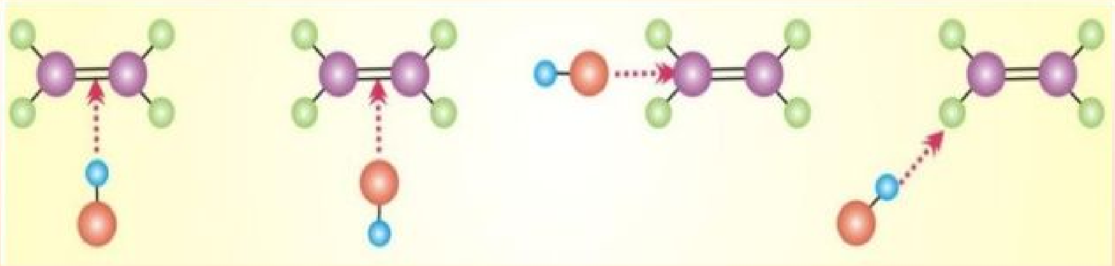


1. Chemical Kinetics

Content

Introduction

In the previous units for example, unit 4 and 5 described the basic aspects of behavior of molecules depending on their physical state and energy requirements for the reaction to occur. Though, we know that the amounts of reactants and products and their molecular nature yet, we have not focused quantitatively on "How fast is the reaction proceed" and requirements to be satisfied to occur a chemical reaction. In this regard the present unit addresses and focuses on the field of *kinetics* where the rates of reactions are concerned. We examine the rate of a reaction, the factors that affect it, the theories that explain those effects, and the stepwise changes reactants undergo as they transform into products. This unit also introduce some general ideas about reaction rates and overview key factors that affect them—concentration/ pressure, physical state, catalyst and temperature. Further, express rate through a rate law and determine its components and see how concentrations change as a reaction proceeds and discuss the meaning of half-life. In addition, we discuss about reaction mechanisms, noting the steps a reaction goes through and picturing the chemical species that exists as reactant bonds are breaking and product bonds are forming.

1.1 Concept of chemical kinetics

We have gained some idea about chemical reactions in unit 5 (energetics). Chemistry is mainly concerned with changes occurring in nature or in substances of interest. Such changes are depicted in a simple way by an equation which is considered a chemical reaction. In the study of any chemical reaction we try to find out the followings.

(a) The feasibility of a chemical reaction, which can be predicted by thermodynamics. For example, energy changes associated with a reaction are expressed by thermodynamic quantities such as ΔH, ΔG, ΔS and we know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible. This also gives us in which direction the reaction occurs.

(b) Extent of a reaction, which explains how far a reaction proceeds to give the desired products and this can be determined from chemical equilibrium (unit 12). This can be quantified with the knowledge of the equilibrium constant.

Along with these, there is another equally important aspect for a given reaction worth paying attention; that is how fast a reaction occurs or the rate of a reaction and factors controlling the rate of a reaction. In this case, time taken by a reaction to reach some known point (extent) has to be studied. Further, how the conversion of reactants to products occurs: that is the mechanism of the reaction has to be known. All these questions can be answered by a branch of chemistry, which deals with the study of reaction rates and their mechanisms, called "chemical kinetics".

If a reaction is to occur, it must be both thermodynamically and kinetically favoured under given conditions such as temperature and pressure of the system. These are relative terms: the reaction must be thermodynamically favoured enough to form the amount of the product desired, and it must be kinetically favoured enough to be completed within the desired time period. For example, nuclear reactions occur very fast (in a fraction of a second) and the conversion of graphite to diamond takes millions of years. This is because it has an enormous activation energy that must be overcome before the reaction may proceed. We must also consider the mechanism of the reaction which is a sequence of events at the molecular level that controls the speed and the desired products of the reaction. Therefore, studying the rates of reactions is very important in many fields. These factors of thermodynamics and kinetics can be simply shown schematically in Figure 1.1 below.

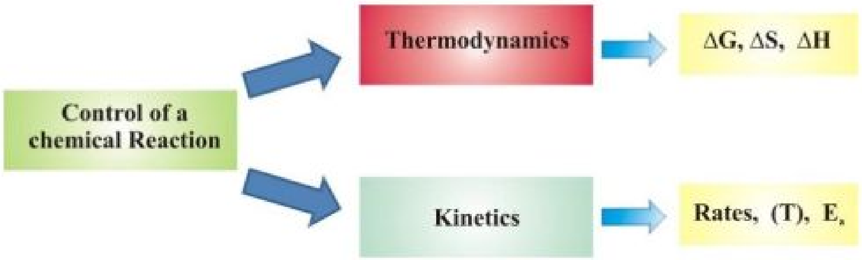


Figure 1.1 Controlling chemical reactions in view of thermodynamics and kinetics

Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions which can alter the reaction rates. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. In these studies, investigations in measurable quantities such as amounts reacted or formed and the rates of consumption or formation come under macroscopic level. At the molecular level, the reaction mechanisms involving orientation, velocities and energy of molecules undergoing collisions have to be considered. These parameters are somewhat hard to measure.

When we consider chemical processes, many chemical processes such as explosive reactions take place in a fraction of a second while the rusting of iron may take a very long time, sometimes in centuries for completion. Ionic reactions in solution, for example the reaction between NaCl(aq) and $AgNO_3$(aq) giving a white precipitate of silver chloride occurs within a very short (but measurable with some advanced techniques) time. In chemical kinetics, at this stage we actually study the rates of reactions which are neither so fast nor so slow. Usually, a chemical reaction involves breaking of bonds in the reactant molecules and making of bonds in the product molecules and it is easy to understand that a reaction that involves breaking of weak bond(s) is faster than a one involving breaking of strong bond(s) at a given temperature. Ionic compounds such as strong electrolytes in solution remain completely ionized and hence in any ionic reaction, no bond is broken. Therefore, an ionic reaction is fast. Different reactions, as they involve variety of bonding in respect of the strength of the bonds to be broken, occur at different rates. Reactions which involve less bond rearrangements are generally faster than those which involve considerable bond rearrangements at a given temperature. Chemical kinetics or reaction kinetics is the study of rates of chemical processes. Chemical kinetics includes investigations of how different experimental conditions can influence the speed of a chemical reaction and gives information about the mechanisms of reactions and transition states, as well as the construction of mathematical models (rate equations) that can describe the characteristics of a chemical reaction. With this it may worth to categorize reactions with respect to their rates as described below.

Very fast (Instantaneous) reactions

These reactions are so fast and occur as soon as the reactants are bought together. These reactions involve ionic species and are thus known as ionic reactions. There are many reactions occurring on the surfaces of catalysts. They are much faster and usually take place in 10^{-12} to 10^{-18} seconds in the time scale. It is almost impossible to determine the rates of these reactions with conventional techniques. However, there are advanced techniques available with ultra-fast laser spectroscopy which in further allow us even to follow electron transfer processes. Some examples we can consider for these very fast reactions are;

Formation of a precipitate of AgCl when highly concentrated solutions of silver nitrate and sodium chloride are mixed:

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

Neutralisation of a strong acid with a strong base when their aqueous solutions are mixed:

$$HCl(aq) + NaOH(aq) \longrightarrow NaCl(aq) + H_2O(l)$$

Very slow reactions

There are certain reactions which occur in extremely slow rates or sometimes never happen at the room temperature. It is therefore, difficult to study the kinetics of such reactions. Examples:

Reaction between hydrogen and oxygen at room temperature: This is highly explosive at high temperatures (~ 1000 K).

Reaction between carbon and oxygen; coke does not catch fire spontaneously in air and remains unreacted.

Moderate reactions

Between the above two extremes, there is a large number of reactions which take place at moderate and measurable rates at room temperature and these allow us to study chemical kinetics under laboratory conditions. Some common examples are given below.

Decomposition of hydrogen peroxide:

$$2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$$

Decomposition of nitrogen pentoxide:

$$2N_2O_5(g) \rightarrow 2N_2O_4(g) + O_2(g)$$

Hydrolysis of an ester:

$$CH_3COOC_2H_5(aq) + NaOH(aq) \rightarrow CH_3COONa(aq) + C_2H_5OH(aq)$$

Inversion of sucrose in aqueous solution:

$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$

Reaction between nitrogen dioxide and carbon monoxide:

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$

Reaction between nitric acid and thiosulfate:

$Na_2S_2O_3(aq) + 2HNO_3(aq) \rightarrow S(s) + 2NaNO_3(aq) + SO_2(g) + H_2O(l)$

Reaction between ferric chloride and potassium iodide:

$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$

Reaction between calcium carbonate and hydrochloric acid:

$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

The rates of chemical processes can be decreased or increased by changing conditions under which they occur. For example, very slow reaction at room temperature; $CO + 2H_2 \rightarrow CH_3OH$, can be speeded up by maintaining temperature around 400 °C, pressure about 300 atm and using a catalyst. The decay of food items can be slowed down by reserving them in refrigerators.

In the study of chemical kinetics, we can predict the rate of a particular reaction under given conditions and that conditions can be adjusted or optimized to make the reactions occur at a desired rate. This is useful in industry to accelerate the formation of industrial products and to predict the mechanism of the reaction.

1.2 Rate of a reaction

Different reactions can occur at different rates. Reactions that occur slowly have a low rate of reaction and reactions that occur quickly have a high rate of reaction. As mentioned above, for example, the chemical change of graphite to diamond and weathering of rocks are very slow reactions; it has a low rate of reaction. Explosions and nuclear reaction are very fast reactions: they have a high rate of reaction.

In general, a reaction can be represented as follows.

$$\text{Reactants} \rightarrow \text{Products}$$

When the reaction proceeds, reactants are consumed while products are formed. As a result, the speed of a reaction or the rate of a reaction can be defined as the change in amount (concentration) of a reactant or product in unit time. That is;

(i) the rate of decrease in amount/ concentration of any one of the reactants, or

(ii) the rate of increase in amount/ concentration of any one of the products at a constant temperature.

Consider a hypothetical reaction at a constant temperature and also assume that the volume of the system remains constant.

$$A \rightarrow B$$

In general, it is more convenient to express the reaction rate in terms of the change in amount with time at a constant temperature. For the reaction above let's consider that at the time t_i *(not at $t = 0$)* the initial amount of A is $(n_A)_i$ moles and after some time t_t, the amount of A is $(n_A)_t$ moles. Therefore, the change in amount of A within the time interval $(t_t - t_i)$ is $[(n_A)_t - (n_A)_i]$ moles.

$$\therefore \text{ The rate of change in the amount of A } = \frac{[(n_A)_t - (n_A)_i]}{t_t - t_i} = \frac{\Delta(n_A)}{\Delta t}$$

Similarly for the product B we can write,

$$\text{The rate of change in amount of B } = \frac{[(n_B)_t - (n_B)_i]}{t_t - t_i} = \frac{\Delta(n_B)}{\Delta t}$$

In the above, $\Delta(n_A)$; change in amount of the reactant has a negative sign because $(n_A)_t < (n_A)_i$. It is important to note that the change in amount in any chemical process is considered to be a positive quantity. Hence in the case of change in amount in a reactant we use a negative sign. So, the rate of change in amount is always a positive quantity. Therefore, the rate of the above reaction can be written as,

$$\text{Rate} = -\frac{\Delta(n_A)}{\Delta t} = \frac{\Delta(n_B)}{\Delta t}$$

With the above understanding, the rate of a reaction can easily be correlated with the change in amount of either reactant(s) or product(s) of the reaction as the rate of consumption of the reactants or formation of the products.

In this simple description, the rate depends upon the change in amount of reactants or products and the time taken for that change to occur. Thus, the variation of the rate of the reaction A → B can be illustrated as shown in Figure 1.2.

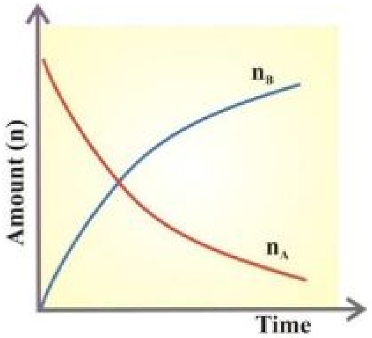
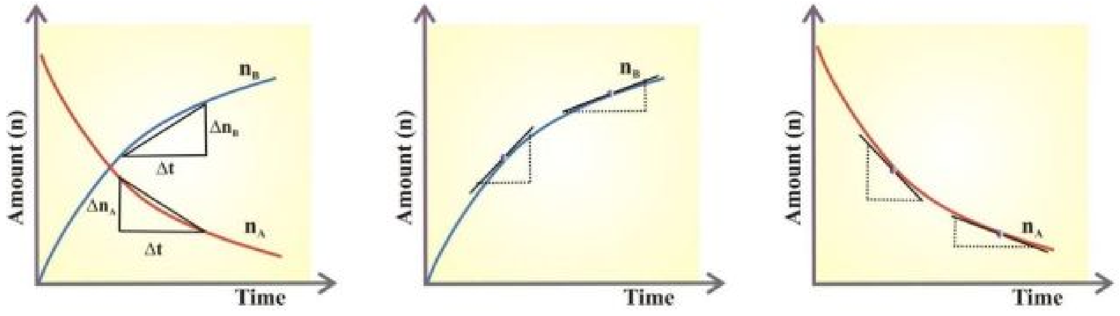


Figure 1.2 The rate of reaction A → B; is the decrease of n_A and increase of n_B with time at a constant temperature. It has to be noted that the rate of the reaction has decreased over the time.

In a mathematical point of view, this quantity $-\frac{\Delta(n_A)}{\Delta t}$ or $\frac{\Delta(n_B)}{\Delta t}$ can be represented as depicted in Figure 1.3(a) where the rate of the reaction is given by the change in amount

$\Delta(n_A)$ *or* $\Delta(n_B)$ over the time interval Δt and usually this rate is defined as *average rate*. Usually the rate changes at a very small time and hence to calculate the rate over the time interval **Δt**, the rates at each time within the interval has to be averaged. The rate at a given instance of time is the slope of the tangent drawn to the curve showing the variation of amount with time as shown in Figures 1.3 (b) and (c) for the product B and reactant A, respectively. It is noted that the slope for the rate of change in amount of A (reactant) is negative indicating that the amount decreases with the time and therefore, we use a negative sign in front of the slope when the rate is calculated. It also shows that the rate also decreases with time as the slope decreases with the time because the reactant is consumed during the progress of reaction.



(a) (b) (c)

Figure 1.3 The rate of reaction A → B; **(a)** Description of rate as the change in amount Δn over time period Δt. The definition of rate as the slope of the tangent drawn to the curve showing the variation of amount of the product B with time **(b)** and the reactant A with time **(c)**. In **(c)**, negative slope indicates that the amount of reactants is decreasing over the time. It is also shown in **(b)** and **(c)** that the rate of the reaction decreases with the time as the slope of the tangent decreases.

In the above we have gone through a very basic idea about the description of reaction rate in which the change in amount (number of moles) is considered the measure of the quantity. If we consider the volume of the container in which the reactions occurs as V and *it does not change during the progress of reaction* then we can define the rate of the reaction as the change in amount of either reactant(s) or product(s) per unit time per unit volume. If the volume V of the system in which the reaction is carrying out is constant, we can write the rate as,

$$\text{Rate} = \frac{\Delta(n_A)}{V\,\Delta t} = \frac{\Delta(C_A)}{\Delta t} \quad \because \; {(n_A)}/{V} = C_A : \text{concentration}$$

Thus we can then express the rate of the reaction as the change in concentration of either reactant(s) or product(s) per unit time as: Rate = $-\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$.

We can therefore, replace the amount in y-axis in the plots of Figures 1.2 and 1.3 with the concentration and hereafter, we use the concentration to represent the change in quantity of a given reaction as shown in Figure 1.4.

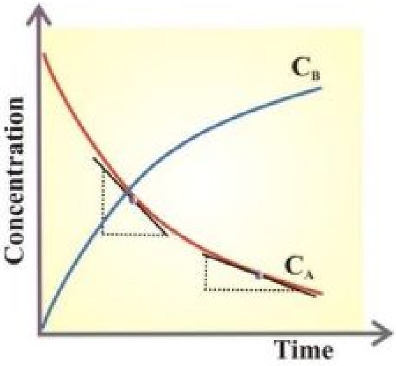


Figure 1.4 The rate of reaction A → B; description of rate as the change in concentration over the time. Rate decreases with the time as is evident from the decrease in the slope of the curve.

We can also see in this plot that the reaction slows down as it proceeds (not the case with reactions) indicating that the reaction rate depends on the concentration of A available to react. Note that when [A] is large, the slope of the curve is steep and hence the reaction is fast. Later in the reaction, [A] is much smaller, and so is the slope. Hence the reaction slows down as A is used up showing that there is a concentration dependence of rate.

Units of rate:

As the rate is defined as the change in concentration at a given time, the units will be **mol dm^{-3} s^{-1}** (if the time is measured in seconds). This unit can easily be applied for the reactions in solutions. When the gas phase reactions are concerned we have to measure the concentrations as partial pressures. Therefore, the units will be **Pa s^{-1}** (or atm s^{-1}).
It can further be understood that the reaction rate will be equal (proportional) to the reciprocal of time (1/t) if the time taken to occur a given change in a reaction is monitored. For a reaction A → B, we write the rate as;

$$\text{Rate} = -\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$$

If the change occurred is a constant and the time taken for that change is t, we write,

$$\text{Rate} = \frac{\text{constant}}{t}$$

or

$$\text{Rate} \ \alpha \ \frac{1}{t}$$

1.3 Reaction rate and stoichiometry

As shown in section 1.2, the rate of a simple reaction of the type A → B at a constant temperature and in a closed rigid vessel (constant volume) can be expressed either as the rate of decrease in concentration of A, $-\frac{\Delta(C_A)}{\Delta t}$ or as the rate of increase in concentration of B, $\frac{\Delta(C_B)}{\Delta t}$. In this reaction we see that one mole of A gives one mole of B, so that the rate can be given as are equal giving $-\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$. Now let us consider a reaction when 2 moles of A giving one mole of B.

$$2A \rightarrow B$$

Because two moles of A are consumed to produce one mole of B, the rate of consumption of A would be twice the rate of production of B. Therefore, we can express the rate of the reaction as;

$$-\frac{1}{2}\frac{\Delta(C_A)}{\Delta t} = \frac{\Delta(C_B)}{\Delta t}$$

Or we write the same as,

$$-\frac{1}{2}\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

Therefore, in general for a reaction: $aA + bB \rightarrow cC + dD$

We can write,

$$\textbf{Rate} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Example 1.1

Consider the decomposition of $H_2O_{2(aq)}$ occurring in a 1.0 dm^3 rigid container at a given temperature according to the following reaction.

$$2H_2O_{2(aq)} \rightarrow 2H_2O(l) + O_2(g)$$

Write the rate of the above reaction in terms of both reactants and products.

