4.8 Rates Of Chemical Reactions And Chemical Equilibrium

Chemical reactions vary extremely in their speed. Some of them proceed over a period of months, years, or even centuries. Others take weeks hours, minutes, or seconds to come to completion. The area of chemistry concerned with the study of the speeds or rates of a reaction is called chemical kinetics

4.8.1 Reaction Rate

As a chemical reaction proceeds, reactants are being used up and new products are formed. The quantity that changes in a chemical reaction is the amount (concentration) of a reactant or product.

The rate or speed of a reaction is the change in concentration of reactants or products per unit of time.

$$\textbf{Rate of reaction} = \frac{\textbf{change in concentration of reactant or product}}{\textbf{change in ime}} = \frac{\Delta C}{\Delta t}$$

From the above expression, it follows that the rate of a reaction is inversely proportional to the time taken by the reaction

$$\textbf{Rate} \propto \frac{1}{\textbf{Time}}$$

4.8.2 Preconditions For Chemical Reactions

For a chemical reaction to take place, the following three major factors should be fulfilled. These factors are called preconditions for chemical reactions.

1. Collisions (or contact) between reactants

Chemists believe that before atoms or molecules can react, they must collide (direct contact) with one another. If collision results in the formation of products, it is known us effective collision and if it does not yield the product, it is known as ineffective collision.

Note: All collisions between reacting molecules are not necessarily effective in bringing a reaction

2. Activation Energy

For the reaction to take place collision must always occur with sufficient energy to break the bonds in the reactants and form new bonds in the products. This minimum energy required by reactant molecules to undergo a reaction during collision is called activation energy.

3. Proper Orientation

Collision of molecules with sufficient energy will not bring a reaction if the reacting molecules are poorly oriented. Thus, the collision between reacting molecules should have the proper orientation

4.8.3 Factors That Affect The Rates Of Chemical Reaction

The rate of a chemical reaction depends largely on the number (frequency) of collisions which take place between the reacting substances and on the collision efficiency. Hence, any influence, that will affect either the frequency of collision of particles or the collision efficiency, will affect the reaction rate. The rate of a reaction is usually affected by one or more of the following factors.

1. Nature Of The Reactants

Under similar conditions the rates of different chemical reactions differ simply because of the nature of the reactants themselves.

For example, if hydrochloric acid, HCl, is added to pieces of magnesium(Mg), Iron (Fe) and copper (Cu) of equal size and shpe, the reaction of Mg with HCl is much more vigours. This is because Mg is more reactive than Fe and Cu

$Mg + 2HCl \longrightarrow MgCl_2 + H_2$ ..... (Very fast reaction)
$Fe + 2HCl \longrightarrow FeCl_2 + H_2$ …… (Slow reaction)
$Cu + 2HCl \longrightarrow FeCl_2 + H_2$ …… (Slow reaction)

2. Temperature

An increase in temperature increases the rate of any reaction and a decrease in temperature generally decreases the rate.

An increase in temperature of a reaction increases the movement (kinetic energy) of the reacting particles and this results in increasing the number of effective collisions between them causing the reaction to proceed faster than the original state

Examples of this generalization surround us. Plants grow more rapidly in warm weather than in cold. Food cooks faster in boiling water than in merely hot water, and it spoils faster at room temperature than when it is refrigerated.

3. Concentration Of Reactants

Chemical reactions take place when the appropriate atoms, ions or molecules approach and collide with one another. The greater the number of collisions, the more rapid wills the reaction rate. Thus, increasing the number of the reacting particles per unit volume (i.e. increasing the concentration) will cause more frequent collisions and hence an increase in the reaction rate. Lowering the concentration has the opposite effect- it decreases the rate of a reaction.

The effect of concentration can be shown by doing several experiments using equal masses of magnesium ribbon, and hydrochloric acid of different concentrations. For example:

i) $Mg + 2HCl(0.5\ mol/lit) \rightarrow MgCl_2 + H_2$ …..(Fast rxn)

ii) $Mg + 2HCl(0.25\ mol/lit \rightarrow MgCl_2 + H_2$ …..(Slow rxn)

Since the concentration of HCl decreases from 0.5 to 0.25 mol/lit, the second reaction has a lower rate.

Materials burn (i.e. react with oxygen) at a certain rate in air, which is only 21% oxygen. The same materials burn much more rapidly in pure oxygen(100% oxygen by volume).

