Chemical Kinetics

The goal of this unit is to answer some important questions: whether a reaction can occur when two or more substances are mixed, how rapid the reaction is, and how far it has gone toward products when all change has apparently ceased.

The principles of thermodynamics, which were studied in the last unit, provide a partial answer to the first question. That is, exothermic reactions usually favour formation of products. Unfortunately, this criterion is insufficient in a practical sense: a reaction may be product-favoured but still require such a long time to occur that it would take several human lifetimes to produce appreciable quantities of products. Such a reaction is of little use if you are trying to make and sell a product. This problem is the concern of chemical kinetics.

Chemical kinetics, the subject of this unit, can be divided into two parts. The first, at the macroscopic level, is the study of rates of reactions: what the rate of reaction means; how to determine a rate by experiment; and how factors, such as the concentrations of reactants and temperature, influence rates. The second part of this subject looks at reactions at the submicroscopic level. Here, the concern is with **reaction mechanisms**, the detailed the pathways taken by atoms and molecules as a reaction proceeds.

The rate of a reaction refers to the change in concentration of a substance per unit of time. During a chemical reaction, the concentration of the reactant or reactants decreases with time, and the concentration of the products increases. To determine the rate of a chemical reaction, two quantities-concentration and time-are measured.

The **rate of the reaction** can then be described as the decrease in concentration of a reactant, or the increase in concentration of a product, per unit time: Δ concentration / Δtime (see Rate Curve I). Hence,

$$\text{Reaction rate} = \frac{\text{change in amount (concentration) of a substance}}{\text{Time taken}}$$

Example: Consider the combustion of butane in air:

$$C_4H_{10\,(g)} + 13/2O_{2\,(g)} \longrightarrow 4CO_{2\,(g)} + 5H_2O_{\,(g)}$$

The rate of the reaction could be expressed as the number of moles of butane reacting per minute, or the number of moles of carbon dioxide gas formed per minute.

The concentration of a substance undergoing reaction can be determined by a variety of methods. It can be related to such measurable quantities as:
(a) pressure (in reactions accompanied by a change in the number of moles of gas), (b) weighing to find the loss in mass, (c) color i.e. colorimetry (d) pH, (e) electric conductivity, (f) dilatometry i.e. reactions with an increase in volume and (g) polarimetry, e.g. sucrose ---> glucose or fructose.

Changes in the concentration of a substance usually lead to a corresponding change in one or more of these quantities. If measurements are made at definite time intervals, the rate of the reaction at any concentration can be obtained.

An example of rate determination is the decomposition of dinitrogen pentaoxide dissolved in a solvent such as liquid carbon tetrachloride:

$$N_2O_{5\,(solvent)} \longrightarrow 2NO_{2\,(solvent)} + 1/2\ O_{2\,(g)}$$

Here the pressure of O_2 gas can be used as an indicator of reaction rate because the increase in O_2 pressure is related to the decrease in the concentration of N_2O_5. For every 1/2 mol of O_2 formed, 1 mol of N_2O_5 disappears. The concentration of N_2O_5 is plotted as a function of time.
The rate of the reaction is expressed as the change in concentration of N_2O_5 divided by the change in time:

$$\text{Average rate of appearance of product} = +\frac{\text{change in [product]}}{\text{change in time}}$$

or more briefly,

$$\text{Rate} = -\frac{\Delta\,[N_2O_5]}{\Delta\,t}$$

The minus sign is needed because the concentration of N_2O_5 decreases with time.

If the rate of the N_2O_5 decomposition reaction were expressed in terms of the rate of appearance of NO_2, it would be twice the rate of disappearance of N_2O_5. The balanced chemical equation tells us that 2 mol of NO_2 is formed from 1 mol of N_2O_5.