Answer

Assuming that the reaction proceeds according to the stoichiometry as shown in the **Figure 1.5**, plot the variations in concentrations of each species in the reaction mixture over the time.

According to the stoichiometry of the reaction; 2 moles of $H_2O_{2(aq)}$ give 2 moles of $H_2O(l)$ and one mole of $O_2(g)$. As the volume of the container is 1.0 dm^3:

Initial concentrations; $H_2O_{2(aq)}$: $H_2O(l)$: $O_2(g)$ = 2.0 : 0.0 : 0.0 mol dm^{-3}

Final concentrations; $H_2O_{2(aq)}$: $H_2O(l)$: $O_2(g)$ = 0.0 : 2.0 : 1.0 mol dm^{-3}

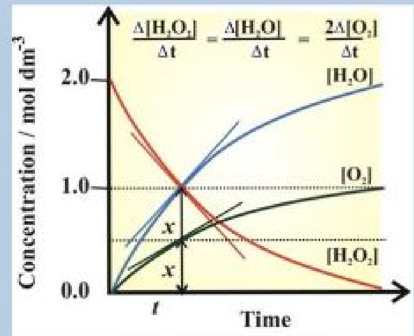


Figure 1.5 The variation of concentrations of the species in reaction $2H_2O_2(aq) \rightarrow 2H_2O(l) + O_2(g)$ at a given temperature

Rate of the reaction can be written as;

$$\text{rate} = -\frac{1}{2}\frac{\Delta[H_2O_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t} \quad \text{or} \quad \frac{-\Delta[H_2O_2]}{\Delta t} = \frac{\Delta[H_2O]}{\Delta t} = 2\frac{\Delta[O_2]}{\Delta t}$$

It has to be noted that the above graphs were drawn with the accurate scale according to the stoichiometry and rate of the reaction. Therefore, from the plots after time t the rates (slopes) can be calculates as:

$$-\frac{\Delta[H_2O_2]}{\Delta t} = -\frac{(-)2x}{t} = \frac{2x}{t};\ \frac{\Delta[H_2O]}{\Delta t} = \frac{2x}{t} \text{ and } \frac{\Delta[O_2]}{\Delta t} = \frac{x}{t}$$

This clearly implies the definition of the rate of this reaction. Therefore, we can understand that the rates of reactions can be experimentally determined or estimated.

Example 1.2

Write the rates of following reactions in terms of both reactants and products.

(i) $Na_2CO_3(aq) + 2HCl(aq) \rightarrow 2NaCl(aq) + CO_2(g) + H_2O(l)$

(ii) $N_2(g) + 3H_2(g) \rightarrow 2NH_3(g)$

Answer

(i) Rate $= -\frac{\Delta[Na_2CO_3(aq)]}{\Delta t} = -\frac{1}{2}\frac{\Delta[HCl]}{\Delta t} = \frac{1}{2}\frac{\Delta[NaCl]}{\Delta t} = \frac{\Delta[CO_2(g)]}{\Delta t}$

(ii) Rate $= -\frac{\Delta[N_2(g)]}{\Delta t} = -\frac{1}{3}\frac{\Delta[H_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[NH_3]}{\Delta t}$

Example 1.3

$N_2O_5(g)$ decomposes as follows:

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

It was found that in a closed rigid vessel at a particular instant the rate of decomposition of $N_2O_5(g)$ was 3.0×10^{-7} mol dm^{-3} s^{-1} at a constant temperature. Write the rates of formation of (i) $NO_2(g)$ and (ii) $O_2(g)$.

Answer

We can write the rate of the reaction as;

$$\text{Rate} = -\frac{1}{2}\frac{\Delta[N_2O_5(g)]}{\Delta t} = \frac{1}{4}\frac{\Delta[NO_2(g)]}{\Delta t} = \frac{\Delta[O_2(g)]}{\Delta t}$$

(i) $\frac{1}{2} \times 3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1} = \frac{1}{4}\ \frac{\Delta[NO_2(g)]}{\Delta t}$

$$\frac{\Delta[NO_2(g)]}{\Delta t} = 6.0 \times 10^{-7}\ \text{mol dm}^{-3}\text{s}^{-1}$$

(ii) $\frac{1}{2} \times 3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1} = \frac{\Delta[O_2(g)]}{\Delta t}$

$$\frac{\Delta[O_2(g)]}{\Delta t} = 1.5 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Example 1.4

In the reaction taking place in a closed rigid container at a constant temperature:

$$2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$$

the rate of formation of NO(g) was found to be 2.0×10^{-4} mol dm^{-3} s^{-1}.

Write the rates of (i) the reaction and (ii) the consumption of NOBr(g).

Answer

We can write; $\text{Rate} = -\frac{1}{2}\frac{\Delta[NOBr(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO(g)]}{\Delta t} = \frac{\Delta[Br_2(g)]}{\Delta t}$

(i) $\therefore$ rate of the reaction $= \frac{1}{2} \times 2.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

$$= 1.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

(ii) $\frac{1}{2}\frac{\Delta[NOBr(g)]}{\Delta t} = 1.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$

$$\therefore \frac{\Delta[NOBr(g)]}{\Delta t} = 2.0 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

Example 1.5

At a given time, the rate of the following reaction with respect to C_2H_4 is 0.20 mol dm^{-3} s^{-1}. Write the rate of the reaction with respect other species in the reaction.

$$C_2H_4(g) + 3O_2(g) \rightarrow 2CO_2(g) + 2H_2O(g)$$

Answer

Rate of the reaction:

$$\text{Rate} = -\frac{\Delta[C_2H_4(g)]}{\Delta t} = -\frac{1}{3}\frac{\Delta[O_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[CO_2(g)]}{\Delta t} = \frac{1}{2}\frac{\Delta[H_2O\,(g)]}{\Delta t}$$

Given that, $\frac{\Delta[C_2H_4(g)]}{\Delta t} = 0.20 \text{ mol dm}^{-3}\text{ s}^{-1}$

$$\frac{\Delta[O_2(g)]}{\Delta t} = 3 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 3 \times 0.20 \text{ mol dm}^{-3}\text{ s}^{-1} = 0.60 \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$\frac{\Delta[CO_2(g)]}{\Delta t} = 2 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 2 \times 0.20 \text{ mol dm}^{-3}\text{ s}^{-1} = 0.40 \text{ mol dm}^{-3}\text{ s}^{-1}$$

$$\frac{\Delta[H_2O(g)]}{\Delta t} = 2 \times \frac{\Delta[C_2H_4(g)]}{\Delta t} = 2 \times 0.20 \text{ mol dm}^{-3}\text{ s}^{-1} = 0.40 \text{ mol dm}^{-3}\text{ s}^{-1}$$

From the above examples we can see that the rate of a reaction is not directly equal to either the rate of disappearance of reactants or the rate of appearance of products.

Therefore, for a reaction taking place at constant temperature and constant volume, rate of the reaction is given by;

$$\boxed{\textbf{Rate} = \frac{\mathbf{1}}{\mathbf{v_j}}\frac{\mathbf{\Delta[J]}}{\mathbf{\Delta t}}}$$

$\boldsymbol{v_j}$ is the stoichiometric coefficient of the substance $\boldsymbol{J}$. $\boldsymbol{v_j}$ is negative for reactants and positive for products.

Example 1.6

Consider the reaction, $A \rightarrow 2B$, which was started with the initial concentration of 0.50 mol dm^{-3} of reactant A. It drops to 0.00 mol dm^{-3} in 10 seconds. During this time the concentration of B increased from 0.00 mol dm^{-3} to 1.00 mol dm^{-3}. Calculate the rate of this reaction as follows.

Answer

We can write the rate of the reaction as; $\text{Rate} = \frac{1}{\nu_j}\frac{\Delta[A]}{\Delta t} = -\frac{\Delta[A]}{\Delta t}$

$$= -\frac{(0.00-0.50)\,\text{mol dm}^{-3}}{10\text{ s}}$$

$$= 0.05\text{ mol dm}^{-3}\text{ s}^{-1}$$

or

$$\text{Rate} = \frac{1}{\nu_j}\frac{\Delta[B]}{\mathrm{d}t} = \frac{1}{2}\frac{\Delta[B]}{\Delta t} = \frac{1}{2} \times \frac{(1.00-0.00)\text{ mol dm}^{-3}}{10\text{ s}}$$

$$= 0.05\text{ mol dm}^{-3}\text{ s}^{-1}$$

Example 1.7

The decomposition of A at 300 K in a solution with constant volume can be followed by monitoring the concentration of A. Initially (at $t = 0$), the concentration of A is 2.00 mol dm^{-3} and after 180 seconds, it is reduced to 1.64 mol dm^{-3}. The reaction takes place according to the equation

$$2A(aq) \rightarrow 4B(aq) + C(aq)$$

Calculate the rate of this reaction.

Answer

$\Delta A = 1.64 - 2.00 = -0.36\text{ mol dm}^{-3}$

$\therefore -\Delta A = 0.36\text{ mol dm}^{-3}$

According to the reaction,

$\text{Rate} = \frac{1}{2}\,[\Delta[A]/\Delta t] = \frac{1}{2} \times 0.36\text{ mol dm}^{-3}/\ 180\text{ s}$

$= 1.0 \times 10^{-3}\text{ mol dm}^{-3}\text{ s}^{-1}$

1.4 Experimental techniques to determine the rates of reactions

As from the example 1.1 and other calculations, we know that the reaction rates are experimentally determined quantities and therefore it is necessary to understand that how the rate of a reaction, is obtained experimentally. In this context, we know to determine the rate of a reaction we have to monitor the concentration of the reactant (or product) as a function of time. That is, in order to determine the rate of a particular reaction, it is necessary to follow either the rate of decrease in concentration of a reactant(s), or the rate of increase in concentration of a product, by choosing an appropriate experimental method at a constant temperature. We can categorize the techniques as non-disruptive and disruptive. In non-disruptive techniques, this is done through a measurement of a rapidly determinable physical property of the reaction mixture. For example, for reactions in solutions, the concentration of a species can often be measured by spectrophotometric techniques if coloured species are involved. If ions are involved, the change in concentration can also be detected by an electrical conductance measurement. Reactions involving gases are monitored by pressure measurements under the constant volume.

Spectrophotometric methods

This is usually employed when at least one of the species involved in the reaction is coloured and its absorbance is monitored as a function of time at a suitable wavelength obtained from the absorption spectrum of either a reactant or a product. As the absorbance is directly proportional to the concentration of the particular species, the rate of the reaction can be monitored by these absorbance measurements as a function of time.

Methods involving the measurement of change in total pressure

As we know, the total pressure of a gas-phase reaction occurring in rigid container at any time will be the sum of the partial pressures of all the gaseous reactants and products. Thus if the stoichiometry of the reaction is known, this can be used to determine either the rate of decrease of a reactant or the rate of increase of a product as a function of the measured total pressure.

Electrical conductance/ conductivity method

Consider, for example, the reaction:

$$R_1COOR_2(aq) + OH^-(aq) \rightarrow R_1COO^-(aq) + R_2OH(aq)$$

The conductivity of hydroxyl ions is much higher than that of the other ions such as ethanoate ions ($R_1 = C_2H_5$). Also the conductivity depends on the concentration of ions and hence, measurement of the conductance is an appropriate method for following the rate of loss of hydroxyl ions in the above process where the decrease in conductivity will be observed.

Optical rotation method

This method is suitable for reactions where the optical activity of the products is different from those of the reactants. For example hydrolysis of sucrose gives glucose and fructose with different optical rotations. An instrument called "polarimeter" is used for the optical rotation measurements. As the optical rotation is related to the concentration, measurement of the optical rotation will then be related to the rate of the reaction.

Refractive index method

This method is especially useful for liquid-phase reactions where the refractive index of reaction mixture changes in the course of the reaction due to increase in the products and decrease in the reactants.

Gas evolution method

If there is one gaseous product in a reaction, the gas evolved can be collected and its volume measured as a function of time. For example, the decomposition of calcium carbonate proceeds by producing CO_2 gas.

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)$$

For these types of reactions, the rate can be determined from a measurement of the volume of gas evolved during the reaction (you will practice such in a laboratory under this unit).

Disruptive techniques: Chemical analysis method

In chemical analysis method, a required sample of the reaction mixture is taken out and analyzed, for example, titration to estimate the acid liberated during the hydrolysis of an ester. In the method of chemical analysis, to obtain the composition of the reaction mixture at a given time it is necessary to ensure that no further reaction takes place between sampling and analysis. This is usually achieved by lowering the temperature (quenching) of the mixture immediately after sampling.

1.5 Factors affecting the rate of a chemical reaction

Usually a balanced chemical equation is used to describe the quantitative relationships between the amounts of reactants present and the amounts of products that can be formed in a chemical reaction. As we have some idea from the previous sections, this balanced equation gives us no information about how fast a given reaction will occur. Such information is obtained by studying the chemical kinetics or rates of a reaction. The rate of the reaction depends on various factors: reactant concentrations, temperature, physical nature and surface areas of reactants, catalyst properties and solvent. By studying the kinetics of a reaction, it is possible to gain insights into how to control reaction conditions to achieve a desired outcome.

It is easy to get an idea that the rate of a chemical reaction can be increased by:
Increasing the concentration of a solution or raising the pressure (for a gas phase reaction), increasing the temperature of the reaction system, increasing the surface area of a solid

and by adding a catalyst. In addition to these, solvent used in an experiment to dissolve solute (reactant) can also affect the rate of reaction.

Insight into these can be understood by considering the basic requirements necessary to satisfy to occur a chemical reaction based on collision theory as discussed below.

1.6 Uses molecular kinetic theory (Collision Theory) to explain the effect of factors affecting the rate of chemical reactions

1.6.1 Collision theory

As we know from unit 4 (gaseous state of matter), collision theory explains the motion of molecules, their kinetic energy and how pressure changes in a system accordingly. Now it is easy to understand that for a reaction to occur the molecules must collide all the time and some fraction- but not all of those collisions will lead to transformation of the reactants to the products. This simply means that all the collisions will not result products. For example, at 1 atm and 20 °C, the $N_{2(g)}$ and $O_{2(g)}$ molecules in 1 cm^3 of air experience about 10^{27} collisions per second. If all that was lead for a reaction atmosphere would consist of almost all NO; but only traces are present. This indicates that the number of collisions can't be the only factor which determines the occurrence of a reaction and a reaction rate. Therefore, following must be satisfied to occur a chemical reaction:

1. The molecules must come into contact leading to a collision.
2. They must collide with enough energy to overcome an energy barrier. This minimum energy required is called the activation energy for the reaction.
3. They must collide in favorable orientation that allows the necessary bond-breaking and forming needed to transform the reactants to the products.

Collision:

According to kinetic molecular theory, the reactant molecules are considered to be hard spheres. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency *(Z)*. In its basic form, collision theory deals with one-step reactions, those in which two particles collide and form products: $A + B \rightarrow$ products. Suppose we have only two particles of A and two of B confined in a vessel.

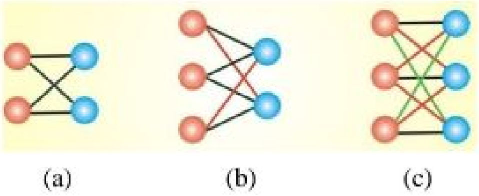


Figure 1.6 Increase in number of collisions with concentration of the reactants A and B in a constant volume of the reaction mixture. **(a)** Two molecules of A and two molecules of B can undergo four collisions. Likewise, in **(b)** when there are three molecules of A and 2 molecules are present total of six (3 × 2) collisions result. Three molecules of each A and B results nine (3 × 3) collisions as in **(c)**. Note that though the number of collision probabilities could predict like this, all the collisions may not result the product of the reaction.

Figure 1.6 shows that four A-B collisions are possible when there are two A and two B molecules. If we have three A and two B molecules, then there are six possible collisions and likewise when there are three A and three B molecules, we have nine possible collisions. Therefore, it can be noted that this probability of collision shows that the number of collisions depends on the *product* of the numbers of reactant particles, not their sum. Thus, collision theory explains that how the rate of a chemical reaction depends on the number of collisions per unit time per unit volume which in turn explains how the increase in concentration increases the reaction rate. Usually, this collision requirement has a large effect on what media are chosen to perform chemical reactions. Solids tend to be very slow reactors because only the atoms on the surface can have collisions with other atoms of other molecules. That's why the rusting of iron is very slow. Most reactions are done either in solution or in the gas phase where freedom of movement of the reactant molecules allows them to easily come into contact. Therefore, the more collisions per unit time per unit volume at a given temperature, the faster is the reaction rate.

Collision orientation

It is easy to understand that in a situation involving two molecules they can only react together when they come into contact with each other. In this encounter, they first have to collide, and then they *may* react. This means that though the molecules collide with each other and all the collisions may not result the product. Reactant molecules must collide with a favorable orientation and they must have necessary activation energy to yield the desired product and such collisions are called *effective collisions.* The reaction rate increases with the increase in number of effective collisions and it is in turn proportional to the total number of collisions.

Example:

Consider the single-step decomposition reaction of BrNO given below.

$$2BrNO_{(g)} \rightarrow 2NO_{(g)} + Br_{2(g)}$$

Now let's see the way the two molecules of BrNO arrange in space as depicted in Figure 1.7. To form $Br_2(g)$ as a product, two Br atoms of the two molecules of BrNO should approach along the same line as shown in the first two collisions. However, if those molecules line up as depicted in third collision, there is no way to collide two Br atoms and hence the collision orientation would not produce the products in the reaction. Therefore, the proper line of approach or the direction of colliding reactant molecules control the rate of reaction.

