Equilibrium

~~Reversible reaction.~~

Introduction

- Changes can be physical or chemical and reversible or irreversible.

- Examples of natural irreversible processes: Natural waterfall, spreading of smoke from burning inscene stick,

Irreversible Chemical reaction:

A reaction which proceeds only in one direction, from reactants to products and the products do not have any tendency to reform the ~~reactiants~~ reactants is called an irreversible reaction.

- Irreversible reactions proceed until one of the reactants is exhausted.
- Their directions is indicated by an arrow ($\rightarrow$) pointing towards the products.

ex

$$C_{(s)} + O_2(g) \longrightarrow CO_2(g)$$

$$2KClO_3(s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$$

Reversible chemical reaction

Reversible reactions are those in which the reactants react to generate the products and the products have the tendency to react and generate the ~~reacto~~ reactants

- Reversible reactions proceed in both directions.
- The directions from reactants to products is the forward reaction where as the opposite reation from products to reactants is the reverse or backward reaction.
- The reversible reaction is denoted by a double arrows in opposite directions ($\rightleftarrows$)
- Reversible reaction does not go to completion

ex.

$$N_2(g) + 3H_2(g) \rightleftarrows 2NH_3(g)$$

- In a closed system, there is no exchange of matter with the surrounding but exchange of heat can occur.

- In a open system, exchange of both matter and heat occurs with the surroundings. An isolated system does not exchange heat nor matter with surrounding.

Decomposition of CaCO, occuring in (a) an open system and (b) a contaneir.

a) In a open system, the decomposition of CaCO is represented as

$$CaCO_3(s) \xrightarrow{heat} CaO(s) + CO_2(g)$$

Since $CO_2(g)$ formed in the reaction escapes This is a unidirectional irreversible reaction

b) In a closed container, the reaction goes in both opposite directions, hence it is a reversible reaction

$$CaCO_3(s) \underset{}{\overset{heat}{\rightleftharpoons}} CaO(s) + CO_2(g)$$

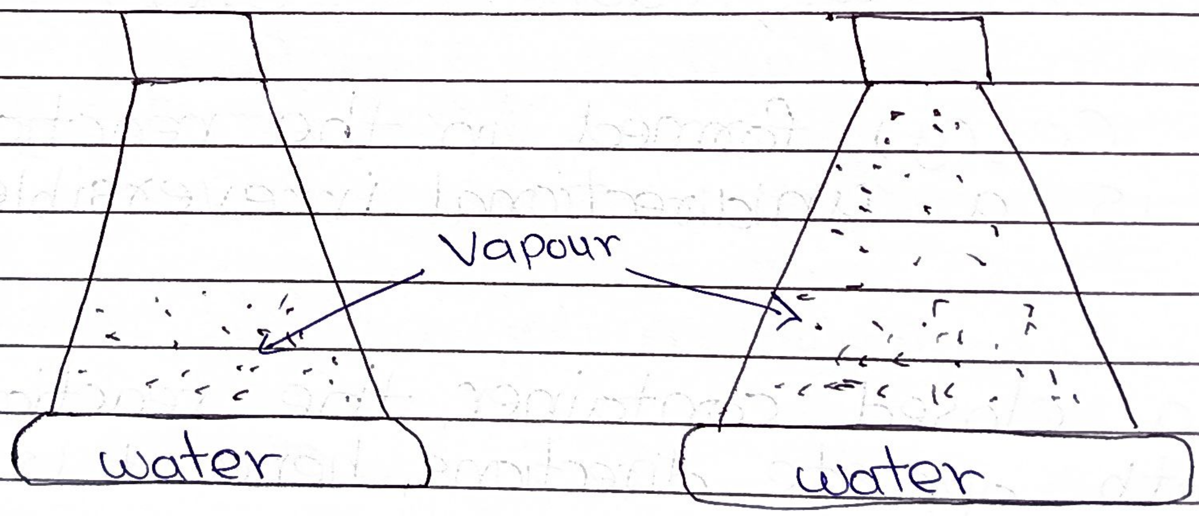
Equilibrium in physical processes

Physical equilibrium:

The equilibrium attained between two phases of the same substance when the rates of forward and reverse changes are equal is called physical equilibrium.

Liquid - Vapour equilibrium

Consider evaporation of liquid water into water vapour in a closed vessel.



~~tnl~~ initially later

water in a closed flask

- Initially the vapour content above liquid in a closed vessel is very less.

- The liquid molecules have tendency to esape into vapour phase increasing vapour pressure

- The vapour molecules have a tendency to condense. Hence, it is a reversible process.

$H_2O\,(l) \rightleftharpoons H_2O\,(\text{vapour})$

- At start, the rate of evaporation is high and the rate of condensation is low. But with times, the rate of evaporation decrease and the rate of condensation increases.

- After a certain ~~ca~~ time, both the opposite rates become equal achieving an equilibrium state

Saturated vapour pressure or aqueous tension.

The pressure exerted by the water molecules in the vapour at equilibrium at a given temperature over the liquid water is called saturated vapour pressure.

Effect of temperature

- As the temperature increases, the saturated vapour pressure increases

- In case of water, the saturated vapoure pressure is [illegible] atm at 100°C, which is

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Solid - liquid equilibrium.

