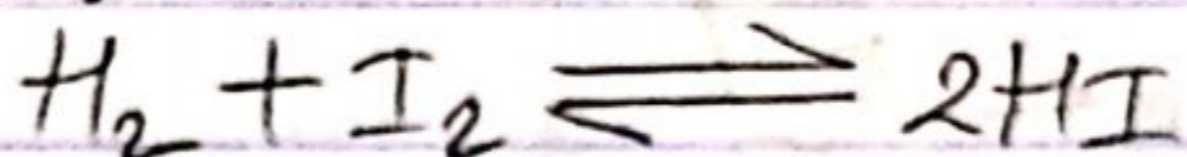
③ When $K_c = 1$, molar concentration of reactant and product are equal.

Special cases :-

* CASE 1 : If $\Delta n = 0$, then

$$K_p = K_c$$

For example :-



$$\text{Here, } \Delta n = 2 - (1+1) = 2 - 2 = 0$$

$$\therefore \Delta n = 0$$

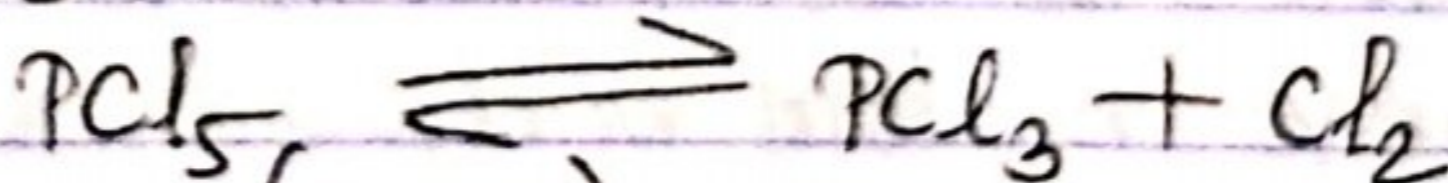
$$\text{So, } K_p = K_c \cdot (RT)^{\Delta n} = K_c \cdot (RT)^0 = K_c$$

$$\boxed{\therefore K_p = K_c}$$

* CASE 2 : If $\Delta n > 0$, then

$$K_p > K_c$$

For example :-



$$\text{Here, } \Delta n = (2+1) - 1 = 2$$

$$\therefore \Delta n = 2$$

$$\text{So, } K_p = K_c \cdot (RT)^{\Delta n} = K_c (RT)^2 = K_c (RT)^2$$

$$\boxed{\therefore K_p > K_c}$$

* CASE 3 : If $\Delta n < 0$, then
 $K_p < K_c$

For Example :-



Here,

$$\Delta n = 2 - (3+1) = -2$$

So,

$$K_p = K_c (RT)^{\Delta n} = K_c (RT)^{-2} = \frac{K_c}{(RT)^2}$$

$$\therefore K_p < K_c$$

VI # Le-chatelier's principle :-

A French chemist Le-chatelier in 1884, study the effect of temperature, pressure, and concentration on the state of equilibrium is known as Le-chatelier's principle.

It states that, "If a system in equilibrium is subjected to change in temperature, pressure and concentration, then equilibrium will shift automatically to that direction so as to nullify the effect of that change."

* Conclusion :-

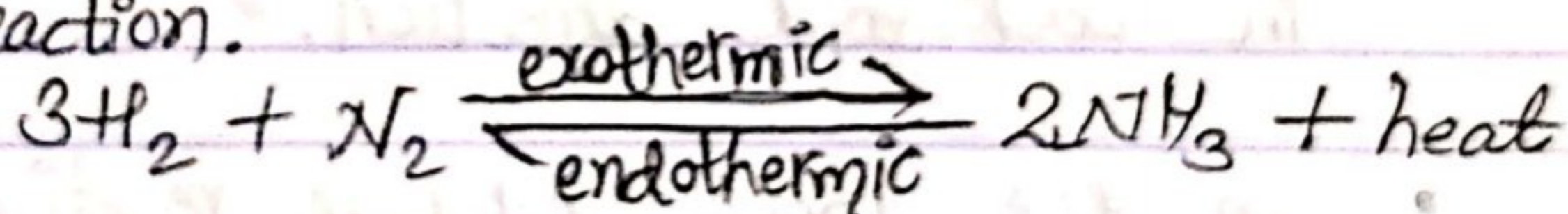
(i) On increasing temperature, equilibrium will

shift towards that direction where heat energy is absorbed, i.e. towards endothermic reaction and vice-versa.

(ii) On increasing pressure, equilibrium will shift towards that direction where no. of moles (volume) of gas is least and vice-versa.

(iii) On increasing concentration, equilibrium will shift towards that direction where increased concentration are consumed, i.e. on increasing concentration of reactant, equilibrium will shift towards product side.

Let us consider an exothermic chemical reaction.



Obviously, the forward reaction is exothermic whereas the backward reaction is endothermic.

- In this reaction, on increasing the temperature, according to Le-Chatelier's principle, equilibrium will shift towards that direction where heat energy is absorbed (endothermic reaction), i.e. reaction in backward direction. Similarly, on decreasing the temperature, equilibrium will shift towards that

direction where heat energy is released (exothermic reaction), i.e. reaction in forward direction.