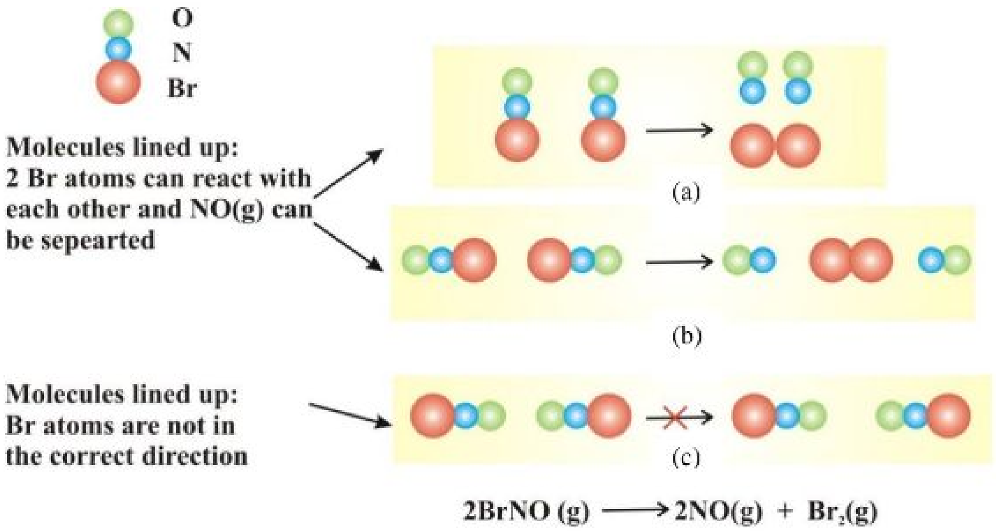
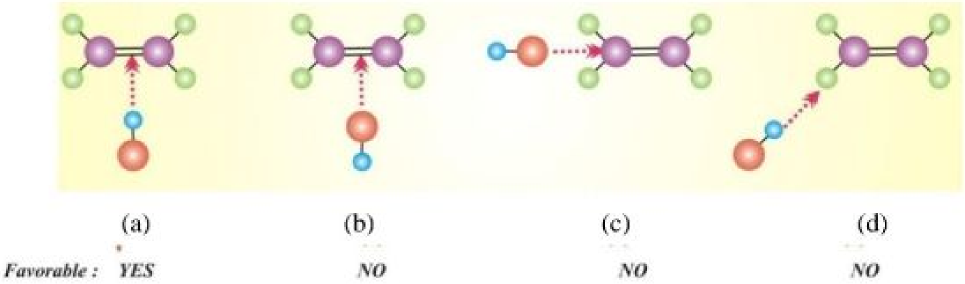


Figure 1.7 Different orientations of collisions between two BrNO molecules. In **(a)** and **(b)**, two molecules lined up properly and result the formation of a Br_2 molecule and two NO molecules. In **(c)** though the molecules lined up, Br atoms are not in the favourable sides/directions to collide and to for in the products.

Consider another single-step reaction between ethene and HCl to produce chloroethane.

$$CH_2{=}CH_2(g) + HCl(g) \rightarrow CH_3CH_2Cl(g)$$

As a result of the collision between the two molecules, the C = C double bond is converted into a single bond attaching hydrogen atom to one of the carbons and a chlorine atom to the other. The desired product of the reaction is only possible if the hydrogen end of the H-Cl bond approaches the carbon-carbon double bond. C = C has a high electron density around it and if the Cl atom approaches it, the Cl atom is repelled leading to no products. The collisions leads to the products and the other possible collisions the collisions which do not lead to products are compared in Figure 1.8.



$$CH_2{=}CH_2(g) + HCl(g) \rightarrow CH_3CH_2Cl(g)$$

Figure 1.8 Possible orientations of collisions between $CH_2{=}CH_2$ and HCl molecules. In **(a)** hydrogen atom of HCl oriented towards the C=C bond and as the C=C bond has negative charge, this collision favours the product. In **(b)**, Cl atom of HCl is repelled thus the reaction is not favoured. In **(c)** and **(d)** product is not favoured.

Surmounting the activation energy barrier

We know that a sample of reactant molecules in motion will have a Boltzmann distribution of molecular kinetic energies. Some molecules will have high energy; some low; many with intermediate energies. Figure 1.9 shows Boltzmann plots for a set of reactants at two different temperatures. Only those reactant molecules with energies greater than a certain minimum (threshold) energy called the ***activation energy, E_a*** (to the right of the plot) will be able to yield products. Because a greater fraction of molecules in the high temperature sample exceed the activation energy, the high-temperature sample will have more effective collisions and will experience a faster reaction rate compared to the sample at low temperature.

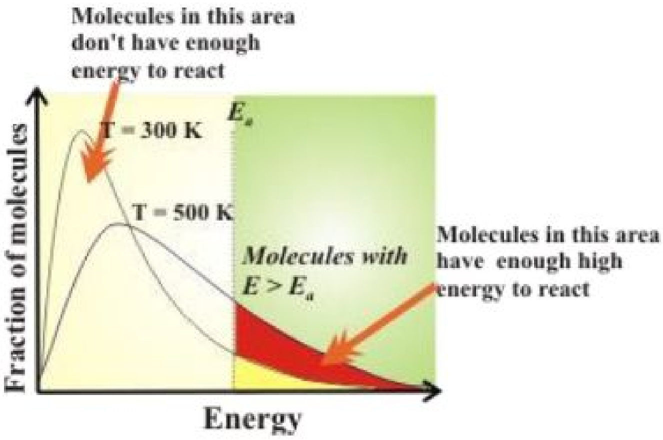


Figure 1.9 The effect of temperature on the distribution of collision energies. At higher temperature fraction of molecules having energy more than the activation energy increases leading to higher reaction rates.

When a favorable collision occurs between molecules overcoming the forces of interactions among the molecules, first an unstable molecule cluster, called the activated complex (transition state) is formed. The life time of the activated complex is very short and transformed to the products (or may break into the reactants again). The activation energy (E_a) depends upon the nature of chemical bonds undergoing rupture and is independent of enthalpies of reaction. The energy diagram for this with the example of the decomposition of BrNO(g) is shown in Figure 1.10 More details on this will be discussed later.

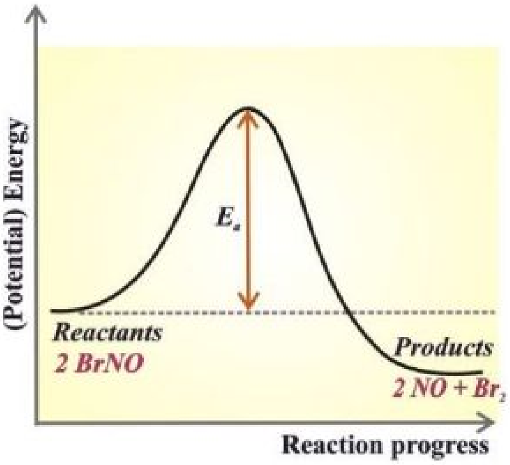


Figure 1.10 Energy diagram in which the activation energy (E_a) is depicted

For example, in the decomposition reaction $2BrNO(g) \rightarrow 2NO(g) + Br_2(g)$, of BrNO(g) two Br-N bonds need to be broken and one Br-Br bond needs to be formed. The energy required to break a Br-N bond is about 243 kJ mol^{-1} and hence this energy must be required to occur the reaction. Based upon the collision model, the energy comes from the kinetic energy of the molecules and once the molecules collide, the kinetic energy is transferred into potential energy which breaks the bonds and rearranges the atoms.

As a summary we can see that a chemical reaction whether exothermic or endothermic has an energy barrier which has to be overcome before reactants can be transformed into products. If the reactant molecules have sufficient energy, they can reach the peak of the energy barrier after an effective collision and then they can go to the right side of the curve and consequently change into products. If the activation energy for a reaction is low, the fraction of effective/ favourable collisions will be large and the reaction will be fast. On the other hand, if the activation energy is high, then fraction of effective collisions will be small and the reaction will be slow. When temperature is increased, the number of collisions and the number of effective collisions per unit time per unit volume will increase and hence the rate of reaction will increase.

Concentration effects

In a chemical reaction of the type A + B → *Products:* reactant molecules of A and B (atoms, or ions) come into contact and converted into products. If there is no contact, the reaction rate will be zero. If the number of molecules per unit volume is increased the reaction rate increases as the collisions between them increase. This means that the reaction rate usually increases as the concentration of the reactants increases. In reactions involving liquids or gases, increasing the concentration of the reactants increases the rate of reaction. In a few cases, increasing the concentration of one of the reactants may not have an effect of the rate (Details of this is discussed in a latter section). The reaction between solid $CaCO_3$ and HCl acid can be used to demonstrate this concentration effect:

$$CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$$

The rate of reaction can be altered by changing the concentration of the acid. (Also size of the calcium carbonate chips can be changed and it comes under the physical nature of the reactant). In this reaction it has been observed that if the $CaCO_3$ chips are large and in excess, then only a small fraction of the solid reacts. The rate will decrease over time as the hydrochloric acid is consumed because the concentration of HCl decreases over the time. Therefore, the rate of reaction can be monitored by measuring the pH of the solution, the decrease in the mass of calcium carbonate, or the increase in the volume of carbon dioxide. The easiest way is the volume measurement of the evolved CO_2 as it is the only gaseous species formed. In a particular experiment if we allow to react a known amount of $CaCO_3$ separately with a known volume of (~ 100 cm^3) of 0.50, 1.00 and 2.00 mol dm^{-3} HCl solutions, and monitor the volume of CO_2 formed with the time, following results could be observed (Figure 1.11).

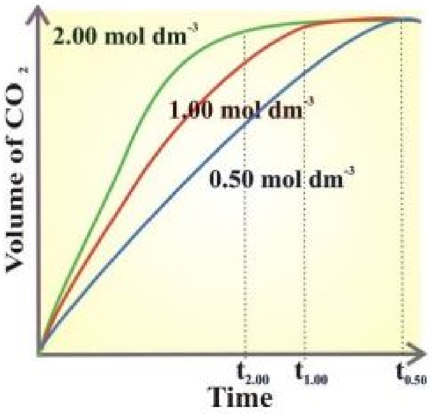


Figure 1.11 The variation in time for the generation of a constant volume of $CO_2(g)$ with the concentration of HCl in a reaction $CaCO_3(s) + 2HCl(aq) \rightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$ at a given temperature.

From the above graph it can be seen that the time taken to produce a constant volume of CO_2 gas decreases ($t_{2.00} < t_{1.00} < t_{0.50}$) with the increasing concentration of HCl. That is the rate of the reaction increases with the increasing concentration of HCl. The reason for this increased rate is explained by the collision theory. At high concentrations collisions per unit time per unit surface area of ($CaCO_3$) among reactants increase and hence the rate of the reaction.

Though the reaction rate increases with concentration, it has to be noted that in certain type of reactions (multi-step) this phenomenon does not exist. For example, consider a reaction which occurs in a series of steps having widely different rates where some of the steps are fast and some of them are slow.

Suppose two reactants A and B react together to give product P in the following two steps:

$$A(aq) \rightarrow X(aq) \quad : \textbf{\textit{slow}}$$
$$B(aq) + X(aq) \rightarrow P \ : \textbf{\textit{fast}}$$

In the above reaction overall rate of the reaction is controlled by the ***slow*** step in which **A** makes X. This is described as the ***rate determining step*** of the reaction.

If the concentration of A is increased, it is clear that the rate of that step increases as described above. However, if the concentration of B is increased, of course, the rate of the step increases but that does not make any impact on the overall rate of the reaction because that the step happens very fast as soon as any X is formed. Therefore, in such a multi-step reaction, increase in the concentration of a particular reactant which involves in the fast step does not show any impact on the reaction rate. Nucleophilic substitution reactions are some of the examples for this type of reactions.

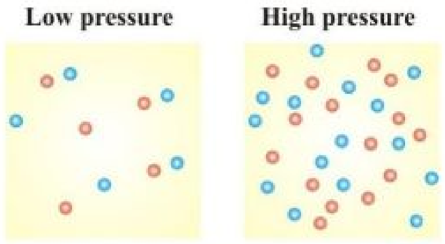
Pressure effects

Increasing the pressure of a reaction involving gaseous reactants increases the rate of reaction. Changing the pressure of a reaction involving only solids or liquids has no effect on the rate. For example, in the manufacture of ammonia by the Haber process, the rate of reaction is increased by the use of very high pressures. Increasing the pressure of a gas is exactly the same as increasing its concentration for a given mass of gas as can be understood from the *ideal gas equation* as follows.

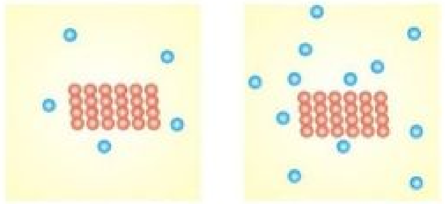
$$PV = nRT$$

For a given mass of gas, we can rearrange the above equation as;

$P = \frac{n}{V} RT = C\,RT$ for a given volume at a constant temperature. As a product *(RT)* is a constant at constant temperature, pressure is directly proportional to the concentration. It is clear that when the pressure is increased collision between two different particles or two of the same particles increases and hence the rate of reaction. This is true for the systems with the both reacting molecules are in gaseous state at constant volume, or whether one is a gas and the other is a solid as described in the Figure 1.11.



Both reactants are gases



One of the reactant is a solid

Figure 1.12 Effect of the pressure: Increase in pressure increases the concentrations of gaseous reactants.

Temperature effects

It has been understood that changing the temperature affects the rate of a reaction. As described in the above with the Maxwell-Boltzmann distribution of molecular energies in a gas increase in the temperature leads the rate of reaction to increase. For many reactions (not for all reactions) happening at around the room temperature, the rate of reaction approximately doubles for every 10 °C rise in temperature. Some reactions are virtually instantaneous (very fast). Examples are precipitation reactions from participant ions in solution to make an insoluble solid, or the reaction between hydrogen ions from an acid and hydroxide ions from an alkali in solution. So heating one of these would not make any acceptable or significant difference in the rate of the reaction.

As described in Unit 4 (gaseous state of matter) the increase in temperature of a system increases the average kinetic energy of its constituent molecules/particles. As the average kinetic energy increases, the particles move faster and collide more frequently per unit time (per unit volume). This leads to increase the fraction of molecules processing energy for productive collisions (or in other words, exceeds the activation energy of the reaction). Both of these factors increase the reaction rate. Hence, the reaction rate of all (most) reactions increases with increasing temperature. Details of this will be discussed in a latter section. Conversely, the rate of reactions decreases with decreasing temperature. For example, refrigeration slows down the growth of bacteria in foods by decreasing the reaction rates of biochemical reactions that enable bacteria to reproduce.

In addition, in the systems where more than one reaction is possible, the same reactants can produce different products under different reaction conditions. For example, in the presence of dilute sulfuric acid and at temperatures around 100 °C, ethanol is converted to diethyl ether:

$$2CH_3CH_2OH(aq) \xrightarrow{H_2SO_4} CH_3CH_2OCH_2CH_3(aq) + H_2O(l)$$

At 180 °C, however, a completely different reaction occurs, which produces ethylene as the major product:

$$CH_3CH_2OH(aq) \xrightarrow{H_2SO_4} C_2H_4(g) + H_2O(l)$$

Physical nature of the reactants

Consider a reaction of two reactant molecules in the same liquid phase. They collide more frequently than when one or both reactants are solids (or when they are in different immiscible liquid phases). If the reactant molecules are uniformly dispersed in a single homogeneous solution, then the number of collisions per unit time per unit volume depends on concentration and temperature. If the reaction is heterogeneous, the reactants are in two different phases (solid/gas), and collisions between the reactants can occur only at the interface between the two phases. The number of collisions between reactants per unit time per unit volume is substantially reduced relative to the homogeneous case, and, hence, so is the reaction rate. Usually rates of reactions depend on the physical state as Gaseous state > Liquid state > Solid state. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase.

In automobile engines, surface area effect on the reaction rate is used. Gasoline is injected into each cylinder, where it combusts on ignition by a spark from the spark plug. The gasoline is injected in the form of microscopic droplets because in that form it has a much larger surface area and can burn much more rapidly than if it were fed into the cylinder as a stream. Similarly, a pile of finely divided iron burns slowly (or not at all), but spraying finely divided dust into a flame produces a vigorous reaction.

In the case of solid reactant, a more finely powdered solid reacts faster than the same mass present as a single lump because the powdered solid has a greater surface area than the single lump.

For example in the calcium carbonate and hydrochloric acid reaction in the laboratory you can observe that the powdered calcium carbonate reacts much faster with dilute hydrochloric acid than if the same mass was present as lumps of marble or limestone.

In the catalytic decomposition of hydrogen peroxide solid manganese(IV) oxide is often used as the catalyst. Oxygen is given off much faster if the catalyst is present as a powder than as the same mass of granules.

For example, in a reaction between magnesium metal and a dilute hydrochloric acid involves collision between magnesium atoms and hydrogen ions. The surface area of the metal here also affects the rate of the reaction. Fine magnesium powder causes evolution of hydrogen gas more rapidly than the magnesium strip.

Not only the physical nature as described earlier but nature of chemical bonds in reactants affects the rate.

Consider the following two reactions:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ ………… (a)

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ ………… (b)

The first reaction (a) is faster than the second because in the first reaction only $N = O$ bond is to be broken where as in the second reaction (b) four C-H bonds are to be broken.

Similarly consider another example of two similar reactions:

$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ ………... (c)

$2CO(g) + O_2(g) \rightarrow 2CO_2(g)$ ……........ (d)

NO bond is weaker than CO bond, hence is broken easily. Thus reaction (c) is faster than (d).

Solvent effects

The nature of the solvent can also affect the reaction rates. The same reaction occurring in different solvents shows different rates depending on the polarities of solvents used.

When the reaction occurs in the same solvent, viscosity is also important in determining reaction rates. In highly viscous solvents, dissolved particles diffuse much more slowly than in less viscous solvents and can collide less frequently per unit time per unit volume. Thus the reaction rates decrease with increasing solvent viscosity.

Catalyst effects

A catalyst is a substance that participates in a chemical reaction and increases the reaction rate by changing the path of the reaction without undergoing a net chemical change itself. For example, the reaction $CO(g) + 2H_2(g) \rightarrow CH_3OH(g)$ is very slow at room temperature and can be speeded up by introducing a catalyst. In addition, the decomposition of hydrogen peroxide in the presence of catalyst occurs in much more rapidly compared to the rate of that reaction without a catalyst. Because most catalysts are specific to certain reactions, they often determine the product of a reaction by accelerating only one of several possible reactions that could occur. In particular reactions with a catalyst the increase in concentration of the reactants sometimes may not increase the rate of reaction. For example, when a small amount of finely powdered solid catalyst is used in a reaction with a high enough concentration of reactant in solution the catalyst surface is totally covered up with reacting particles. Increasing the concentration of the solution even more cannot make any effect because the catalyst is already working at its maximum capacity. Details of these effects on the reaction rate and mechanisms will be discussed in a separate section.