- Consider a mixture of ice and water in a perfectly insulated thermos flask at 273 K

Ice (s) $\rightleftharpoons$ water (l)

In this, Solid ice exists in equilibrium with water

ex.

1) $I_2(s) \underset{\text{Condensation}}{\overset{\text{Sublimation}}{\rightleftharpoons}} I_2(g)$

2) Camphor (s) $\rightleftharpoons$ Camphor (g)

3) Ammonium chloride (s) $\rightleftharpoons$ Ammonium choloride (g)

Equilibrium in chemical process.

Chemical equilibrium :

When there is no further change in concentration of reactant and product, we say that the reaction has attained equilibrium, with the rates of forward and reverse reactions being equal

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

Law of mass action and equilibrium constant

Equilibrium constant (K_c):

The chemical equilibrium is mathematically described in terms of equilibrium constant (K_c).

Mathematical expression for Kc

Consider a reversible reaction

$$A(g) + B(g) \rightleftharpoons C(g) + D(g)$$

Rate ~~for~~ of forward reaction

$$r_f \propto [A] \times [B]$$

$$r_f = K_f [A] \times [B]$$

Rate of backward reaction

$r_b \propto [C] \times [D]$

$r_b = k_b [C] \times [D]$

At equilibrium $R_f = R_b$

$k_f [A] \times [B] = k_b [C] \times [D]$

$$\frac{k_f}{k_b} = \frac{[C] \times [D]}{[A] \times [B]}$$

k_f and k_b are constant

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

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

where K_c is equilibrium constant

Rate of Chemical Reactions

$$= -\frac{d[\text{Reactan}]}{dT} = \frac{d[\text{Product}]}{dT}$$

Law of action

The law of mass action states that the rate of a chemical reactions is directly proportional to the product of the active masses of the reactants, with each active mass team raised to a power equal to its respective stoichiometric coefficients in the balenced equation at a given temperature.

Exaplanation

~~Condis~~ Consider a general equation

$aA + bB \rightarrow$ Products

If $[A]$ and $[B]$ are the active masses

$$\text{Rate} \propto [A]^a \times [B]^b$$

Hence

$$\text{Rate} = k\,[A]^a \times [B]^b$$

This equation is called rate equation

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Equilibrium constant with respect to partial pressure (K_P)

Consider a gaseous reversible reaction,

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

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

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

Relationship between K_P and K_C

Consider a general reversible reaction

$$aA_{(g)} + bB_{(g)} \rightleftharpoons cC_{(g)} + dD_{(g)}$$

Now substituting equations for P_A, P_B, P_C, P_D in eq

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

Note:

For a mixture of ideal gases, the partial pressure of each component is directly proportional to its concentration at constant temperature

For component A

$$P_A V = n_A RT$$

$\frac{n_A}{V}$ is molar concentration of A in mol dm^{-3}

$$P_A = \frac{n_A}{V} \times RT \qquad \text{where } [A] = \frac{n_A}{V}$$

$$P_A = [A]RT$$

For a chemical equilibrium reaction, both equilibrium constants are equal

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

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

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

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

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

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

$\therefore \; \Delta n$ is (number of moles of gaseous product) − (number of moles of gaseous reactants)

$R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}$

Homogeneous and Heterogenous equilibria

Homogeneous : In a Homogeneous equilibrium state all the reactants are in the same phase.

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

Heterogenous :

In a heterogenous equilibrium results from a reversible reaction involving reactants and products those are in different phase

ex.

$NH_3(g) + Cl_2(g) \rightleftharpoons NH_4Cl(s)$

Equilibrium constant for heterogenous equilibria

As a started earlier, equilibrium in a system having more than one phase is called heterogenous equilibrium.

Calculate units of equilibrium constant

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

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

$$\text{Units of } K_c = \frac{[\text{mol dm}^{-3}]^2}{[\text{mol dm}^{-3}][\text{mol dm}^{-3}]}$$

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

1.

2.

3.

onstant

Characteristics of equilibrium constant

1. The value of equilibrium constant is inpendent of initial concentrations of either the reactants or products.

2. Equilibrium constant is temperature depender Hence Kc, Kp change with change in temperature.

3. Equilibrium constant has a characteristic value for a particular reversible reaction represented by a balanced equation at a given temperature

Application of equilibrium constant

Some applications of equilibrium constant are discussed below

Predication of the direction of the reaction

For the reaction

$aA + bB \rightleftharpoons cC + dD$

the equilibrium constant is

where all concentrations are equilibrium concentrations
The ratio is called reaction quotient Q_c when the concentrations are not necessarily equilibrium concentrations

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

If $Q_c < K_c$ the reaction will proceed from left to right, in forward direction, generating more product to attain the equilibrium

If $Q_c = K_c$ the reaction is at equilibrium and hence no net reaction occurs

If $Q_c > K_c$ the reaction will proceed from right to left, requiring more reactants to attain equilibrium.

Link between chemical equilibrium and chemical Kinetics

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

K_f = Velocity

K_r = rate constants of reverse reactions

Le chatealier's principle and factors altering the Composition of equilibrium

The principal goal of chemical synthesis is to achieve maximum conversion of reactants to products with minimum expenditure of energy.

Le chatelier's Principle

It states that, when a system at equilibrium is subjected to a change in any of the factors determining the equilibrium conditions of a system, system will respond in such a way as to minimize the effect of change.