- In this reaction, on increasing the pressure, according to Le-Chatelier's principle, the equilibrium will shift towards that direction where numbers of moles is the least, i.e. reaction in forward direction. Similarly, on decreasing the pressure, equilibrium will shift towards that direction where number of moles is most, i.e. reaction in backward direction.

- In the above chemical reaction, on increasing the concentration according to Le-Chatelier's principle, equilibrium will shift towards that direction where increased concentration are consumed, i.e. on increasing the concentration of either H_2 , N_2 or both, equilibrium will shift towards products (i.e. NH_3) side.

Application of Le-Chatelier's principle :-

towards the forward side. So increase in pressure, equilibrium will shift towards the forward side and more ammonia will be formed. On other hand, decrease in pressure, equilibrium will shift towards the backward and production of ammonia will be low.

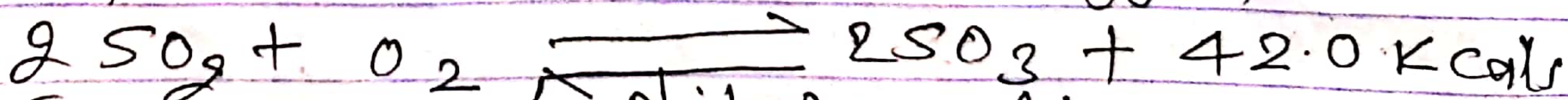
c) Effect of change in concentration:
 When concentration of N_2 or H_2 is increased at equilibrium, then equilibrium will shift towards the forward side. i.e. on increasing concentration of any species (reactants or products) then equilibrium will shift in that direction where increased concentration is consumed.

Hence formation of NH_3 is favoured by
 a) low temperature (optimum temperature is about $450^\circ C$)

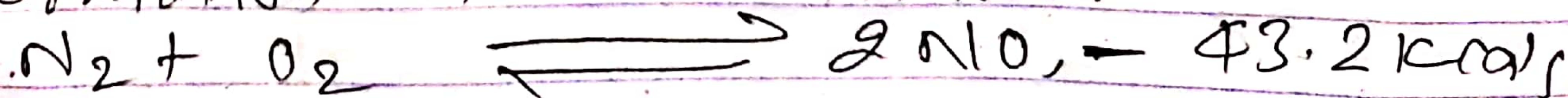
b) High pressure

c) High concentration

2. Formation of sulphur trioxide from sulphur dioxide and oxygen.

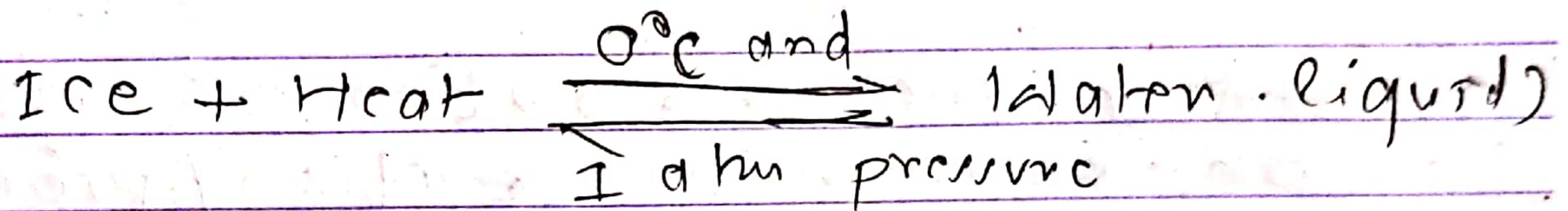


3. Formation of Nitric oxide:



⊕ Application of Le-Chatelier's principle is physical equilibrium:-

1. Let us take an example of melting of ice,

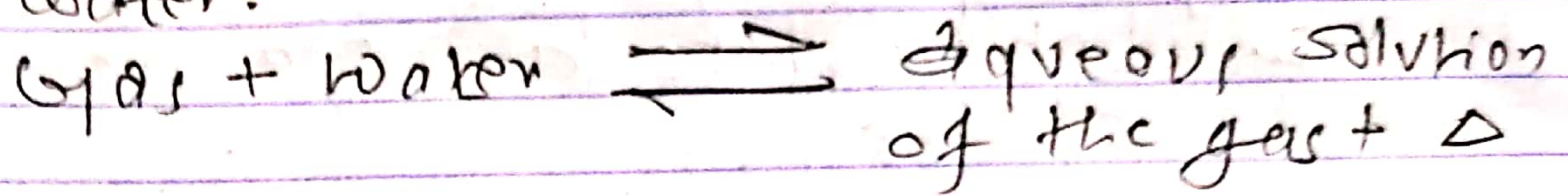


a) Effect of change in temperature
Since the melting of ice endothermic process, increase in temperature, equilibrium will shift in forward side form more liquid water and decrease in temperature shifts the equilibrium backward to form more ice.

b) Effect of change in pressure:
For the given mass of water, ice has more volume than liquid water. On increasing the pressure the equilibrium shifts to that side where volume is decreased, i.e. towards liquid water side. On decreasing the pressure, the equilibrium shift to that where volume is more i.e. towards ice side.