1.7 Controlling the rate of a reaction by appropriately manipulating the concentration of reactants

1.7.1 Expressing the rate of a reaction: Average, instantaneous and initial rates

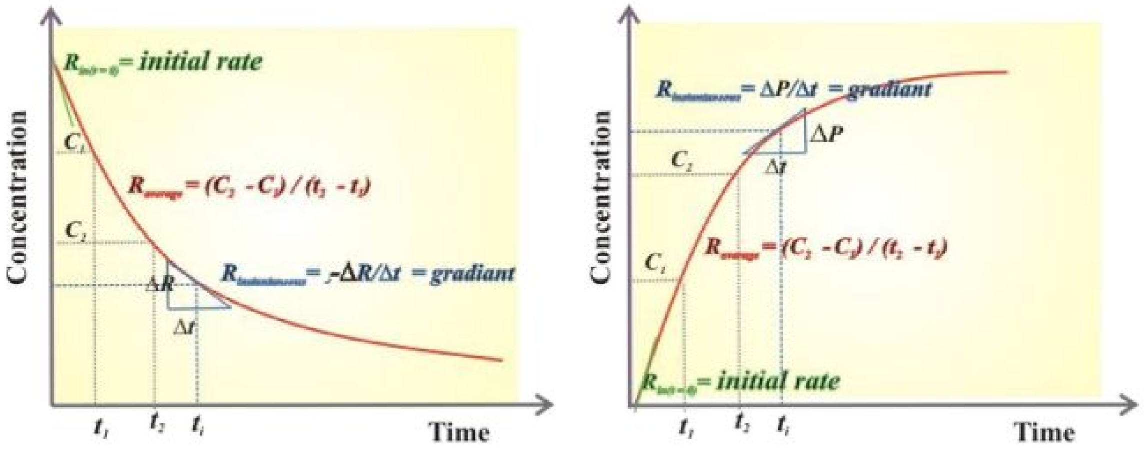
As described earlier *the rate varies as a reaction proceeds.* Consider the following hypothetical gas phase reaction between **A** and **B**.

$$\mathrm{A(g)} + \mathrm{B(g)} \rightarrow \mathrm{C(g)}$$

For every molecule of **A**, a molecule of **B** reacts and hence **[A]** and **[B]** decrease at the same rate and we can write:

$$\text{Rate} = -\frac{\Delta[\mathrm{A}]}{\Delta t} = -\frac{\Delta[\mathrm{B}]}{\Delta t}$$

Assume that the reaction is started with a known [A] in a closed vessel at 298 K and the concentration of is manured A at 10 second intervals after adding B. The obtained data can be plotted as shown in Figure 1.13. Rate *decreases* during the progress of the reaction because the *reactant* concentration decreases with the time (As **A** molecules react, the number of effective collisions decreases and hence the rate). If we plot the concentration of the products with the time the opposite curve will result. With the help of the plot of concentration vs time, following three types of rates can be defined.



(a) (b)

Figure 1.13 Definitions and graphical expression of reaction rates; average, instantaneous and initial rates: (a); change in rate for the reactants and (b); change in rate for the products. Note that the quantity of rate takes negative sign (as the slope is negative) and that for the products is positive. Therefore, in the calculations rate of consumption of reactants is multiplied by (-1).

Average rate

Over a given period of time, the **average rate** is the slope of the line joining two points along the curve. The average rate over the first 100 s time interval is the change in concentration during that time interval divided by the time taken. For example, when $C_1 = 3.50 \times 10^{-5}$ and $C_2 = 0.50 \times 10^{-5}$ mol dm^{-3},

$$\text{Rate}_{0-100} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,0.50 \times 10^{-5} - \;3.50 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,100 - 0\,]s}$$
$$= \;3.0 \times 10^{-7}\ \text{mol dm}^{-3}\ \text{s}^{-1}$$

This shows that during the first 100 s of the reaction, [A] decreases with the *average* of 3.0×10^{-7} mol dm^{-3} each second. However, this does not imply that the rate at any point along the curve is 3.0×10^{-7} mol dm^{-3} s^{-1}. We can clearly understand that the slope of the curve decreases with the time and hence the rate (average) should also decrease.

That means the rate over shorter intervals may be lower or higher than the average. In the above estimation in whole 100 s interval the decrease in [A] does not show the rate over any shorter time period. This *change* in reaction rate is evident when we calculate the average rate over two shorter periods. For example, in the first 10 s the average rate is given by ($C_1 = 3.50 \times 10^{-5}$ and $C_2 = 3.00 \times 10^{-5}$ mol dm^{-3});

$$\text{Rate}_{0-10} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,3.00 \times 10^{-5} - \;3.50 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,10 - 0\,]s}$$
$$= \;5.0 \times 10^{-7}\text{mol dm}^{-3}\ \text{s}^{-1}$$

Likewise the average rate in the 50-60 s interval is when $C_1 = 1.00 \times 10^{-5}$ and $C_2 = 0.75 \times 10^{-5}$ mol dm^{-3}.

$$\text{Rate}_{50-60} = -\frac{\Delta[A]}{\Delta t} = -\frac{[\,0.75 \times 10^{-5} - \;1.00 \times 10^{-5}]\ \text{mol dm}^{-3}}{[\,60 - 50\,]\ \text{s}}$$
$$= \;2.50 \times 10^{-7}\text{mol dm}^{-3}\ \text{s}^{-1}$$

Instantaneous rate

Average rate which is a constant for the time interval interested cannot be used to predict the rate of a reaction at a particular instant. So, to express the rate at a particular instant of time the instantaneous rate is determined. Rate of the reaction at a certain time is called as an instantaneous rate. The slope of a line tangent to the curve at any point gives the instantaneous rate at that time.

For example, the instantaneous rate at 50.0 s is;
To calculate this it is necessary to calculate the slope of the tangent line drawn to the curve at 50.0 s. Related points considered are ($65, 1.25 \times 10^{-5}$) and ($35, 0.75 \times 10^{-5}$)

$$\text{Rate}_{50} = -\frac{\Delta[\text{A}]}{\Delta t} = -\frac{[(0.75 - 1.25)\times 10^{-5}]\ \text{mol dm}^{-3}}{[\ 65 - 35\ ]\text{s}} = 1.70 \times 10^{-7}\text{mol dm}^{-3}\ \text{s}^{-1}$$

It is very clear that the instantaneous rate is different from the average rate and in general, we use the term *reaction rate* to mean *instantaneous* reaction rate.

Initial rate

The instantaneous rate at the moment the reactants are mixed (that is, at $t = 0$) is the **initial rate.** Initial rate is calculated from the slope of the line tangent to the curve at $t = 0$ s (Figure 1.13). Measurements of initial rates is usually used in chemical kinetics to find other kinetic parameters.

When there is a reversible reaction the use of initial rate poses some complications. As a reaction proceeds in the *forward* direction (products → reactants), product increases, causing the *reverse* reaction (products → reactants), to occur more quickly. To find the overall (net) rate, we would have to calculate the difference between the forward and reverse rates. But, for the initial rate, $t = 0$, so product concentrations are negligible. So the rate of the reverse reaction would not affect the estimations.

As such in the simple way the initial rate or the instantaneous rate at t = 0, occurs when reactants have just been mixed and before any product accumulates.

1.7.2 Effect of concentration on reaction rate

Rate law

From the above section it is known that the frequency of effective collisions controls reaction rates. The more effective collisions mean the faster the rate. There are two ways to increase the frequency of collisions between molecules: increase the number of molecules in a constant volume at a given temperature or increase the kinetic energy of them by raising temperature. Increasing the number of molecules in a constant volume means the increase in concentration.

As was explained previously, for many reactions involving liquids or gases, increasing the concentration of the reactants increases the rate of reaction due to the increase in collision frequency. In some cases, increasing the concentration of one of the reactants may not affect the rate and also doubling the concentration of one of the reactants may not double the rate of the reactions always. Therefore, it is necessary to understand the behavior of concentration dependence of the reaction rate quantitatively with some models.

Consider a simple reaction;

$$A \rightarrow B$$

We can write,

$$\text{Rate} \propto [A]$$

$$\therefore \text{Rate} = k\,[A]$$

where ***k*** is the proportionality constant and is called the "**rate constant".** The above expression is called the **rate law expression** or **rate law** of the reaction A → B. In this reaction we can say that the rate of the reaction is proportional to the concentration of A. If we assure that doubling the concentration of A doubles the rate and we can then write the rate law as;

$$\text{Rate} = k\,[A]^1 = k[A]$$

Consider the following decomposition reaction.

$$NH_4NCO_{(aq)} \rightarrow (NH_2)_2CO_{(aq)}$$

It has been experimentally found that the rate of the above reaction is proportional to the above square of the $NH_4NCO_{(aq)}$ concentration. That is when the concentration of $NH_4NCO_{(aq)}$ is doubled the rate will quadruple. Therefore, the rate law for the reaction can be written as,

$$\text{Rate} = k\,[NH_4NCO_{(aq)}]^2$$

From the above it can be noted that there are three parts appear in the rate law;

***k:* rate constant;** For a given reaction it has a number and (appropriate) units. Rate constant is different for different reactions and is different for the same reaction at different temperatures.

$[NH_4NCO_{(aq)}]$: the concentration of the reactants; If more than one reactant is present, any or all of them may be present in the equation. Sometimes it is the case that one or more reactants will not be appearing in the rate law.

2: the order of the reaction with respect to the relevant reactant; This is more often an integer like 1,2. but fractions are also possible sometimes. If the order is one, 1 is not written in the rate law expression. The order of the reaction can also be more than 2. However, they are not included in this discussion.

Experimentally derived rate laws for two reactions are given below.

$2NO_{(g)} + O_{2(g)} \rightarrow NO_{2(g)}$: Rate $= k\,[NO_{(g)}]^2[O_{2(g)}]$

$NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$: Rate $= k\,[NO_{2(g)}]^2$

Now consider a general reaction between reactants A and B;

$$aA + bB \rightarrow \textit{Products}$$

The rate law for the reaction can be written as,

$$\text{Rate} = \boldsymbol{k}\,[\text{A}]^x[\text{B}]^y$$

From the above examples concentrations of **A** and **B** have to be raised to some power ***x*** and **y** to show how they affect the rate of the reaction. These powers are called the **orders of the reaction** with respect to **A** and **B**. The sum of x and y, **(x + y)** is called as the **overall order** of the reaction.

> *i.e the sum of powers of the concentration terms of the reactants written in the rate law expression is called the overall order of that chemical reaction.*

If the order of reaction with respect to **A** is 0 (zero), this means that the concentration of **A** doesn't affect the rate of the reaction. Mathematically, any number raised to the power zero is equal to 1. That is why that particular concentration term disappears from the rate equation.

> *Therefore, rate law is the expression in which reaction rate is given in terms of molar concentration of reactants with each term raised to some power, which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.*

Let's consider some examples of observed rate laws and note the reaction orders.
For the reaction between NO and H_2 gases,

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$

the rate law is

$$\text{Rate} = k\,[NO_{(g)}]^2\,[H_{2(g)}]$$

This reaction is second order with respect to NO. And, even though $H_{2(g)}$ has the stoichiometric coefficient of 2 in the balanced equation, the reaction is first order with respect to $H_{2(g)}$. It is third order overall.

For the reaction between nitrogen monoxide and ozone,

$$NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$$

the rate law is

$$\text{Rate} = k\,[NO(g)]\,[O_3(g)]$$

This reaction is first order with respect to $NO_{(g)}$ and first order with respect to $O_3(g)$, thus it is second order overall.

For the hydrolysis of 2-bromo-2-methylpropane,

$$(CH_3)_3CBr(l) + H_2O(l) \rightarrow (CH_3)_3COH(l) + HBr(aq)$$

the rate law is

$$\text{Rate} = k\,[(CH_3)_3CBr(l)]$$

This reaction is first order with respect to 2-bromo-2-methylpropane and zero order with respect to $H_2O(l)$, despite its coefficient of 1 in the balanced equation. If we want to note that water is a reactant, we can write the rate law as follows.

$$\text{Rate} = k\,[(CH_3)_3CBr(l)]\,[H_2O(l)]^0$$

This is a first order reaction overall.

The above examples give an important point:

> *Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation and must be determined experimentally. Although the rate constant is really a number with appropriate units, when describing a general rate law, we usually just write* ***k*** *but any value is true only at one temperature.*

The rate of a reaction is always expressed in terms of mol $dm^{-3}\ s^{-1}$. We can classify the reactions as *zeroth, first, second, etc.* order reactions. Assuming time is measured in seconds, The corresponding units of the *rate constant can be derived* as follows.

Zero order reactions

Consider the reaction; A → products

If the reaction is zero order, the rate law is,

$$\text{Rate} = k$$

The units of k must be the same as that of rate, **mol $\mathbf{dm^{-3}\ s^{-1}}$.**

First order reactions

Consider the reaction; A → products

If the reaction is first order, the rate law is,

$$\text{Rate} = k\,[A]$$

$$\text{Units of } k; = \frac{\text{Rate}}{[A]} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}} = \mathbf{s^{-1}}.$$

Second order reactions

Consider a reactions A → products or A + B → products

If the reaction is second order, the rate law is,

$$\text{Rate} = k\,[A]^2 \quad \text{or} \quad \text{Rate} = k\,[A][B]$$

$$\text{Units of } k; = \frac{\text{Rate}}{[A]^2} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol}^2\text{ dm}^{-6}} = \mathbf{mol^{-1}\ dm^3\ s^{-1}}.$$

Example 1.8

Methyl acetate reacts with hydroxide ion according to the following equation.

$$CH_3COOCH_3(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + CH_3OH(aq)$$

The rate law is;

$$\text{Rate} = k\,[CH_3COOCH_3(aq)][OH^-(aq)]$$

What is the order of reaction with respect to each reactant, and the overall reaction order?

Answer

Because there are no superscripts to the right of each concentration term in the rate law, it means they are each first order. The reaction is first order in $CH_3COOCH_3(aq)$ and first order in $OH^-(aq)$. It is second order overall $(1 + 1 = 2)$.

For example let's consider experimentally derived rate laws for the following reactions;

$2NO(g) + O_2(g) \rightarrow NO_2(g)$: Rate $= k\,[NO(g)]^2[O_2(g)]$

The reaction is second order with respect to $NO(g)$ *and first order with respect to* $O_2(g)$. *Overall order of the reaction is 3.*

$NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$: Rate $= k\,[NO_2(g)]^2$

The reaction is second order with respect to $NO_2(g)$ *and zero order with respect to* $CO(g)$. *Overall order of the reaction is 2.*

Example 1.9

Identify the reaction order from each of the following rate constants.

Answer

(i) $k = 5.6 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$

The unit of second order rate constant is $dm^3\ mol^{-1}\ s^{-1}$

$\therefore k = 5.6 \times 10^{-5}\ dm^3\ mol^{-1}\ s^{-1}$ *represents the second order reaction.*

(ii) $k = 3 \times 10^{-4}\ s^{-1}$.

The unit of a first order rate constant is s^{-1}

$\therefore k = 3 \times 10^{-4}\ s^{-1}$ *represents the first order reaction.*

Table 1.1 summarizes the difference in rate of a reaction and rate constant to avoid the confusion between them.

Table 1.1 The difference in rate of a reaction and rate constant

Rate of reaction	Rate constant
It is the speed of conversion of reactants into products.	It is a proportionality constant.
It is measured as the rate of decrease of concentration of reactants or the rate of increase of concentration of products with time.	It is equal to the rate of reaction when the concentration of each of the reactants is unity.
It depends upon the initial concentration of reactants.	It is independent of the initial concentration of the reactants. It has a constant value for a given reaction at a fixed temperature.

1.7.3 Graphical representation of change in rate with concentration for zero, first and second order reactions

Zero order reactions

Zero order reactions means that the rate of the reaction is independent of the concentration of the reactants or we can say that the rate is proportional to zeroth power of the concentration of reactants. Consider the reaction,

$$\mathrm{A} \rightarrow \text{Products}$$
$$\text{Rate} = \mathrm{k}\,[\mathrm{A}]^0 = \mathrm{k}$$

Therefore, for any given concentration of A, the rate does not change implying that the rate is a constant with the concentration. Hence the plot of rate against the concentration is a horizontal straight line as shown in Figure 1.14 (a). In other words, the change in concentration over the time is a constant which can be obtained from the slope of the graph of concentration over the time as shown in Figure 1.14(b).

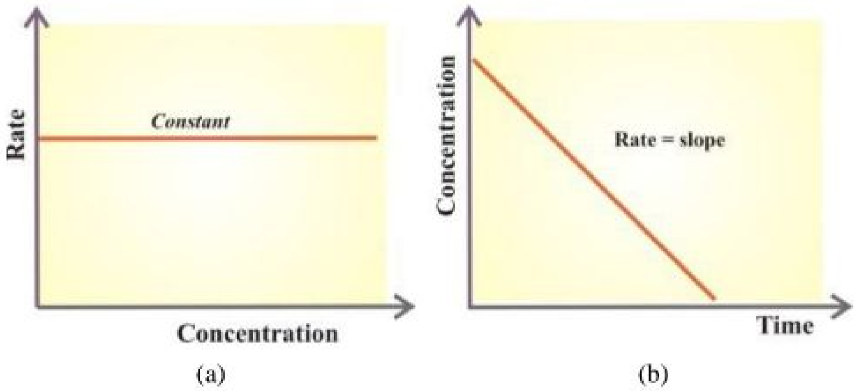


Figure 1.14 (a) Variation of reaction rate over the concentration of the reactant and (b) Variation of concentration of the reactant over the time for a zero-order reaction.

The behaviour of the zero order reaction can be treated as follows too.
Consider a reaction:

$$A + B \rightarrow \text{Products}$$

Rate of the reaction is,

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

Assume that the concentration of B is very high and change in its concentration is negligible during the course of reaction. Therefore, the rate of reaction can be written as,

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

As the reaction is zero order with respect to A, Rate = k' = constant

Therefore, the graph of rate verses the concentration is again a horizontal straight line as described above.

Some photochemical reactions and a few heterogeneous reactions are examples for zero-order reactions. Such reactions are not common.

Photochemical reaction between hydrogen and chlorine:

$$H_2\,(g) + Cl_2\,(g) \xrightarrow{h\nu} 2HCl\,(g)$$

This photochemical reaction is a zero-order reaction. The reaction is studied by placing H_2 and Cl_2 gases over water. The rate of reaction is studied by noting the rate at which water rises in the vessel due to dissolving of HCl formed. The rate of rise of water is the same as the rate of disappearance of H_2 and Cl_2, i.e., the concentration of the gaseous phase will not change with time, although the quantities will change.

Decomposition of $N_2O_{(g)}$ on a hot platinum surface:

$$N_2O(g) \rightarrow N_2(g) + 1/2\,O_2(g)$$

$$\text{Rate} = k\,[N_2O]^0 = k \text{ or,}$$

$$\frac{\Delta[N_2O]}{\Delta t} = k$$

Decomposition of $NH_3(g)$ in the presence of molybdenum or tungsten is a zero-order reaction.

$$2NH_3(g) \xrightarrow{Mo} N_2(g) + 3H_2(g)$$

The surface of the catalyst is almost completely covered by NH_3 molecules. The adsorption of gas on the surface cannot be changed by increasing the pressure or concentration of NH_3. Thus, the concentration of gas phase remains constant although the product is formed. Therefore, this reaction has zero order kinetics.

Other examples for zero order reactions are:

Iodination of acetone in the presence of $H^+(aq)$ ions:

$$CH_3COCH_{3(aq)} + I_{2(aq)} \xrightarrow{H^+(aq)} ICH_2COCH_{3(aq)} + HI_{(aq)}$$

Experimentally found that the rate equation of this reaction does not containing $[I_2]$ factor, i.e.,

$$\text{Rate} = k\,[CH_3\,COCH_{3(aq)}][H^+_{(aq)}]$$

Indicating that the reaction is zero order with respect to $[I_{2(aq)}]$

Characteristics of zero order reactions

The concentration of the reactants decreases linearly with time.