Note: That the rate of the reaction decreases as the reactant concentration decreases. The concentration of N_2O_5 drops sharply at the beginning of the reaction, but it decreases more slowly near the end of the reaction, (**see rate curve I**). This can be verified by comparing the rate of disappearance of N_2O_5 calculated for various time intervals such as for a 15-min interval during the first hour with the rate of reaction calculated for the time interval from 6.5 h to 9.0 h.

The rate calculated by this procedure is the **average rate** over the chosen time interval – defined as a measure of average rate of reaction over a given period of time; calculated by dividing the total change in the amount of reactants or products by the time for the reaction to finish:

$$\text{Average rate of loss of reactant} = -\frac{\text{change in [reactant]}}{\text{change in time}}$$

$$\text{Average rate of appearance of product} = +\frac{\text{change in [product]}}{\text{change in time}}$$

The steepness of the graph reflects the rate of the reaction i.e. steeper the curve, faster the rate, (see Rate Curve II). average rate is the change in concentration over a period of time: if in 10 seconds the change in concentration is 1.0 mol dm^{-3} from 1.1 mol dm^{-3}, then average rate of change is (1.1 - 1.0) $moldm^{-3}$ / 10 s = 0.01 mol dm^{-3} s^{-1}
If the time were measured in seconds, what would be the units of the rate?
(Rates can have all kinds of units as time might be measured in seconds, hours, days, etc.

We might also ask what the **instantaneous rate** is at a single point in time. The instantaneous rate - defined as a measure of the rate of the reaction at a particular instant in time – determined by drawing a line tangent to the concentration – time curve at a particular time (**see rate curve III and IV**), and obtaining the rate from the slope of the tangent.

The instantaneous rate at the start of the reaction is known as the **initial rate** (see Rate Curve V)

The difference between an average rate and an instantaneous rate has an analogy in the speed of an automobile. A car may travel at 60 km in 5 min for an average speed of 12 km per min. At any instant in time, however, the car may have moved much slower or much faster, as indicated by the car's speedometer.

Consider a reaction: $A + 2B \longrightarrow C$

The mathematical notation for rate of change of [C] with time is: $\frac{d\,[C]}{d\,t}$

(pronounced 'dee cee by dee tee', 'd' is used rather than Δ, to show that the change is taking place over a vanishingly small time. The rate of change of concentration of different species may be different. As [C] is increasing, [A] is decreasing. As one molecule of A disappears, one of C appears, so:

$$\frac{d\,[C]}{d\,t} = -\frac{d\,[A]}{d\,t}$$

As the equation tells us that 2 molecules of B are used up for every one of A, then:

$$\frac{d\,[B]}{d\,t} = 2\frac{d\,[A]}{d\,t}$$

Reaction Rates and Stoichiometry

1. Give the relative rates for disappearance of reactants and formation of products for the following reaction: $4PH_{3\,(g)} \longrightarrow P_{4\,(g)} + 6H_{2\,(g)}$

Solution

To equate rates, we have to divide Δ [reagent] / Δt by the stoichiometric coefficient in the balanced equation.

$$\text{Reaction rate} = -\frac{1}{4}\frac{\Delta[PH_3]}{\Delta t} = +\frac{\Delta[P_4]}{\Delta t} = +\frac{1}{6}\frac{\Delta[H_2]}{\Delta t}$$

Because 4 mol of PH_3 disappears for every mol of P_4 formed, the rate of formation of P_4 can only be one-fourth of the rate of disappearance of PH_3. Similarly, P_4 must appear at only one-sixth of the rate that H_2 appears.

2. What are the relative rates of appearance or disappearance of each product and reactant, respectively, in the decomposition of nitrosyl chloride, NOCl?

$$2\,NOCl_{(g)} \longrightarrow 2\,NO_{(g)} + Cl_{2\,(g)}$$

3. Sucrose decomposes to fructose and glucose in acid solution. A plot of the concentration of sucrose as a function of time is given here. What is the rate of change of the sucrose concentration over the first 2 h? What is the rate of change over the last 2 h?