4. Surface Area (Surface Contact)

Surface area affects largely rates of heterogeneous reactions (reactions involving reactants existing in different states). It has very little or no influence on the rtes of homogeneous reaction (reactants in the same phase or state)

In general, a reduction in the particle size leads to an increase in the rate of a reaction by increasing the total surface area exposed for the reaction. The higher the surface area of contact, the better the chance of collision and the faster the rate of reaction will be.

For example, large pieces of wood burns slowly in air, but if that same wood is chopped into smaller pieces, it burns rapidly.

A finely powdered chalk ($CaCO_3$) reacts faster with HCl than a cube of chalk

i) $CaCO_3$ (cubic) + HCl(aq) $\longrightarrow$ CaCl(aq) + H_2O(l) + CO_2(g) $\Rightarrow$ Slow reaction

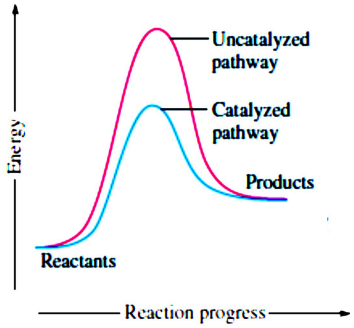
ii) $CaCO_3$ (powder) + HCl(aq) $\longrightarrow$ CaCl(aq) + H_2O(l) + CO_2(g) $\Rightarrow$ Fast reaction

5. Catalyst

A catalyst is a substance that changes the speed (rate) of a chemical reaction without itself being consumed in the reaction. For example MnO_2 acts as a catalyst for the decomposition of $KClO_3$

i) 2KCl($\xrightarrow{\text{Heat}}$ 2KCl + $3O_2$ (Slow reaction, no catalyt)

ii) 2KC $\xrightarrow{\text{Heat}}$ 2KCl + $3O_2$ (Fast reaction, with catalyst)



A catalyst speeds up the rate of a reaction by providing an alternative reaction pathway with lowering activation energy as shown in the figure.

A catalyst cannot start a reaction, unchanged in mass and chemical composition at the end of the reaction

1.8.2 Chemical Equilibrium

1.Reversible And Irreversible Reactions

A chemical reaction that can proceed only to the right giving a product that is stable and that cannot revert to the original reactants is known as irreversible or one way reaction.

Irreversible reactions are also described as reactions which 'go to completion'. The sign (→) in an equation shows that the reactions is irreversible.

For example when magnesium is reacted with dilute hydrochloric acid, the products are hydrogen and magnesium chloride.

$$Mg(s) + 2HCl(aq) \rightarrow MgCl_2(aq) + H_2(g)$$

There is no way that the reverse reaction will take place. Hydrogen will not react with magnesium chloride under any conditions, to produce magnesium and hydrochloric acid.

$$H_2(g) + MgCl_2(aq) \rightarrow Mg(s) + 2HCl(aq) = \text{Impossible}$$

Reactions that can take place simultaneously in two mutually opposite directions are said to be reversible or two – way reactions. To indicate that a chemical reactions is reversible, double arrows (⇌) pointing in opposite directions are used in the equation as shown below

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

As indicated above, the reaction proceeding from left to right is conventionally called the forward reaction and the opposite reaction is called the reverse or the backward reaction.

A characteristics feature of reversible reaction is that they do not go to completion unless the products are removed from the sphere of reaction and is responsible for the establishment of chemical equilibrium

2. Chemical Equilibrium And Equilibrium Constant

Chemical equilibrium is the state of balance attained in a reversible reaction in which the rate of the forward and back ward reactions are exactly equal.

Rate of forward reaction = Rate of backward reaction ⇒ Chemical equilibrium

☞ Note that Chemical Equilibrium

i) is applicable only to reversible reactions

ii) is a dynamic process in which the reaction does not stop, but both the forward and backward reactions continue at equal rates

At the state of chemical equilibrium, there is no net change in the concentration of reactants and products and are not necessarily equal to each other.

Consider a reversible reaction represented by the following general equation:

$$aA + bB \rightleftharpoons cC + dD$$

where A, B, C, and D denote reactants and products, and a, b, c, and d are coefficients in the balanced chemical equation.

The equilibrium-constant expression for a reaction is an expression obtained by multiplying the concentrations of products, dividing by the concentrations of reactants, and raising each concentration term to a power equal to the coefficient in the chemical equation.