The time required for the reaction to be complete, i.e., time at which [A] is zero is given by;

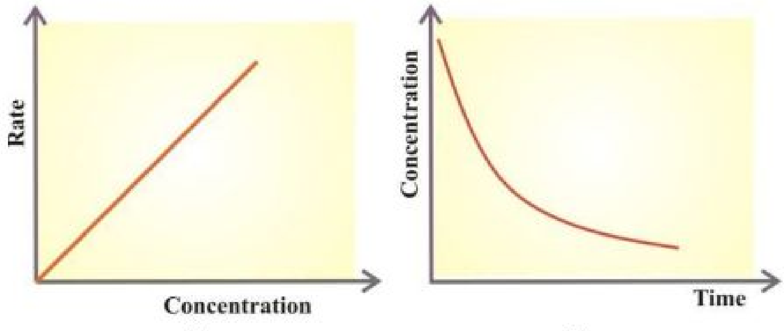
$$t_{completion} = \frac{[A]_0}{k} = \text{(Initial concentration)/ (Rate constant)}$$

First order reactions

In this class of reactions, the rate of the reaction is proportional to the first power of the concentration of the reactant. For example, considering the same reaction; A → products

$$\text{Rate} = k\,[A]$$

This takes the form; $y = mx$ and the graph of rate against the concentration will be a straight line going through the origin (0,0) as shown in Figure 1.15(a). The plot of the variation of concentration over the time will be a curve as shown in Figure 1.15(b).



(a) (b)

Figure 1.15 **(a)** Variation of reaction rate over the concentration of the reactant (gradient = rate constant) and **(b)** Variation of concentration of the reactant over the time for a first-order reaction.

Let us consider this in another way.
We can write,

$$\text{Rate} = k\,[\text{A}]$$

Taking log of both sides; $\log(\text{Rate}) = \log[\text{A}] + \log(k)$

Therefore, the graph of log (Rate) against log[A] will be $y = mx + c$ type having the slope of one (1) and the intercept of log (k) as shown in Figure 1.17 (will be shown later).

As discussed previously, the rate constant of a first order reaction has only (inverse) time unit. It has no concentration unit. This means that the numerical value of k for a first order reaction is independent of the unit in which concentration is expressed. ($k = \frac{\text{rate}}{\text{concentration}} = \frac{\text{mol dm}^{-3}\text{s}^{-1}}{\text{mol dm}^{-3}}$)Therefore, even if the concentration unit is changed the numerical value of k for a first order reaction will remain unchanged. However, it would change with the change in time unit. Say, k is 6.0×10^{-3} min^{-1}, then it can also be written as 1.0×10^{-4} s^{-1} .i.e. The numerical value of k has changed.

Following are some examples for the first order reactions.

Decomposition of $H_2O_2(aq)$ in aqueous solution

$$H_2O_2(aq) \rightarrow H_2O(l) + \tfrac{1}{2}O_2(g)$$

Hydrolysis of methyl acetate in the presence of mineral acids

$$CH_3COOCH_3(aq) + H_2O(l) \rightarrow CH_3COOH(aq) + CH_3OH(aq)$$

Inversion of cane sugar in the presence of mineral acids

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \xrightarrow{H^+} C_6H_{12}O_6(aq) + C_6H_{12}O_6(aq)$$

Decomposition of ammonium nitrite in aqueous solution

$$NH_4NO_2(aq) \rightarrow N_2(g) + 2H_2O(l)$$

Hydrolysis of diazo derivatives

$$C_6H_5N{=}NCl(aq) + H_2O(l) \rightarrow C_6H_5OH(aq) + N_2(g) + HCl(aq)$$

In the cases where gas phase reactions are considered, it is necessary to use pressure terms instead of concentration terms in the rate law. For example, a reaction $A(g) \rightarrow B(g) + C(g)$ is a first order reaction. If the initial (at t = 0) pressure of the system is P_1 and the pressure of the system changed to P_2 after time t, it is necessary to understand the way we write the rate law of the reaction.

In this case we can assume that the partial pressure of A is decreased by -x due to its decomposition and hence the pressures built up by each of B and C would be +x. Therefore we can construct the system as follows.

	$A(g)$ →	$B(g)$ +	$C(g)$
Initial	P_1	0	0
At time *t*	$P_1 - x$	x	x

Therefore, total pressure at time $t = (P_1 - x) + x + x = P_1 + x = P_2$

$\therefore x = P_2 - P_1$

t Pressure of A at $t = P_1 - x = P_1 - (P_2 - P_1) = 2P_1 - P_2$

Thus these pressure terms can be used for the estimation of orders and rate constants of the reactions.

Second order reactions

In this class of reactions, the rate of the reaction is proportional to the second power of the concentration of the reactant or if the concentration of the respective reactant is doubled the rate will be quadrupled. For example, considering the same reaction; A → products

$$\text{Rate} = k\,[\text{A}]^2$$

This takes the form; $y = mx^2$ and the graph of rate against the concentration will be a upward-curve passes through the origin (0,0) as shown in the Figure 1.16(a). The variation of concentration against time will be a curve; however, slope would be higher than that for the first order plot as seen in Figure 1.16(b).

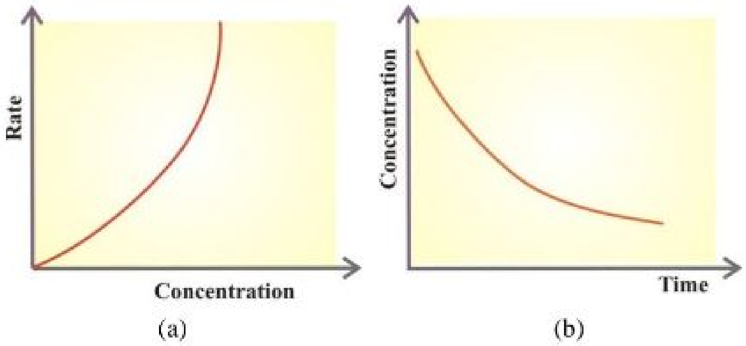


Figure 1.16 (a) Variation of reaction rate over the concentration of the reactant and (b) Variation of concentration of the reactant over the time for a second-order reaction.

Let us consider this in another way,
We can write,

$$\text{Rate} = k\,[\text{A}]^2$$

Taking log of both sides; $\log(\text{Rate}) = 2\log[\text{A}] + \log(k)$

Therefore, the graph of log(rate) against log[A] will be $y = mx + c$ type having the slope of two (2) and the intercept of log(*k*). As a summary Figure 1.17 compares the above cases in order to understand the differences in zeroth, first and second order reactions easily.

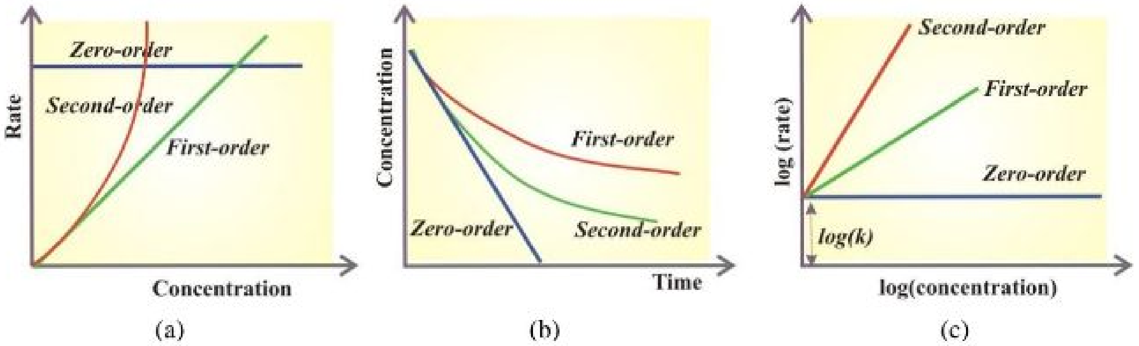


Figure 1.17 Comparison of first order, second order and zero order reactions; **(a)** Variation of reaction rate with concentration. The plot is a horizontal line for the zero order reaction because the rate does not change no matter what the value of [A]. The plot is an upward-sloping line for the first order reaction because the rate is directly proportional to [A]. The plot is an upward-sloping curve for the second order reaction because the rate increases exponentially with [A]. **(b)** Variation of concentration over time. The decrease in [A] does not change as time goes on for a zero order reaction. The decrease slows down as time goes on for a first order reaction. The decrease is even more for a second-order reaction. **(c)** Variation of log(rate) with log(concentration). The plot is a horizontal line for the zero order reaction. The plot is a straight line with the slope one for the first order reaction and the plot is a straight line with the slope two for a second order reaction.

Example 1.10

Consider the following first order reaction.

$$N_2O_5(g) \rightarrow 2NO_2(g) + \tfrac{1}{2}O_2(g)$$

At 328 K, when the concentration of $N_2O_5(g)$ was 2.00×10^{-2} mol dm^{-3} the rate of the decomposition was found to be 1.00×10^{-2} mol dm^{-3}s^{-1}. Calculate the first order rate constant of the reaction at 328 K.

Answer

$$\text{Rate} = k\,[\text{A}] = 1.00 \times 10^{-2} \text{ mol dm}^{-3}\, s^{-1}$$

$$\therefore k = \frac{1.00 \times 10^{-2}\ mol\ dm^{-3}\ s^{-1}}{2.00 \times 10^{-2}\ mol\ dm^{-3}} = 0.50\ s^{-1}$$

Example 1.11

Consider the reaction between oxygen and nitrogen monoxide.

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

Rate law of the reaction is $\text{rate} = k\ [O_{2(g)}]\ [NO(g)]^2$ at 300 K.

When the concentrations of $O_2(g)$ and NO(g) were 1.00×10^{-2} and 2.00×10^{-2} mol dm^{-3}, respectively, the rate was found to be 3.20×10^{-3} mol dm^{-3} s^{-1} at 300 K. Calculate the rate constant for the reaction at 300 K.

Answer

$$k = \frac{\text{rate}}{[O_{2(g)}]\ [NO(g)]^2}$$

$$= \frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{[1.00 \times 10^{-2}\text{mol dm}^{-3}]\ [2.00 \times 10^{-2}\ \text{mol dm}^{-3}]^2}$$

$$k = 8.00 \times 10^2\ \text{dm}^6\ \text{mol}^{-2}\ \text{s}^{-1}$$

Example 1.12

Consider the hypothetical reaction given below at a given temperature.

$$aA + bB \rightarrow cC + dD$$

In a particular experiment carried out at a given temperature, the rate of the reaction was found to be 5.00×10^{-4} mol dm^{-3} s^{-1} when the concentrations of A and B are 1.00×10^{-5} mol dm^{-3} and 2.00 mol dm^{-3} respectively. It has also been observed that the rate doubles as the concentration of A is doubled. Calculate the rate constant of the reaction.

Answer

For the reaction we can write the rate law as,

$$\text{rate} = k\ [A]^x\ [B]^y$$

It is given that the rate doubles as the concentration of A is doubled. Therefore, we can conclude/find that the reaction is first order with respect to A. Next, it is necessary to understand the dependence of rate on the concentration of B, which is much higher than the concentration of A ($1.00 \times 10^{-5} \lll 2.00$ mol dm^{-3}). Thus, it is evident that the reaction rate does not depend on the concentration of B, or assuming that [B] remains unchanged during the reaction. Now the rate law of the reaction can be rewritten as,

$$\text{Rate} = k'\ [A]$$

$$k' = \frac{5.00 \times 10^{-4}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{1.00 \times 10^{-5}\ \text{mol dm}^{-3}} = 50\ \text{s}^{-1}$$

Following example gives an idea about the relation between order and the concentration of the reactants. Consider a hypothetical reaction,

$$aA + bB \rightarrow cC + dD$$

and the rate low of the reaction is given by; Rate = $k\,[A][B]^2$

(a) Consider that the initial concentrations of both A and B are 1.0 mol dm^{-},^{3}

$$\text{Rate}_1 = k\,[1.0][1.0]^2 \text{ mol }^3\text{dm}^{-9} = k \text{ mol }^3\text{dm}^{-9}$$

If the concentration of A is doubled while keeping the concentration of B constant at 1.0 mol dm^{-3},

$$\text{Rate}_2 = k\,[2.0][1.0]^2 \text{ mol }^3\text{dm}^{-9} = 2k \text{ mol }^3\text{dm}^{-9}$$

i.e. The rate is doubled when the concentration of A is doubled revealing that the reaction is first order with respect to A.

(b) If the concentration of B is doubled while keeping the concentration of A constant at 1.0 mol dm^{-3},

$$\text{Rate}_3 = k\,[1.0][2.0]^2 \text{ mol }^3\text{dm}^{-9} = 4k \text{ mol }^3\text{dm}^{-9}$$

i.e. The rate is quadrupled when the concentration of B is doubled revealing that the reaction is second order with respect to B.

1.7.4 Methods to determine the order of a reaction and rate constant (Rate law)

From the above last two examples, when a concentration of one reactant is in large excess compared to the other reactant it has been assumed that the concentration of that reactant can be considered a constant during the course of reaction. This postulate can be used to investigate the kinetics of reactions involving more than one reactant and the experiments can be designed as such.

There are two fundamentally different approaches to this; follow a particular reaction all the way through, and process the results from that single reaction or investigate the change occurred in the *initial rate* of the reaction as concentrations of the reactants are changed. In the first approach experiments are carried out by keeping the concentrations of all the reactants except one is in large excess. Thus for example, for the reaction:

$$aA + bB \rightarrow cC + dD$$

The rate law is: Rate = $k\,[A]^x[B]^y$

Let B to be in large excess relative to $[A]_0$, so that [B] can be considered constant during a course of reaction. Thus we may write:

$$\text{Rate} = k'\,[A]^x$$

where:

$$k' = k\,[B]^y$$

By taking logarithm of both sides we get:

$$\log(\text{Rate}) = \boldsymbol{y}\log[\text{A}] + \log(k')$$

which is the equation of a straight line and by plotting log(Rate) against log[A] with gradient **y** and intercept of $\log(k`)$, the order and the rate constant of the reaction would be estimated.

The process can then be repeated by letting A in excess to determine $\boldsymbol{x}$ and k.

Method of initial rates

As we know, the rate laws are not derived from the reaction equation and are derived from experimental data. The method of initial rates is an experimental method to investigate the kinetics of reaction leading to find the rate constant and orders of a given reaction, in which a reaction is run multiple times with different initial concentrations of each reactant. The initial rate of each experiment is compared with the initial concentrations of the reactants to determine its order. The method is most often performed in the following way:

In a simple way of initial rate experiments involve measuring the time taken for some easily measurable or recognizable event that happens very early in a reaction. This could be the time taken for, say, to liberate a *given volume* of a gas, to from a measurable amount of a *precipitate* or for a *colour change* to occur. Further, some *titrations* can be performed by stopping a reaction after a given period of time.

Then the concentration of one of the components of the reaction is changed, keeping everything else such as the concentrations of other reactants, the total volume of the solution and the temperature and so on constant. Then the time taken for the same event to take place has to be measured with that new concentration. This has to be repeated for a range of concentrations of the substance interested in. It is worth to cover a reasonably wide range of concentrations, taking perhaps five or more different concentrations varying from the original one down to half of it or less.

This means that for each reactant, it is needed to run at least a pair of reactions in which that reactant's concentration is doubled (changed) while all other reactant concentrations and conditions are held constant. This isolates the effect on rate to that single reactant. Most often one of three things happens to the initial rate when the reactant concentration is doubled:

(a) The rate does not change: This means that the rate is independent of that reactant. The reaction is zero order with respect to that reactant.

(b) The rate doubles: This means that the rate is proportional to the concentration of that reactant. The reaction is first order with respect to that reactant.

(c) The rate quadruples: This means that the rate is proportional to the square of the concentration of that reactant. The reaction is second order with respect to that reactant.

Once the order for each reactant is found, take any of the experiments and substitute in concentration values and the measured rate to determine the numerical value of the rate constant *k*.

Exploration of the results from initial rate experiments

Consider a simple example of an initial rate experiment in which a gas being produced. This could be a reaction between a metal and an acid, for example, or the catalytic decomposition of hydrogen peroxide. Assume that the volume of the evolved gas being measured with the time and that can be shown as a plot of volume of gas given off against time as shown in the Figure 1.18.

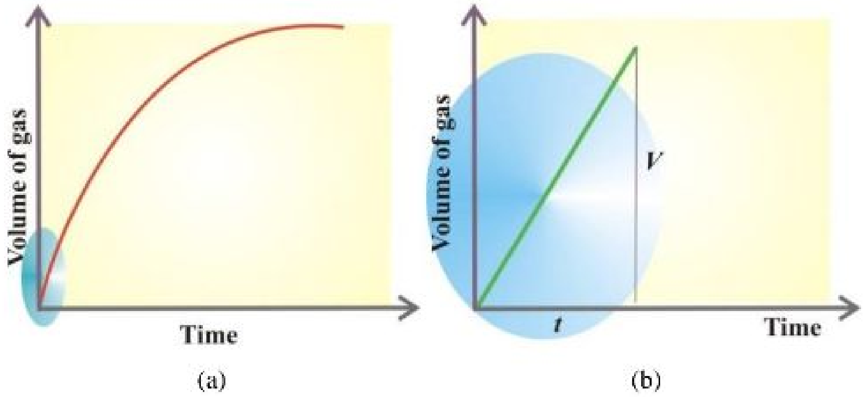


Figure 1.18 Measuring the volume of an evolved gas in an initial rate experiment. (**a**) Change in volume over the time, volume increases very fast at the beginning and slows down when the reaction progresses. (**b**) Expanded view of the shaded area of (**a**) Increase in volume at the very beginning of the reaction is linear and therefore it is possible to measure the time taken to produce a constant volume of gas by varying the concentration of the desired reactant at a given temperature.

We know that a measure of the rate of the reaction at any point is found by measuring the slope of the graph. Since we are interested in the initial rate, it is necessary to find the slope at the very beginning (say at $t \sim 0\ s$). Of course, it is impossible to observe some changes at the time = 0, and therefore, we measure the time taken for a given/constant change to happen in the system (like a constant volume). However, since the concentration of the species at the very beginning is almost the initial concentration, it is assumed that during the event measured, the change in concentration of that particular reactant is negligible.

In the Figure 1.18(a), variation of volume over time in the entire range shows a curve. By enlarging the circled area, i.e. enlarging the very beginning of the first curve, it can be seen that it is approximately a straight line at that point (Figure 1.18(b)). That is a reasonable approximation once very early stage in the reaction is considered. This can also be obtained by drawing a tangent line to the curve at the $t \sim 0$. The slope in this case is simply V/t. Now suppose the experiment is carried out again with different (lower) concentrations of the reagent and the time taken to evolve the same volume of the gas is measured at the very beginning of the reaction as earlier. Following types of graphs as shown in Figure 1.19 would result for the formation of a constant volume of a gas in which different time measurements could be obtained.