Estimate the instantaneous rate at 4 h. (see **rate curve VI** on sheet "Instantaneous Rate")

Reaction Conditions and Rate

For a chemical reaction to occur, reactant molecules must come together so that atoms can be exchanged or rearranged. Atoms and molecules are mobile in the gas phase or in solution, and so reactions are often carried out in a mixture of gases or between solutes in a solution. Under these circumstances, four factors affect the speed of a reaction.

1. The Nature of the Reactants

Generally, reactions that involve simple exchanges are rapid, while those that involve bond-breaking and bond-making are slower at room temperature.
Example: *reactions of aqueous ions are extremely fast:*

$$Ag^{+1}{}_{(aq)} + Cl^{-1}{}_{(aq)} \rightarrow AgCl_{(s)}$$

The ***state of the reactants is important.***
Depending on concentration, gases tend to be reactive.
Example: liquid gasoline is inflammable but it is less reactive than gasoline vapour and the air (oxygen source) and the mixture burns rapidly.

Solids are generally less reactive than liquids of the same substance, (naturally, the liquid substance is at higher temperature).
Solids can only react on their outside, i.e. the **surface area is an important factor for solids.**
Rate of the reaction is directly proportional to surface area exposed.
The reason a powder is more reactive is that the surface area of the solid has been greatly increased.
Powdered coal is much more reactive than lump coal.
An iron nail does not burn very well, but if you grind down the nail to iron filings or powder, it burns rapidly. (The “sparkles” in fireworks are iron filings.)
Chopped wood (kindling) burns much faster than the log from which it was cut.
DEMO:
The combustion of lycopodium powder: (a) The spores of this common moss burn only with difficulty when piled in a dish, (b) If the surface area is increased, and a finely divided powder is sprayed into a flame, combustion is rapid.

2.Concentration of Reactants

The natural gas methane, $CH_{4\,(g)}$, in a Bunsen burner burns in air:

$$CH_{4\,(g)} + O_{2\,(g)} \rightarrow CH_{4\,(g)} + 2H_2O_{\,(l)}$$

However, if the concentration of the $CH_{4\,(g)}$ and $O_{2\,(g)}$ are increased , combustion occurs at a faster rate.
The more concentrated one or the more of the reactants there are, the faster the reaction will be i.e. the rate of the reaction will increase.
Note: In the case of gases, high pressure is the same as high concentration. An increase in pressure of a gas increases the temperature and decreases the volume i.e. increases the concentration

3.Temperature

In your own experience you know that heating things can bring about a more rapid reaction. That is why, for example, we cook food, and in the laboratory we often heat the reactants to make reactions occur faster.

2. Catalysts

Catalysts are substances that accelerate chemical reactions but are not themselves transformed. This process is known as **catalysis.**
For example, hydrogen peroxide, H_2O_2, can decompose to water and oxygen.

$$H_2O_{2\,(l)} \longrightarrow O_{2\,(g)} + 2H_2O_{\,(l)}$$

If the peroxide is stored in a cool place in a clean plastic container, it is reasonably stable for many months; the rate of the decomposition reaction is extremely slow. But, in the presence of a manganese salt, an iodide-containing salt, or a biological substance called an enzyme, an energetic reaction occurs as shown by vigorous bubbling and the rapid escape of steam (the water is given off as steam because of the high heat of reaction).

An insect called the bombardier beetle uses the process as its defence mechanism. It uses a biological catalyst, an enzyme, to cause the reaction to occur with explosive speed. By combining the organic compound hydroquinone with a peroxide in the presence of an enzyme, it produces a stream of superheated steam and an irritating chemical to spray on its enemies.

1. A catalyst which increases the rate of one reaction may have no effect on another.

2. **Autocatalysis:** a process in which one of the products of a reaction acts as a catalyst for the reaction.

3. **Promoter:** a substance which increases the power of a catalyst, so speeding up the reaction.