The equilibrium constant Kc (or K_{eq}) is the value obtained for the equilibrium-constant expression when equilibrium concentrations are substituted. For the previous reaction, you have

i) Rate of forward reaction = $K_f [A]^a[B]^b$ ⇒ K_f = rate constant for the forward reaction

ii) Rate of reverse reaction = $K_r[C]^c[D]^d$ ⇒ K_r = rate constant for the reverse reaction

Since at equilibrium, rate of forward reaction equals rate of backward reaction, it follows

$K_f [A]^a[B]^b = K_r[C]^c[D]^d$ ⇒ Rearranging the equation gives:

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

Example-1: The following equilibrium has been studied at 450 K.

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

In an experiment, the concentrations of the reactants and products are found to be:

$[SO_3] = 0.254$ M; $[O_2] = 0.054$ M; $[SO_2] = 1.27$ M;

Calculate the equilibrium constant of the reaction at this temperature?

Solution: The equilibrium constant expression for the above reaction is given by:

$$\boldsymbol{Keq} = \frac{[SO_3]^2}{[SO_2]^2[O_2]}$$; substituti ng the concentrat ion, we find that

$$\boldsymbol{Keq} = \frac{(0.254)^2}{(1.27)^2(0.054)} = 4.62$$

Factors That Affect Chemical Equilibrium

Equality of the forward and reverse reactions determined by a particular set of conditions is known as the position of equilibrium. The equilibrium position, once established between any given substances, will last indefinitely if the conditions remain unchanged. Any change that alters the rate of forward or reverse reaction disturbs the original equilibrium. The system then seeks a new position of equilibrium.

The movement of a reaction from one state of equilibrium to another, as a result of a change in conditions is called a shift of position of chemical equilibrium.

When chemical equilibrium shifts, it is important to know the direction in which the shift will occur. The direction of a shift in equilibrium can be predicted qualitatively by using Le-chatelier's principle which can be stated as follows.

" If a chemical reaction at equilibrium is subjected to a stress (a change in temperature, concentration or pressure) then the positon of equilibrium of the system will shift in a direction that tends to reduce or minimize the effect of the change."

In applying Le chatelier's principle to chemical equilibrium. We will consider there important stresses.

1. The Effect Of Temperature Changes On Equilibrium

The effect of temperature changes on equilibrium depends on whether the reaction is exothermic or endothermic. Reversible reactions are exothermic in one direction and endothermic in the other.

In general, an increase in temperature shifts the position of equilibrium in the direction of an endothermic reaction. A decrease in temperature, conversely, shifts the equilibrium in direction of the exothermic process.

Consider the reaction given below:

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \; ; \quad \Delta H = -9.4 \text{ KJ}$$

Since the forward reaction is exothermic (ΔH is negative), the position of equilibrium shifts to:

i) right (in the direction of product, HI) when the temperature is lowered (decreased)

ii) left (in the direction of reactants, (H_2&I_2) when the temperature is increased

2. The Effects Of Pressure Or Volume Changes.

We would not expect pressure changes to have any marked effect on the position of equilibrium in reactions where all the reactants and products are either solids or liquids, because the volumes of these phases are little affected by even quite large changes in pressure.

Changes in pressure measurably affect systems in equilibrium only when gases are involved, and when the reaction produces unequal number of molecules of gaseous reactants and products.

If a system is at equilibrium and its volume is decreased, thereby increasing its total pressure, the equilibrium position will shift in the direction of formation of a smaller amount (number of moles) of gaseous molecule.

A decrease in pressure (increase in volume) shifts the equilibrium in the direction of formation of larger amount gas molecules. For example, in the reaction:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$(1 + 3 = 4 \text{ moles of reactants}) \neq (2 \text{ moles of gaseous product})$$

There are 4 moles of reactants and 2 moles of products. Therefore the position of equilibrium

shifts to the:

i) left (in the direction of reactants, (N_2&H_2)) when the pressure is lowered (decreased)

ii) right (in the direction of product, NH_3, formation) when the temperature is increased

When the number of moles of reactants and products are equal , pressure has no effect on position of chemical equilibrium as shown below.

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O$$
$$(1 + 1 = 2 \text{ moles of reactants}) = (1 + 1 = 2 \text{ moles of gaseous product})$$

3. The Effect Of Concentration Changes On Equilibrium.

Concentration is the amount or the number of reactants or products per unit volume. According to Le Chatelier's principle, any change in the concentration of a reactant or a product will led to a change in the concentration of the substance on the other side of the equation .

When the concentration of one of the reactants or products is increased to a system at equilibrium, the system will shift, away from the added component to reduce the amount of the reactant or product added. For example, in the reaction:

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

If the concentration of SO_3 is increased, the equilibrium shifts to the left in order to reduce the amount of SO_3 added.