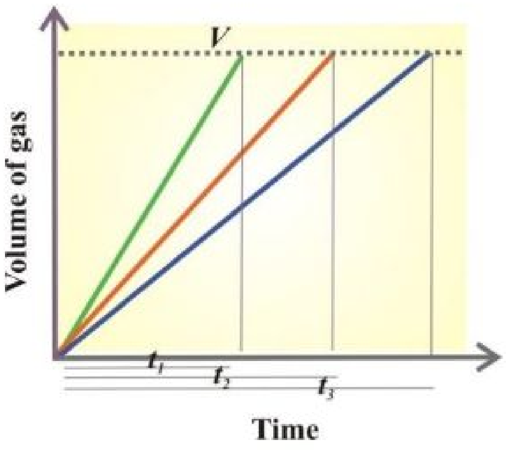


Figure 1.19 Measuring time taken to produce a constant volume of a gas with different concentrations of the reactant in an initial rate experiment. When there is no linearity at the beginning of the reaction, gradient of the tangent has to be determined.

From these experiments the initial rates (in terms of volume of gas produced per second) can be deduced as:

Experimet 1 : Initial rate$_1$ = V/t_1
Experimet 2 : Initial rate$_2$ = V/t_2

In the above two experiments as the time taken to evolve a constant volume (V) of a gas is measured it is easy to compare the initial rates obtained. It is clear from the above two that the initial rate is inversely proportional to the time taken and therefore;

$$\text{Initial rate} \propto \frac{1}{t}$$

Thus, normal in experiments of this type, $\frac{1}{t}$ can be used as a measure of the initial rate without any further calculations. Therefore, the initial rates measured by varying concentrations of respective reactant(s) can be used to determine the orders of reactions and finally the value of the rate constant. Following examples give some insight into this type of experiments.

Example:

Consider a hypothetical reaction at a given temperature:

$$A + 2B \rightarrow C + D$$

The rate law, expressed in general terms, is

$$\text{Rate} = k[A]^m[B]^n$$

To find the values of **m** and **n**, a series of experiments was carried out in which one reactant concentration was changed while the other was kept constant. The initial rate measured in each case is shown in the table shown below. Using the data given in the table calculate the values of ***m, n*** and ***k.***

Table 1.2 Data set for calcultion

Experiment	Initial [A]/ mol dm^{-3}	Initial [B]/ mol dm^{-3}	Initial rate/ mol dm^{-3} s^{-1}
1	2.5×10^{-2}	3.0×10^{-2}	1.75×10^{-3}
2	5.0×10^{-2}	3.0×10^{-2}	3.50×10^{-3}
3	2.5×10^{-2}	6.0×10^{-2}	3.50×10^{-3}

1. *Finding m, the order with respect to A*

   By comparing experiments 1 and 2, in which [A] doubles and [B] is constant, we can obtain m. First, take the ratio of the general rate laws for these two experiments:

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k\,[A]_1^m\,[B]_1^n}{k[A]_2^m\,[B]_2^n}$$

   In experiments 1 and 2, $[B]_1$ and $[B]_2 = 3.0 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

   Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[A]_1^m}{[A]_2^m}$$

$$\frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{3.50 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}} = \frac{(2.5 \times 10^{-2}\ \text{mol dm}^{-3})^m}{(5.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^m$$

$$\therefore\ \boldsymbol{m = 1}$$

   Thus, the reaction is first order *with respect to* A, because when [A] doubles, the rate doubles.

2. *Finding n, the order with respect to B.*

   Comparing experiments 3 and 1 in which [A] is held constant and [B] doubles:

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{k\,[\text{A}]_1^m\,[\text{B}]_1^n}{k[\text{A}]_3^m\,[\text{B}]_3^n}$$

   In experiments 1 and 3, $[\text{A}]_1$ and $[\text{A}]_3 = 2.5 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

   Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{[\text{B}]_1^n}{[\text{B}]_3^n}$$

$$\frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\,\text{s}^{-1}}{3.50 \times 10^{-3}\ \text{mol dm}^{-3}\,\text{s}^{-1}} = \frac{(3.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}{(6.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}$$

$$\frac{1}{2} = \left(\frac{1}{2}\right)^n$$

$$\therefore\ \boldsymbol{n = 1}$$

   Thus, the reaction is also first order with respect to B, because when [B] doubles, the rate doubles.

   Therefore the rate law of the reaction is

$$\text{Rate} = k\,[\text{A}][\text{B}]$$

   The value of k can be obtained by substituting appropriate values in the rate expression as for the experiment 1 ;

$$1.75 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1} = k\,(2.5 \times 10^{-2})(3.0 \times 10^{-2})\ \text{mol}^2\,\text{dm}^{-6}$$

$$k = \frac{1.75 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{7.50 \times 10^{-4}\ \text{mol}^2\,\text{dm}^{-6}} = 2.3\ \text{mol}^{-1}\,\text{dm}^3\,\text{s}^{-1}$$

Note: What would be the initial rate of the above reaction if the concentrations of both A and B are doubled at the same time?

When both [A] and [B] doubled, the rate should quadruple to $7.00 \times 10^{-3}\ mol\ dm^{-3}s^{-1}$ *and therefore, that confirms the rate law derived from the experiment.*

Note especially, that while the order with respect to B is 1, the coefficient of B in the balanced equation is 2. Thus, as mentioned earlier, reaction orders must be determined from experiment.

Example 1.13

Consider the real reaction between oxygen and nitrogen monoxide at 300 K.

$$O_2(g) + 2NO(g) \rightarrow 2NO_2(g)$$

The general rate law is,

$$\text{Rate} = k\,[O_2(g)]^m[\,NO(g)]^n$$

Using the data given in the table below derive the rate law of the reaction at 300 K.

Experiment	Initial $[O_2(g)]$ or $[O_2(g)]_0$/ mol dm^{-3}	Initial [NO(g)] or $[NO(g)]_0$/ mol dm^{-3}	Initial rate mol dm^{-3} s^{-1}
1	1.0×10^{-2}	2.0×10^{-2}	3.20×10^{-3}
2	2.0×10^{-2}	2.0×10^{-2}	6.40×10^{-3}
3	1.0×10^{-2}	4.0×10^{-2}	12.80×10^{-3}
4	3.0×10^{-2}	2.0×10^{-2}	9.60×10^{-3}

$[O_2(g)]_0$ and $[NO(g)]_0$ are the initial concentrations.

Answer

1. Finding m, the order with respect to $O_2(g)$.

   By comparing experiments 1 and 2, in which $[O_2(g)]$ doubles and [NO(g)] is constant, we can obtain m. First, take the ratio of the general rate laws for these two experiments:

   $$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{k\,[O_2]_1^m\,[NO]_1^n}{k[O_2]_2^m\,[NO]_2^n}$$

   In experiments 1 and 2, $[NO]_1 = [NO]_2 = 2.0 \times 10^{-2}\ \text{mol dm}^{-3}$ and k is a constant as the temperature is constant.

   Therefore, we can write;

   $$\frac{\text{Rate}_1}{\text{Rate}_2} = \frac{[O_2]_1^m}{[O_2]_2^m}$$

   $$\frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}}{6.40 \times 10^{-3}\ \text{mol dm}^{-3}\ \text{s}^{-1}} = \frac{(1.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}{(2.0 \times 10^{-2}\ \text{mol dm}^{-3})^m}$$

   $$\frac{1}{2} = \left(\frac{1}{2}\right)^m$$

   $$\therefore\ \boldsymbol{m = 1}$$

   Thus, the reaction is first order with respect to O_2, because when $[O_2(g)]$ doubles, the rate doubles.

   Experiment 4 also supports the value of m (m =1); rate increases thrice when the concentration is increased by three times.

2. Finding n, the order with respect to NO(g).

Comparing experiments 1 and 3 in which $[O_2]$ is held constant and [NO] doubles:

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{k\,[O_2]_1^m\,[NO]_1^n}{k[O_2]_3^m\,[NO]_3^n}$$

In experiments 1 and 3, $[O_2]_1$ and $[O_2]_3 = 1.0 \times 10^{-2}$ mol dm^{-3} and k is a constant as the temperature is constant.

Therefore, we can write;

$$\frac{\text{Rate}_1}{\text{Rate}_3} = \frac{[NO]_1^n}{[NO]_3^n}$$

$$\frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{12.8 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}} = \frac{(2.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}{(4.0 \times 10^{-2}\ \text{mol dm}^{-3})^n}$$

$$\frac{1}{4} = \left(\frac{1}{2}\right)^n$$

$$\therefore\ \boldsymbol{n = 2}$$

Thus, the reaction is second order with respect to NO, because when [NO] doubles, the rate increases four times.

Therefore the rate law of the reaction is

$$\text{Rate} = k\,[O_2(g)]\,[\,NO(g)]^2$$

Note: In some cases we may not have exactly simplifying numbers in this calculations. For example if the initial rate of the experiment 1 is 3.10×10^{-3} mol dm^{-3}s^{-1}, then we get $\frac{3.10 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{6.40 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}} = 0.485$ and hence $0.485 = \left(\frac{1}{2}\right)^m = (0.500)^m$.

This can be solved by taking log as;

$\log(0.485) = m \log(0.500)$

$$m = \frac{\log(0.485)}{\log(0.500)} = 1.04\ or\ m = \frac{\log(0.500)}{\log(0.500)} = 1\ \ (as\ 0.485 \sim 0.500)$$

As m has to be an integer, m = 1

The value of k can be obtained by substituting appropriate values in the rate expression as for the experiment 1.

$$3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1} = k\,(1.0 \times 10^{-2})(2.0 \times 10^{-2})^2\ \text{mol}^3\ \text{dm}^{-9}$$

$$k = \frac{3.20 \times 10^{-3}\ \text{mol dm}^{-3}\text{s}^{-1}}{4.0 \times 10^{-6}\ \text{mol}^3\ \text{dm}^{-9}} = 8.00 \times 10^2\ \text{mol}^{-2}\ \text{dm}^6\ \text{s}^{-1}$$

In addition to the above type of calculations, the data obtained by several experiments can be plotted as a plot of $\frac{1}{t}$ against the varying concentrations of the reactant. If the reaction is first order with respect to that substance, then straight line will result. That's because in a first order reaction, the rate is proportional to the concentration.

If the plot is a curve, then it isn't first order. It *might* be second order (or some sort of fractional order).

The best way for this analysis with several data of initial rates is constructing a *log graph*. As previously discussed, for a reaction involving A, with an order of ***n*** with respect to A, the rate equation is:

$$\textbf{Rate} = k\,[\textbf{A}]^n$$

Taking the log of each side of the equation, you get:

$$\log(\text{Rate}) = n \log[\text{A}] + \log k$$

Therefore the plot of log(Rate) against log[A], would give a straight line with slope n, that is the order of the reaction. The intercept of the plot is log(k) and hence k can be obtained.

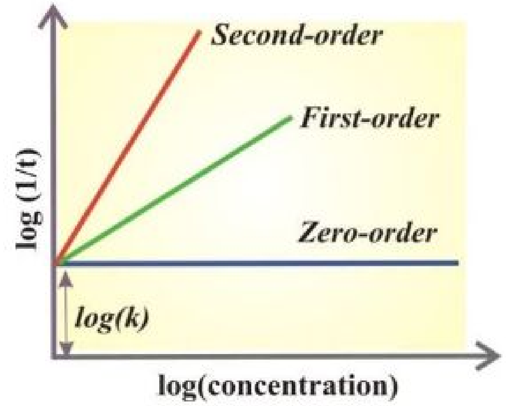


Figure 1.20 Shapes of graphs that could be obtained from initial rate experiments (Figure 1.17(a) can also be obtained)

Some kind of laboratory experiments can be designed and carried out by measuring time measurements to occur for a constant extent of the reaction and then by plotting the appropriate graphs, the order of the reaction(s) can be deduced. Following are some examples which are included in your practical manual.

Thiosulphate-acid reaction

Addition of dilute nitric acid (HNO_3) to sodium thiosulphate ($Na_2S_2O_3$) solution at room temperature results in a slow formation of a pale yellow precipitate of sulphur through the following reaction.

$$Na_2S_2O_3(aq) + 2HNO_3(aq) \rightarrow S(s) + 2NaNO_3(aq) + SO_2(g) + H_2O(l)$$

In this system, there is a simple, but very effective, way of measuring the time taken for a small fixed amount of sulphur precipitate to form. As a precipitate is formed in the reaction, it is possible to measure the time taken to form a fixed amount of precipitate under different concentrations of reactants at a given temperature as follows.

Keep a flask or small beaker on a piece of paper with a cross mark (X) drawn on it, and then look down through the reaction mixture until the cross disappears. First, put a known amount of thiosulphate solution in to a beaker and then add a small amount of dilute acid solution with known different concentrations and measure the time it takes for the cross to disappear (Detailed experiment is discussed in your practical manual). In this experiment, the actual concentration of the sodium thiosulphate does not have to be known because in each case, its relative concentration can be estimated with the total volume of the reaction mixture. The solution with 40 cm^3 of sodium thiosulphate solution plus 10 cm^3 of water has a concentration which is 80% of the original one, for example. The one with 10 cm^3 of sodium thiosulphate solution plus 40 cm^3 of water has a concentration which is 20% of the original one.

After collecting data on the time measurements, the data can be plotted as the variation of 1/t with the thiosulphate concentration and from that the reaction order with respect to the reactant thiosulphate can be deduced. In addition to this, the effect of temperature on the reaction rate could also be investigated as described in the practical manual.

Iodine clock experiments

There are several reactions given the name "iodine clock". They are all reactions which give iodine as one of the products and help measure the time taken for the formation of constant amount of iodine. This is the simplest of them, because it involves the most familiar reagents. For example, kinetics of the reaction of the oxidation of iodide ions by hydrogen peroxide under acidic conditions can be monitored by such "iodine clock" experiments. In the acidic medium iodide ions reacts with hydrogen peroxide as follows.

$$H_2O_2(aq) + 2I^-(aq) + 2H^+(aq) \rightarrow I_2(aq) + 2H_2O(l)$$

In this reaction the amount of iodine ($I_2(aq)$) produced can be monitored by using starch when a small amount has been formed. Iodine reacts with starch solution to give a deep blue colored complex turning the solution blue. If a little volume (few drops) of starch solution is added to the reaction mixture initially, as soon as the first trace of iodine was formed, the solution would turn blue. However, just the addition of starch will not help to follow the kinetics as the colour change occurs instantaneously. Therefore, another way to remove the iodine produced is used. As iodine also reacts with sodium thiosulphate solution that can be used to consume some iodine produced.

$$2S_2O_3^{2-}(aq) + I_2(aq) \rightarrow 2I^-(aq) + S_4O_6^{2-}(aq)$$

If a very small known amount of sodium thiosulphate solution is added to the reaction mixture (including the starch solution), it will react with the iodine that is initially produced, and so the iodine will not affect the starch and no blue colour is displayed. However, when that small amount of sodium thiosulphate has been used up, there is nothing to stop the next bit of iodine produced from reacting with the starch. The mixture suddenly goes blue and the time taken to appear the blue colour can be measured for different experimental conditions.

In this experiment, effect of changing the hydrogen peroxide concentration, or the iodide ion concentration, or the hydrogen ion concentration - each time, keeping everything else constant would let you find the orders with respect to each reactant taking part in the reaction.

Note that a similar experiment is included in the practical manual to follow the kinetics of the reaction;

$$2I^-(aq) + 2Fe^{3+}(aq) \rightarrow I_2(aq) + 2Fe^{2+}(aq)$$

In addition to the above - mentioned reactions, the method of initial rate can be used to monitor the kinetics of the catalytic decomposition of hydrogen peroxide by monitoring the volume of oxygen gas produced at a given temperature.

Above examples show that the kinetics of reactions can be investigated by carefully designed experiments. It has to be noted that following requirements must be fulfilled once such experiments are carried out.

(i) Controlling the temperature of the system with a good thermostat (this will be learnt during practical) as rates change (exponentially) with temperature.
(ii) Choosing an accurate timing device.
(iii) An appropriate method for determining the concentration of reactant or product. This can be done through a measurement of a rapidly determinable physical property of the reaction mixture.

Following the course of a single reaction

Rather than doing a whole set of initial rate experiments, information about orders of reaction can also be obtained by following a particular reaction from start to finish.

There are two different ways to do this. Withdraw samples of the mixture at intervals and find out how the concentration of one of the reagents is changing by doing an appropriate titrations. Or by measuring some physical property of the reaction which changes as the reaction proceeds - for example, refractive index, absorbance, etc. Then the set of values obtained for concentration can be plotted against time and the rates of reaction at different points need to be extracted from the graph. Finally, by plotting log(rate) against log(concentration) the order of reaction can be estimated.

Half-life of a reaction ($t_{1/2}$)

As the reaction proceeds, the concentration of the reactant(s) decreases and another measure of the rate of reaction relating the concentration to the time is the half-life. The concept of half-life is useful for describing the rough speed of a reaction. The half-life of a reaction is the time it takes for the consumption of reactants by half of the initial amount. In other words, the half-life of a reaction is the time in which the concentration of a reactant is reduced to one half of its initial concentration. It is represented as $\mathbf{t_{1/2}}$ and this is affected by temperature. This can be represented by the Figure 1.21.

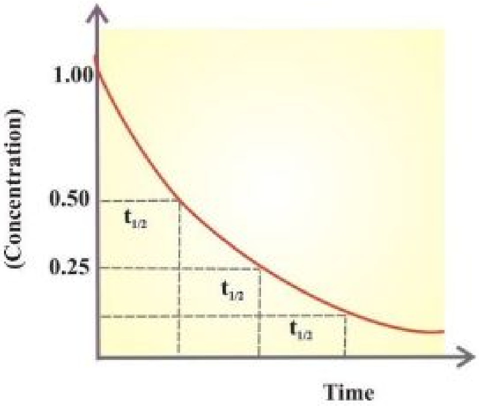


Figure 1.21 Definition of half-life (for a first order reaction)

For example, consider the first order decomposition of hydrogen peroxide. The table below shows the concentration of H_2O_2 in increments of 600 min.

Table 1.3 Concentration of H_2O_2 in increments of 600 min

Time/ min	Number of half-lives	Fraction remaining	$[H_2O_2]$/ mol dm^{-3}
0	0	1	0.020
600	1	1/2	0.010
1200	2	1/4	0.005
1800	3	1/8	0.0025
2400	4	1/16	0.0013
3000	5	1/32	0.00065

Note that in the first 600 min, the concentration drops from 0.020 mol dm^{-3} to 0.010 mol dm^{-3}. That is, it drops in half. The half-life of the reaction is therefore 600 min. Then, when another 600 min passes (from $t = 600$ to $t = 1200$) and the concentration drops in half again: from 0.010 mol dm^{-3} to 0.0050 mol dm^{-3} the half-life is still 600 min. Successive half-lives produce reaction mixture with concentration fractions of 1/2, 1/4, 1/8, 1/16 and 1/32 as shown in the table.