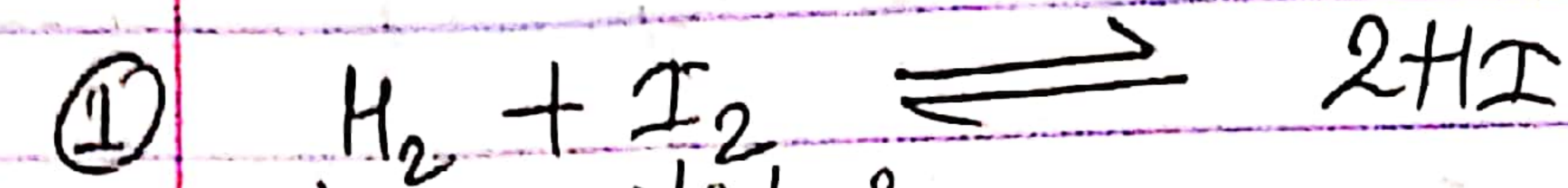
This implies that, melting of ice is favoured at high temperature and high pressure.

2. Let us consider dissolution of a gas in water.

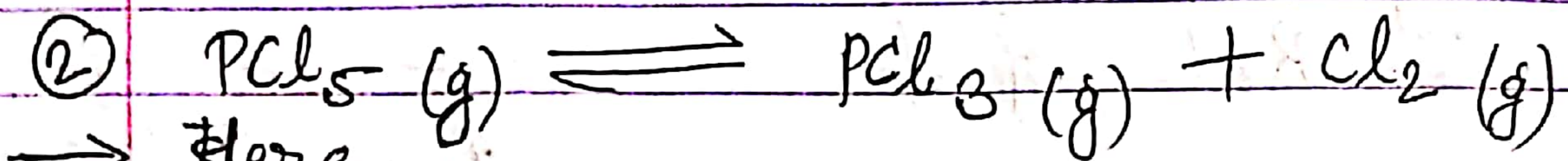


Since the dissolution of gas is an exothermic reaction/process and proceeds by the decrease in the volume, the favourable condition for the dissolution of the gases is low temp. and high pressure.

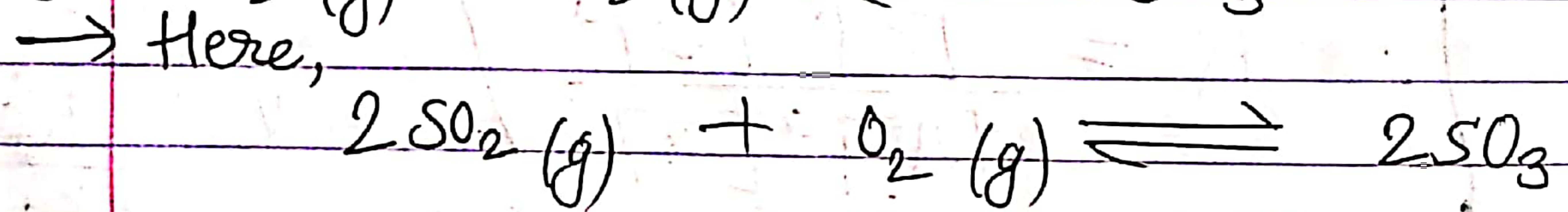
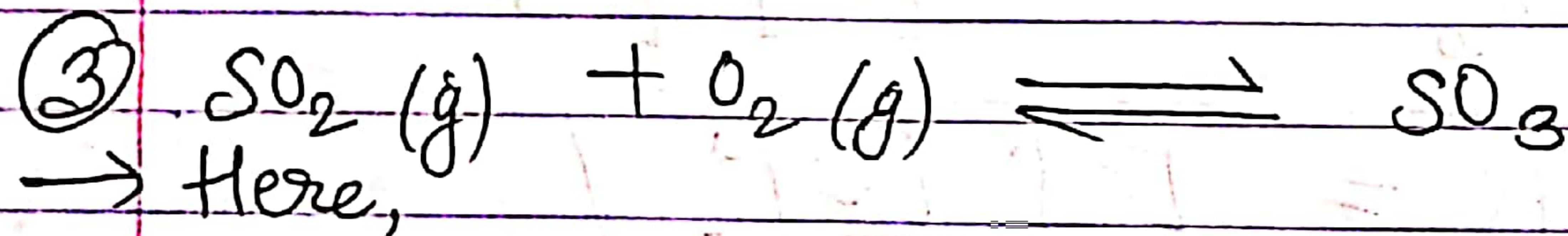
⇒ Expression of equilibrium constant for the following reaction :-



→ At equilibrium,
$$K = \frac{[\text{HI}]^2}{[\text{H}_2][\text{I}_2]}$$



→ Here,
At equilibrium,
$$K = \frac{[\text{PCl}_3][\text{Cl}_2]}{[\text{PCl}_5]}$$



At equilibrium,
$$K = \frac{[\text{SO}_3]^2}{[\text{SO}_2]^2[\text{O}_2]}$$