When the concentration of either a reactant or a product of an equilibrium mixture is decreased, the system will shift, toward the removed component (in a direction which forms this reactant or product).

In the above reaction, if the concentration of SO_2 and O_2 is reduced, the equilibrium will shift to the left to increase the amount of the reactants reduced

4. The Effect of Catalysts on Equilibrium.

The addition of a catalyst to a system at equilibrium has no effect on the value of an equilibrium constant or equilibrium concentration. It increases the rate of both the forward and reverse reactions equally, so that the equilibrium is reached rapidly. Thus, a catalyst has no effect on the position of chemical equilibrium

Unit - Five
Physical States Of Matter

5.1 Introduction

The Physical state of a substance is the form in which it exists under a given set of conditions of temperature and pressure. Matter can exist in three different physical states: Solid, liquid and gas. The three states of matter can be distinguished from one another by their unique characteristics as shown in the table below.

PROPERTY	SOLID	LIQUID	GAS
Shape And Volume	Has a definite Shape and Volume	Definite volume But no definite Shape	Has no definite Shape or volume
Density	High	Medium	Low
Fluid Nature (ability to flow)	Does not flow (Is not fluid)	Flows readily (Is fluid)	Flows readily (Is fluid)
Intermolecular Attraction	Is very large (Strong)	Is less as Compared with Solids	Is the least (Almost none)
Intermolecular Space	Is practically Absent(Very close)	Fairly close	Very far apart (Very large)
Movement of Particles	Highly restricted (they only Vibrate)	Move about freely	Move at very High speed
Arrangement of particles	Highly ordered	Less ordered (Disordered)	Extremely disordered
Effect Of Heat	Do not expand or contract Very much	Expand or Contract much More than solids	Expand or contract to a large extent
Diffusion	Occurs extremely slowly	Occurs slowly	Occurs rapidly
Compressibility	Is virtually incompressible	Is virtually incompressible	Easily and highly compressible

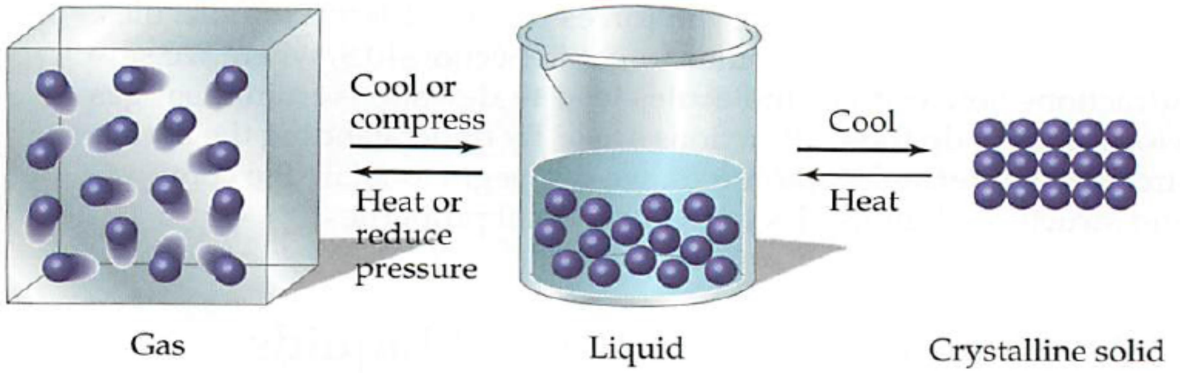


Figure: Molecular level comparison of gases, liquids and solids

5.2 The Gaseous State

5.2.1 The Kinetic Molecular Theory Of gases

kinetic-molecular theory is a model that explains gas behavior in terms of particles in random motion whose volumes and interactions are negligible. The theory is based on the following basic assumptions or postulates.

1. Particle volume. A gas consists of a large collection of individual particles. The volume of an individual particle is extremely small compared with the volume of the container. In essence, the model pictures gas particles as points of mass with empty space between them.

2. Particle motion. Gas particles are in constant, rapid, random, and straight-line motion, except when they collide with the container walls or with each other.

3. Particle collisions. Collisions are elastic, which means that, somewhat like minute billiard balls, the colliding molecules exchange energy but they do not lose any energy through friction. Thus, their total kinetic energy(E_k) is constant. Between collisions, the molecules do not influence each other by attractive or repulsive forces.