Half-life of a first order reaction

Half-life of a first order reaction is given by, $\mathbf{t_{1/2}} = \frac{0.693}{k}$ *

k is the rate constant.

Since k is a constant for a given reaction at a given temperature and the expression does not contains any concentration term, the half-life of a first order reaction is a constant independent of initial concentration of reactant.

This means that if we start with 2.00 mol dm^{-3}, and of a reactant reacting with first order kinetics and after 20 minute it is reduced to 1.00 mol dm^{-3}, and the half-life of the reaction will be 20 minutes. In other words, during the first 20 minutes 50% of the reaction completes, then in 40 minutes 75%, in 60 minutes 87.5% and so on. This can also be understood from the Figure 1.21.

Example 1.14

A certain first-order reaction has a half-life of 20.0 minutes.

(i) Calculate k for the reaction.

(ii) How much time is required for this reaction to be 75% complete?

Answer

(i) Half-life of a first order reaction is given by $\mathbf{t_{1/2}} = \frac{0.693}{k}$.

$$20.0 \text{ min} = \frac{0.693}{k}$$

$$k = \frac{0.693}{20 \text{ min}} = 3.47 \times 10^{-2} \text{ min}^{-1}$$

(ii) If the reaction is 75% complete that means there is 25% of the reactant is left or the reaction has occurred up to the second half life cycle. Therefore, the time taken to complete the reaction by 75% is two-half-lives, i.e 40 min.

Show that in a first order reaction, time required for completion of 99.9% is 10 times the half-life ($t_{1/2}$) of the reaction.

When 99.9% is completed the remaining amount is 0.100 % or 0.001

The value of remaining concentration after 10 half-life cycles

Can be written as $\frac{1}{2^n} = \frac{1}{2^{10}} = \frac{1}{1024} = 0.001$

Therefore, the time required for the completion of 99.9% of a first order reaction is 10 times the half-life.

Half-life of a zero order reaction is given by;

$$\mathbf{t_{1/2}} = \frac{[\mathrm{A}]_0}{2k} \; *$$

$[\mathrm{A}]_0$ is the initial concentration. Therefore, half-life of the zero-order reaction depends on the initial concentration.

* *Derivation of this equation will not be tested at the G. C. E. (A/L) Chemistry examination.*

1.8 The effect of the physical nature (surface area) on the reaction rate

In the section 1.1 a little description on the effect of the physical nature of the reactant on the rate has been given. When the reactions involve solid reactants, increasing the surface area by turning the solid into a fine powder enhances the rate of reaction due the increase in the number of collisions between reacting particles.

As described earlier, rates of reactions depend on the physical nature as Gaseous state > Liquid state > Solid state. The reaction rate of a heterogeneous reaction depends on the surface area of the more condensed phase. In the case of solid reactant, the more finely powdered solid reacts faster than the same mass present as a single lump because the powdered solid has a greater surface area than the single lump.

For example in the reaction between calcium carbonate and hydrochloric acid you can observe in the laboratory that powdered calcium carbonate reacts much faster with dilute hydrochloric acid than the same mass of marble or limestone in lumps.

In the catalytic decomposition of hydrogen peroxide solid manganese(IV) oxide is often used as the catalyst. Oxygen is given off much faster if the catalyst is present as a powder than when the same mass of it is present as granules.

In these cases with increasing surface area of the solid, the frequency of collisions increases and the rate of the reaction thus increases.

For example, the reaction between magnesium metal and a dilute hydrochloric acid involves collision between magnesium atoms and hydrogen ions. The effect of surface area can be understood by the Figure 1.22.

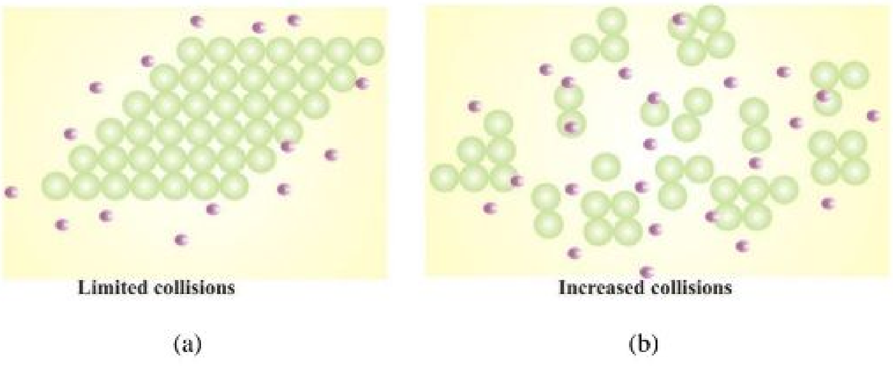


Figure 1.22 Effect of particle size on the reaction rate; (a) A particle has a little area to collide with the reactant molecules, molecules collide only with the outer surface. (b) When the solid sample with the same number of atoms is powdered to fine particles, surface area for the collisions with reactant molecules increases and hence the rate of reaction.

1.9 Effect of catalysts on the rate of reactions

Increasing the rate of a reaction has many advantages in industry. Higher temperatures can speed up a reaction, but energy for industrial processes is costly and many organic and biological substances are heat sensitive. More commonly, by far, a reaction is accelerated by a **catalyst,** a substance that increases the rate *without* being consumed. Thus, only a small, non stoichiometric amount of the catalyst is required to speed the reaction.

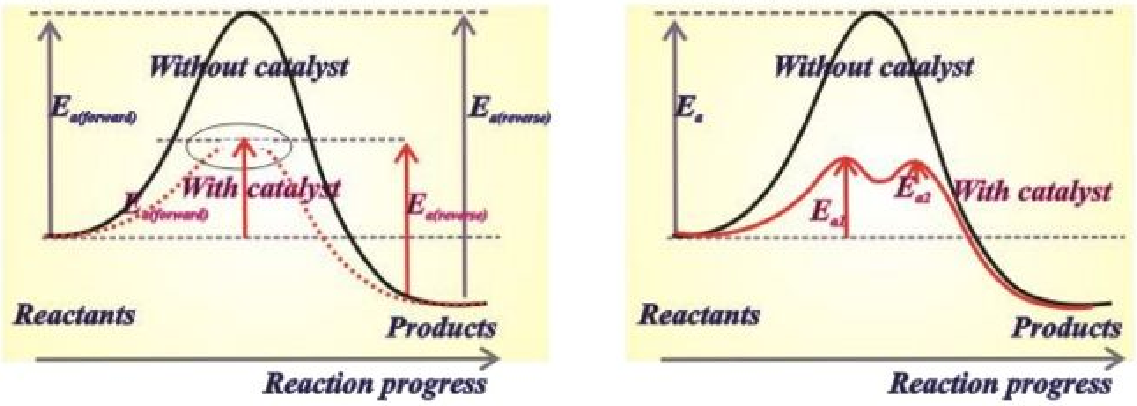
A catalyst is a substance that accelerates a reaction but undergoes no net chemical change. *It functions by providing an alternative path with lower activation energy of the reaction and avoids the slow, rate-determining step of the unanalyzed reaction, and results in a higher reaction rate at the same temperature.*

As we know, there are two basic types of catalysts namely heterogeneous and homogeneous catalyst. Heterogeneous catalyst is in a different phase (for example, a solid catalyst for a gas-phase reaction). A homogeneous catalyst is a one that is in the same phase as the reaction mixture (for example, acid catalyzed reactions in aqueous solution).

The following examples elaborates the function of a catalyst on the reaction rate. The activation energy for the decomposition of hydrogen peroxide in solution is 76 kJ mol^{-1} and the reaction is slow at room temperature. When a little amount of iodide ions is added, the activation energy falls to 57 kJ mol^{-1}, and the rate constant increases by a factor of 2000.

In addition, enzymes (categorized as biological catalysts), are very specific and can have a dramatic effect on the reactions they control. The activation energy for the acid hydrolysis of sucrose is 107 kJ mol^{-1} but the enzyme saccharase reduces it to 36 kJ mol^{-1}, corresponding to an acceleration of the reaction by a factor of 1012 at body temperature (310 K).

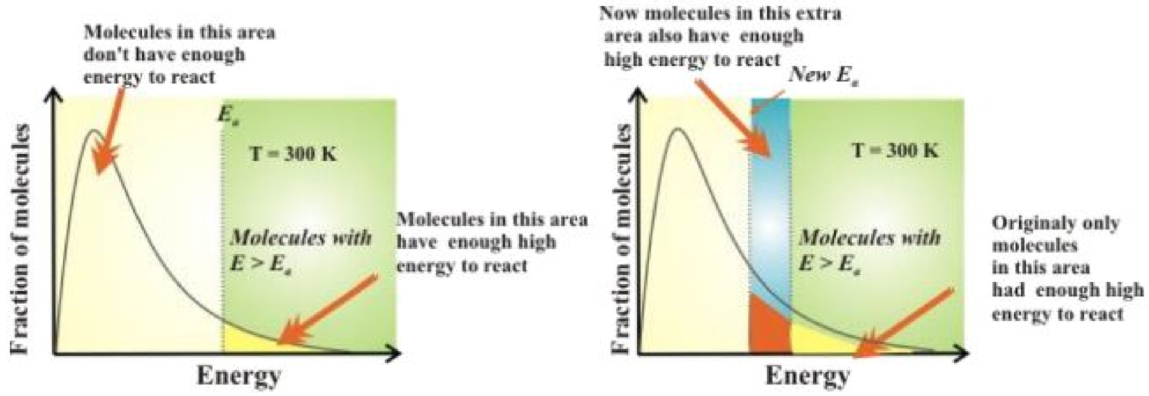
There are some substances which decrease the rate of reaction and such substances are called inhibitors. Obviously, the substances accelerating the rate will be a catalyst. Catalyst are generally foreign substances but sometimes one of the product formed may act as a catalyst. Such a catalyst is called an "auto catalyst" and the phenomenon is called auto catalysis. The function of the catalyst on the reaction rate can be depicted as illustrated in the Figure 1.23



(a) (b)

Figure 1.23 Comparison of the reaction profiles with and without a catalyst. The addition of a catalyst to a reaction increases the rate by providing a new, lower-energy alternative pathway. **(a)** Reaction goes through a different mechanism and **(b)** for example reaction goes through two transition states.

In a chemical reaction collisions result products only if the particles collide with a certain minimum energy or the activation energy for the reaction. The position of activation energy can be marked on a Maxwell-Boltzmann distribution curve as illustrated in Figure 1.24(a).



(a) (b)

Figure 1.24 Comparison of Maxwell - Boltzmann distributions with and without a catalyst at 300 K (same temperature). The addition of a catalyst to a reaction increases the rate by increasing the fraction of molecules having enough energy to react through an alternative pathway by increasing the collision frequency and hence the rate of the reaction.

Only those particles represented by the area to the right of the activation energy will react when they collide. The great majority does not have enough energy, and will simply bounce apart. Therefore, to increase the rate of a reaction it is necessary to increase the number of effective collisions by increasing the fraction of molecules with enough energy. In one way, this can be done by providing an alternative pathway for the reaction to happen with lower activation energy. In other words, the activation energy should be moved to the lower energy side (left) of the Maxwell Boltzmann distribution as shown in Figure 1.24(b). Adding a catalyst to a reaction has exactly this effect on activation energy. i.e. a catalyst provides an alternative path for the reaction with a lower activation energy compared to the un-catalyzed reaction as depicted in Figure 1.23.

It is very important to note that;

> *"A catalyst provides an alternative path for the reaction with lower activation energy." It does not "lower the activation energy of the reaction".*

This means that the original value of the activation energy of the reaction remains the same and the new catalyzed-path has lower activation energy. It is just like going through a tunnel without climbing a mountain.

1.10 Uses of reaction mechanisms to describe the rate of chemical reactions

In any chemical reaction or change, some bonds are broken and new bonds are formed. Usually, these changes such as bond breaking/ formation and rearrangements are too complicated to happen simply in one stage. Instead, the reaction may involve a series of steps one after the other. A reaction mechanism describes the one or more steps involved in the reaction in a way which makes it clear exactly how the various bonds are broken and formed.

A chemical reaction that takes place in one and only one step i.e., all that occurs in a single step is called an **elementary reaction**.

A chemical reaction occurring in a sequence of two or more steps is called a multi-step or complex reaction. As described above, the sequence of steps through which a multi-step reaction takes place is called the reaction mechanism. Each step in a mechanism is an elementary reaction. Reaction mechanisms cannot be calculated or predicted; instead, all reaction mechanisms must be determined experimentally.

Therefore, a chemical reaction in which one or more chemical species react directly to form products in a single step reaction and with a single transition state is called an elementary reaction. In this elementary reaction the molecules collide exactly as the stoichiometric equation of the reaction.

Further, in an elementary reaction no reaction intermediates are involved. Also their presence is not a requirement to describe the chemical reaction on a molecular scale.

1.10.1 Molecularity of a reaction

The molecularity of an elementary reaction is defined as the minimum number of molecules, atoms or ions of the reactant(s) required for the reaction to occur and is equal to the sum of the stoichiometric coefficients of the reactants in the balanced chemical equation.

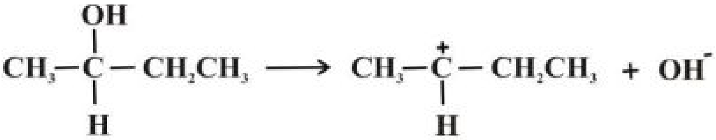
In general, molecularity of a simple reactions is equal to the sum of the number of molecules of reactants involved in the balanced stoichiometric equation.

When multi-step reaction mechanism is written, the minimum number of reacting particles (molecules, atoms or ions) that comes together or collide in the **rate determining step** to form a product or products is called the molecularity of a reaction.

Therefore, chemical reactions can be categorized simply by the number of reacting species in an elementary step. A reaction is **unimolecular** when only a single reactant molecule is involved and is **bimolecular** when two reactant molecules are involved. For example, in a **unimolecular reaction**, a single molecule decomposes itself or changes its atoms into a new arrangement, as in the isomerization of cyclopropane to propene. In a **bimolecular reaction**, a pair of molecules collides and exchange energy while atoms or groups of atoms undergo some other kind of change getting converted into a product or products.

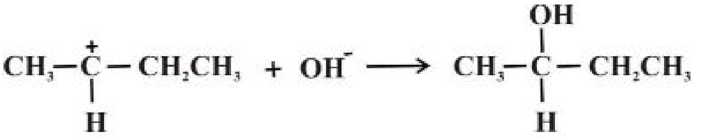
Molecularity is a theoretical concept; it cannot be zero, negative, fractional, infinite and imaginary.

Consider a following reaction in which a bond breaking step involves a single entity breaking up into two pieces. The C-O bond breaks. A single reactant forms two products. Because only one reactant molecule is involved, this step is unimolecular.



$$CH_3-\underset{H}{\overset{OH}{C}}-CH_2CH_3 \longrightarrow CH_3-\underset{H}{\overset{+}{C}}-CH_2CH_3 + OH^-$$

The following **bond forming step** which involves bringing two molecular fragments together to form a single product, a C-O bond is formed. Two reactants form a single product. Because two reactant molecules are involved, this step is **bimolecular**.



$$CH_3-\underset{H}{\overset{+}{C}}-CH_2CH_3 + OH^- \longrightarrow CH_3-\underset{H}{\overset{OH}{C}}-CH_2CH_3$$

Usually, there are few reactions with termolecular elementary behaviour as the collision of three molecules at the same time is somewhat difficult (However, such reactions occur through multi steps).

1.10.2 Examples of single step reactions

Many chemical reactions are simple events that occur in a single step. Acid-base reactions mostly occur in a single step. The protonation of ammonia by a hydronium ion involves the transfer of an H^+ ion from H_3O^+ to NH_3. This single step is a concerted bond-breaking and forming process.

$$H_3O^+(aq) + NH_3(aq) \rightarrow H_2O(l) + NH_4^+(aq)$$

The reaction occurs via a single step involving two species and is called as **bimolecular elementary reaction**.

The decomposition of $N_2O_4(g)$ is a single bond breaking step.

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

The reaction occurs via a single step involving one species and is called as **unimolecular elementary reaction**.

Followings examples show some elementary reactions with different molecularities.

Table 1.4 Elementary reactions with different molecularities

Reaction	Molecularity
$PCl_5 \rightarrow PCl_3 + Cl_2$	Unimolecular
$2HI \rightarrow H_2 + I_2$	Bimolecular
$NO + O_3 \rightarrow NO_2 + O_2$	Bimolecular
$2SO_2 + O_2 \rightarrow 2SO_3$	Termolecular
$2CO + O_2 \rightarrow 2CO_2$	Termolecular
$2FeCl_3 + SnCl_2 \rightarrow SnCl_2 + 2FeCl_2$	Termolecular

There are some chemical reactions whose molecularity appears to be more than three from stoichiometric equations, e.g.

$4HBr(aq) + O_2(g) \rightarrow 2H_2O(l) + 2Br_2(l)$

$2MnO_4^-(aq) + 16H^+(aq) + 5C_2O_4^{2-}(aq) \rightarrow 2Mn^{2+}(aq) + 10CO_2(g) + 8H_2O(l)$

In the first reaction molecularity seems to be '5' and in the second reaction molecularity seems to be '23'. Such reactions do not occur in a single step and involve two or more steps; each step has its own molecularity not greater than three. Following describes the basic features of reactions which occurs through multistep.

1.10.3 Multistep reactions

Chemical processes that occur in a series of elementary steps has their own set of rules.

(i) The overall reaction is the sum of the elementary reaction steps.

(ii) A species that is formed in one step and then used up in a later step is an **intermediate**.

(iii) A species that is used in one step and increase the rate of the reaction, then regenerated in a later step is acting as a **catalyst**.

(iv) Neither intermediates nor catalysts are seen in the overall reaction rate law.

Example 1:

The decomposition of ozone takes place in two steps.

Step 1: $O_3(g) \rightarrow O_2(g) + O(g)$; unimolecular, bond breaking

Step 2: $O_3(g) + O(g) \rightarrow 2O_2(g)$: bimolecular, bond forming and breaking

As learned in Unit 5, the idea of adding a series of reactions to give a net reaction is used here to determine the overall reaction that takes place in a series of steps.

In this case, O(g) is present on both sides.