4. **Inhibitor:** a substance that slows a reaction, some work by reducing the power of a catalyst.

5. **Enzyme:** a catalyst found in living things which increases the rate of reaction in a natural chemical process.

6. **Surface Catalyst:** a catalyst which attracts the reactants to itself. It holds them close to each other on its surface, so that they react.

7. **Homogeneous Catalyst:** a catalyst that is in the same physical state as the reactants.

8. **Heterogeneous Catalyst:** a catalyst that is in a different physical state to the reactants.

Collision Theory

"Reactant concentrations can affect reaction rate" is a macroscopic observation. Reaction rate may be described in terms of what happens in the microscopic world of atoms and molecules. A need to find explanations for the factors that govern reaction rates is required. We small base our explanations on the collision theory of reaction rates which assumes that molecules must collide with one another in order to react. The collision theory of reaction rates states that the rate of a reaction is proportional to the number of collisions that occur in a given time period. Usually the number of collisions that produce actual reactions, called **effective collisions** is very small. There are two reasons for this:

1. Steric factor: for a collision to result in a reaction, the molecules must approach each other in the right orientation

2.Energy factor: for a collision to result in a reaction, the molecules must have a certain minimum energy: enough to start breaking bonds.

<u>To explain the factors that affect reaction rates in terms of collision theory</u>

1. Nature of reactants

Which will give up electrons faster: sodium or copper?

2. Surface Area

Reaction takes place on the surface, increasing the surface area will increase the number of collisions between reacting molecules, (note: applies to reactions in which the reactants are in more than one phase). Example: $CaCO_{3\ (s)} + Hcl_{(aq)} \longrightarrow$

The results will show that smaller the size of the particles of calcium carbonate, the faster the reaction will take place.

3. Concentration

Obviously, the more molecules there are the collisions there can be, hence to increase the speed of a reaction – add more reactants.

Example: $Na_2S_2O_{3\ (aq)} + 2\ Hcl \longrightarrow S_{(s)} + SO_{2\ (g)} + 2NaCl_{(aq)} + H_2O_{(l)}$

Sulphur appears as very small particles of solid suspended in the solution. When the reaction container is placed on a cross(X) marked on a sheet of paper and viewed, the time taken for the disappearance of the crss will indicate the time for the reaction to occur. Thus, the speed of the reaction is inversely proportional to the time taken for the reaction to finish.

If the experiment is repeated, keeping the concentration of thiosulphate constant, but varying the concentration of the hydrochloric acid, it will be found that:

$$\text{Speed of reaction} \propto \text{concentration of acid}$$

When 1/(time for cross to disappear) is plotted against concentration, a straight line is obtained, indicating that for this reaction:

$$\frac{1}{\text{Time}} \propto \text{concentration}$$

The pressure of gaseous reactants:
When gases react, molecules have first to collide before they can react. If the pressure is increased, molecules of gas are pushed closer together. As a result, they collide more frequently and react more rapidly.

4. Temperature
An increase in temperature will increase the energy of the molecules. Thus, it is not surprising therefore that an increase in temperature should increase reaction rates for two reasons:

1.

2.

The Maxwell-Boltzmann Distribution of Molecular Energies will help to explain the increase in reaction rate due to temperature.

At the lower temperature there are not many molecules with sufficient energy or minimum energy (threshold or activation energy) to lead to a reaction.

At the higher temperature the distribution flattens out, the average speed is higher and there are more molecules with sufficient energy (activation energy) to react.

There are more collision as the molecules are moving faster, however, the significant factor is the fraction of molecules with the sufficient energy (the minimum energy, i.e. the activation energy) to react.

Generally, a 10 ˚ C change in temperature will double the rate of a non-instantaneous reaction.

Light
Light is another form of energy that will speed up chemical reactions. Example, the formation of silver from silver salts that takes place when a photographic film is exposed to light.