Step 1: $O_3(g) \rightarrow O_2(g) + O(g)$
Step 2: $O_3(g) + O(g) \rightarrow 2O_2(g)$

$2\,O_3(g) + O(g) \rightarrow 3\,O_2(g) + O(g)$

∴ Overall reaction: $\mathbf{2\,O_3(g) \rightarrow 3\,O_2(g)}$

In this example, it can be seen that the O(g) atom formed in the step 1 is consumed in the step 2 and it doesn't appear in the overall reaction. That doesn't mean that it does not exist at least for a little while. A chemical species that is formed in one step of a mechanism and then used in a later step is called an intermediate. Intermediates never appear in the overall reaction equation. Sometimes they can be observed while the reaction progresses, but other times they are formed and used up so quickly and are not seen.

Example 2:

The decomposition of hydrogen peroxide in the presence of iodide ion occurs in two steps.

Step 1. $H_2O_2(aq) + I^-(aq) \rightarrow IO^-(aq) + H_2O(l)$; bimolecular
Step 2. $IO^-(aq) + H_2O_2(aq) \rightarrow I^-(aq) + H_2O(l) + O_2(g)$: bimolecular

∴ Overall reaction $2\,H_2O_2(aq) \rightarrow 2\,H_2O(l) + O_2(g)$

In this case, the $IO^-(aq)$ ion is formed in the first step and then consumed in the second step. $IO^-(aq)$ is an intermediate in this reaction. Conversely, $I^-(aq)$ ion is used in the first step and then regenerated in the second step. Therefore, $I^-(aq)$ act as a catalyst in this reaction

Example 3:

Chlorofluorocarbons break down in the upper atmosphere to give chlorine atoms. These are involved in the breakdown of ozone via the following mechanism.

Step 1. $Cl(g) + O_3(g) \rightarrow ClO(g) + O_2(g)$
Step 2. $ClO(g) + O_3(g) \rightarrow Cl(g) + O_2(g)$

Overall reaction: $2O_3(g) \rightarrow 2O_2(g)$

Reactions in step 1 and 2 are both bimolecular. Cl(g) is a reactant in the Step 1, but is regenerated in Step 2. Cl is therefore a catalyst. ClO is generated in Step 1, but is consumed in Step 2. ClO is therefore an intermediate.

1.10.4 The rate laws of elementary reactions

The rate law for elementary reactions can deduced directly from their molecularity. For example, the rate law of a unimolecular elementary reaction is first-order with respect to the reactant. Consider the reaction where P denotes products (several different species may be formed).

$$A \rightarrow P$$

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

A unimolecular elementary reaction is first-order because the number of A molecules that decays in a short interval is proportional to the number available to decay. Therefore the rate of decomposition of A is proportional to its molar concentration.

An elementary bimolecular reaction has a second-order rate law:

$$2A \rightarrow P$$

$$\text{Rate} = k\,[A]^2$$

Or we can write the reaction as;

$$A + B \rightarrow P$$

$$\text{Rate} = k\,[A][B]$$

A bimolecular elementary reaction is second order because its rate is proportional to the rate at which the reactant species meet, which in turn is proportional to their concentrations. Therefore, if we consider that a reaction is a single-step, bimolecular process, we can write down the rate law.

Note that the converse of this rule does not follow, that is, for example *second order rate law does not imply that the reaction is bimolecular.* Also, care must be taken to ensure that the reaction /step that we are considering is really elementary. For example, the reaction

$H_2(g) + I_2(l) \rightarrow 2HI(g)$ may look simple, but it is not elementary, and in fact, it has a very complex reaction mechanism, and hence the rate law cannot be deduced by merely looking the reaction.

With the above descriptions, for an elementary reaction of the general type;

$$aA + bB \rightarrow cC + dD$$

rate law is written as,

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

The order of an elementary reaction with respect to a given reactant is exactly same as the stoichiometric coefficient. Therefore, for the above elementary reaction, order with respect to the reactant A is ***a*** and the order with respect to the reactant B is ***b***. The overall order of the reaction is ***(a + b)***.

It is very important to understand the difference between molecularity and reaction order:

The ***reaction order*** is an empirical quantity, and obtained from the experimental rate law.

The ***molecularity*** refers to an elementary reaction proposed as an individual step in a mechanism.

The following table summarizes some examples.

Table 1.5 Summary of molecularity

Molecularity	Elementary step	Rate law
Unimolecular	A → Products	Rate = k [A]
Bimolecular	A + A → Products	Rate = k $[A]^2$
Bimolecular	A + B → Products	Rate = k [A] [B]
Termolecular	A + A + A → Products	Rate = k $[A]^3$
Termolecular	A + A + B → Products	Rate = k $[A]^2[B]$
Termolecular	A + B + C → Products	Rate = k [A][B][C]

1.10.5 Reaction mechanisms and the rate law

As described earlier, a species acting as an intermediate or a catalyst does not appear in the rate law. Then it is necessary to understand how the rate law is derived for such systems. Usually, in a mechanism there are some steps that occur very slowly and some other steps that occur very rapidly. The overall rate of a reaction is controlled by the rate of the slowest step. The slowest step of a reaction is known as the **rate determining step (RDS)**. Therefore, in experiments, when the rates are measured, the rate of the rate determining step is actually measured as long as there is a lot of differences among the rates of the various steps.

Consider the following example; in which the reaction occurs in two steps. First the reactant A is transformed into another species B; then in the next step it acts as a reactant which is transformed into the desired product P.

$$A \overset{k_1}{\rightarrow} \mathrm{B}$$

$$\mathrm{B} \overset{k_2}{\rightarrow} \mathrm{P}$$

k_1 and k_2 are the rate constants of respective steps.

Assume that $k_2 >> k_1$. In such a case, whenever a molecule B is formed, it decays rapidly to P indicating that the rate of the reaction depends only on the first step and that the step would be the rate determining step of the reaction.

Consider another example in which the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ occurs through following mechanism.

$$NO_2(g) + NO_2(g) \overset{k_1}{\rightarrow} NO_3(g) + NO(g) : \text{ slow; rate determining step}$$
$$NO_3(g) + CO(g) \overset{k_2}{\rightarrow} NO_2(g) + CO_2(g) : \text{ fast}$$

In this reaction the first step is the rate determining step and hence we can say that the rate of reaction depends only on the rate constant k_1. This can further be proven from the experiments in determining the empirical rate law of the reaction. The empirical rate law of the reaction is

$$\text{Rate} = k\,[NO_2]^2$$

i.e. the reaction $NO_2(g) + CO(g) \rightarrow NO(g) + CO_2(g)$ is 2nd order with respect to $NO_2(g)$ and zero-order with respect to $CO_{(g)}$.

In the mechanism given above NO_3 functions as a **reaction intermediate,** which is formed and used up during the reaction. Even though it does not appear in the overall balanced equation, a reaction intermediate is essential for the reaction to occur. Intermediates are less stable than the reactants and products.

Rate laws for the two elementary steps written above are;

$$\text{Rate}_1 = k_1\,[NO_2]^2$$
$$\text{Rate}_2 = k_2\,[NO_3][CO]$$

Three key points to notice about this mechanism are

(i) If $k_1 = k$, the rate law for the rate-determining step (step 1) becomes identical to the observed rate law.

(ii) Because the first step is slow, $[NO_3]$ is low. As soon as any NO_3 forms, it is consumed by the fast second step, so the reaction takes as long as the first step does.

(iii) CO does not appear in the rate law (reaction order = 0) because it takes part in the mechanism *after* the rate-determining step.

Example:

Consider the reaction between nitrogen dioxide and fluorine as an example:

$$2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)$$

The experimental rate law is that it is first order in NO_2 and in F_2.

$\therefore$ Rate = $k\,[NO_{2(g)}]\,[F_{2(g)}]$

The accepted mechanism is

Step 1; $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$: slow; rate determining

Step 2; $NO_2(g) + F(g) \rightarrow NO_2F(g)$: fast

Note that here the free fluorine atom is a reaction intermediate.

Let us consider the mechanism and how the rate law of the reaction is explained.

Sum of the two elementary reaction steps is the overall balanced equation.

Step 1; $NO_2(g) + F_2(g) \rightarrow NO_2F(g) + F(g)$

Step 2; $NO_2(g) + F(g) \rightarrow NO_2F(g)$

Overall reaction: $\mathbf{2NO_2(g) + F_2(g) \rightarrow 2NO_2F(g)}$

And both steps are bimolecular.

The rate laws for the elementary steps are:

$\text{Rate}_1 = k_1 [NO_{2(g)}] [F_{2(g)}]$

$\text{Rate}_2 = k_2 [NO_{2(g)}] [F_{(g)}]$

It can be seen that the step 1 is the rate-determining step, and with $k_1 = k$, it is the same as the overall rate law.

In this mechanism it has to be noted that the second molecule of NO_2 is involved *after* the rate-determining step, so it does not appear in the overall rate law.

From the above examples it can be noted that though the reaction proceeds through several steps, rate law of the reaction follows the rate determining step (slowest step) of the mechanism.

Consider the reaction between 2-bromo-2-methylpropane with hydroxide (OH^-) ions:

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

In the overall reaction the bromine atom is replaced by an OH group.

The first step that happens is that the carbon-bromine bond breaks to give ions via a unimolecular reaction;

$$(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + :Br^- \ : \textit{slow}$$

Carbon-bromine bonds are reasonably strong, so this is a slow change. If there is a high concentration of hydroxide ions, the positive ions will combine with them and this step of the reaction will be very fast. A new covalent bond is made between the carbon and the oxygen, using one of the lone pairs on the oxygen atom via a bimolecular (fast) reaction;

$$(CH_3)_3C^+ + :OH^- \rightarrow (CH_3)_3COH \ : \textit{fast}$$

The mechanism shows that the reaction takes place in two steps and describes exactly how those steps happen in terms of bonds being broken or made. It also shows that the steps have different rates of reaction; one slow and one fast.

The emperical rate law of the above reaction has been found to be as follows,

$$\text{Rate} = k[(CH_3)_3CBr]$$

The reaction is first order with respect to the $(CH_3)_3CBr$, and zero order with respect to the hydroxide ions. The concentration of the hydroxide ions does not affect the rate of the overall reaction.

If the hydroxide ions were taking part in the slow step of the reaction, increasing their concentration would speed up the reaction. Since its concentration does not seem to matter, they must be taking part in a later fast step.

Increasing the concentration of the hydroxide ions will speed up the fast step, but that will not not have a noticeable effect on the overall rate of the reaction as that is governed by the speed of the slow step.

Example: *Predicting a suitable mechanism*
Suppose an elementary bimolecular reaction between A and B which was experimentally found to be first order with respect to both A and B.
So the rate equation is:
Rate = k [A][B]

Let us consider the following two mechanisms;
Mechanism 1

$$\mathrm{A} \rightarrow \mathrm{C} + \mathrm{D}\ ; slow$$
$$\mathrm{B} + \mathrm{C} \rightarrow \mathrm{E}\ ; fast$$

Mechanism 2

$$\mathrm{A} + \mathrm{B} \rightarrow \mathrm{D} + \mathrm{E}\ ; slow$$

In this case, the reaction is first order with respect to both A and B, so one molecule of each must be taking part in the slow step. That means, mechanism 2 is the possible one.

Mechanism 1 must be wrong. One molecule of A is taking part in the slow step, but no B. The rate equation for that would be:
Rate = k[A]

1.10.6 Consecutive (elementary) reactions

As noted from the above reaction steps/mechanisms, the reaction which goes through an intermediate can be expressed as,

$$\mathrm{A} \overset{k_1}{\rightarrow} \mathrm{I} \overset{k_2}{\rightarrow} \mathrm{P}$$

The above reaction is defined as a consecutive unimolecular reaction because one reactant is involved in each step and the first step is the rate determining step of the reaction. For such a process:

(i) The concentration of A decreases through unimolecular decomposition of A, and is not replenished. Thus we have the rate equation

$$\text{Rate} = -k_1[\mathrm{A}]$$

(ii) The intermediate I is formed from A at a rate k_1[A], and decreases through decay to P at rate k_2[I]. This event happens very fast.

(iii) The product P is formed from I at a fast rate k_2[I], and it does not decrease.

Therefore, from these it can be simply noted that

(i) The concentration of the reactant A decreases with time;

(ii) The concentration of the intermediate I rises to a maximum and then falls to zero within a short time interval;

(iii) The concentration of the product P rises from zero to some value depending on the stoichiometry of the reaction.

These can be illustrated as shown in the Figure 1.25.

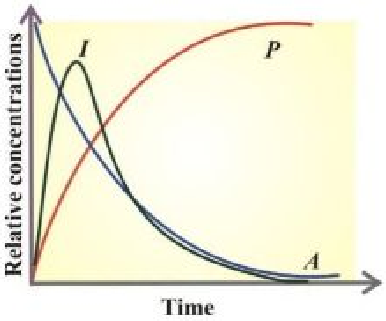


Figure 1.25 The concentrations of A, I, and P in the consecutive reaction $A \overset{k_1}{\rightarrow} I \overset{k_2}{\rightarrow} P$. Intermediate I is formed and consumed in the next step making its concentration zero with the time.

We can look at the above in another direction as follows.

The reaction $A \overset{k_1}{\rightarrow} I \overset{k_2}{\rightarrow} P$ occurs in two steps.

Step 1; $A \overset{k_1}{\rightarrow} I$

Step 2; $I \overset{k_2}{\rightarrow} P$

Overall reaction: $A \overset{k}{\rightarrow} P$

From the above we can deduce how the concentrations of A, I, and P will change over time. It is important to consider the relative rates of each step to understand the variation in concentrations of the species participating in the reaction. In any case, the concentration of A will decrease as the reaction proceeds, and the concentration of the product P will increase. But what would be the concentration of the intermediate, I? It is formed in one step and consumed in another. Its concentration must be zero at the start of the reaction, and must be zero when the reaction is complete, but non-zero in between. This is best observed by examining concentration-time curves. Figure 1.26 shows concentration-time curves of these species in three cases.

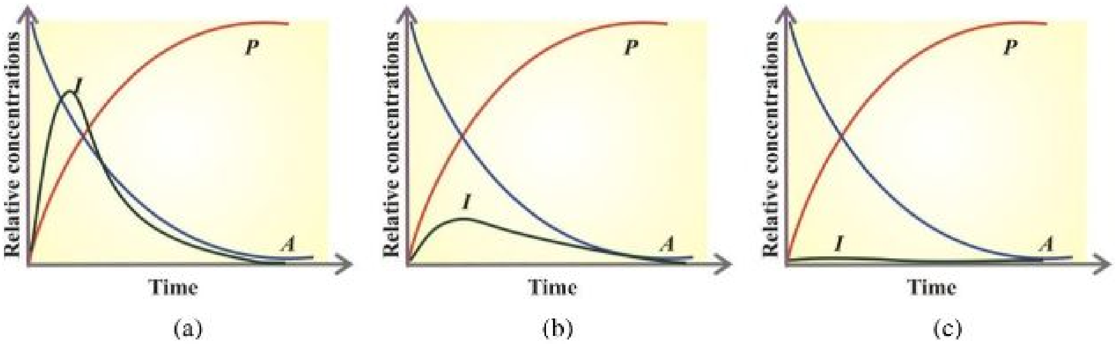


Figure 1.26 **(a)** Step 1 faster than Step 2. **(b)** Step 2 a little faster than Step 1. (c) Step 2 much faster than Step1.

In (a) the first step is somewhat faster than the second step. Initially, as A → I occurs, the rate of formation of I is greater than its rate of consumption in Step 2. So, the concentration of I increases over time. Then, as reactant A is depleted and the concentration of I increases, the rate of formation of I decreases and its rate of consumption increases. At this point, the concentration of I starts to decrease. Eventually the concentrations of both A and I drop to near zero as the reaction nears completion. (b) shows a case where Step 2 is somewhat faster than Step 1. In this case, I is consumed more quickly and its concentration does not build up as much as in (a). (c) shows a case where Step 2 is much faster than Step 1. In this case, I is consumed almost instantly as it is formed. The concentration of I never rises to an appreciable level and I may never be concentrated enough to observe in an experiment.

If a case like (c) occurs, it is important to know that the intermediate ever existed or not. Additional experiments can be designed to show that the intermediate was present, even if not directly observed. One of the methods is the addition of another reagent that would react with the postulated intermediate and observing the expected product. Then we can have evidence for the existence of the intermediate.

1.10.7 Cases where a pre-equilibrium exists in a mechanism

Example 1:

Suppose the mechanism for a reaction $A + B \rightarrow P$

$$A \rightleftharpoons I \ ; fast$$
$$I + B \rightarrow P \ : slow$$

This time the slow step is the second step and the intermediate I reaches an equilibrium with the reactants A and B. This mechanism involves a **pre-equilibrium**, in which an intermediate is in equilibrium with the reactants.

A pre-equilibrium arises when the rates of formation of the intermediate and its decay back into reactants are much faster than its rate of formation of the products.

The rate of the reaction will be governed by the slow step, and so the rate equation of the slow step is : Rate $= k\,[\mathrm{B}]\,[\mathrm{I}]$

In the rate law the concentration of the intermediate I is appearing and however, it is known that I is in equilibrium with A. Therefore the equilibrium constant K_c for the first step is;

$$K_c = \frac{[\mathrm{I}]}{[\mathrm{A}]}$$

$$\therefore\ [\mathrm{I}] = K_c[\mathrm{A}]$$

Therefore the rate of the reaction is:

$$\mathrm{Rate} = k\,[\mathrm{B}]\,K_c\,[\mathrm{A}] = k\,K_c\,[\mathrm{A}][\mathrm{B}]$$

This can further be modified with the relation between rate constants and equilibrium constant of the reaction. If the rate constants for the forward and backward reactions are k_f and k_r, respectively, we can write;

$$K_c = \frac{k_f}{k_r}$$

Finally,

$$\therefore \mathrm{Rate} = k\,\frac{k_f}{k_r}[\mathrm{A}][\mathrm{B}]$$

$$\mathrm{Rate} = k'\,[\mathrm{A}][\mathrm{B}]$$

The above shows that the rate law is similar to that of an elementary bimolecular reaction.

Consider another example.

Suppose the mechanism for a reaction $\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$

$$\mathrm{A} + \mathrm{B} \rightleftharpoons \mathrm{I}\ ;fast$$

$$\mathrm{I} + \mathrm{A} \rightarrow \mathrm{P}\ : slow$$

The overall reaction is ; $2\mathrm{A} + \mathrm{B} \rightarrow \mathrm{P}$

The rate of the reaction will be governed by the slow step, so the rate equation of the slow step is : Rate $= k\,[\mathrm{A}]\,[\mathrm{I}]$

In the rate law the concentration of the intermediate I is appears. However, it is known that I is in equilibrium with A and B, so the equilibrium constant K_c for the first step is;

$$K_c = \frac{[\mathrm{I}]}{[\mathrm{A}][\mathrm{B}]}$$

$$\therefore\ [\mathrm{I}] = K_c[\mathrm{A}][\mathrm{B}]$$

$$\therefore\ Rate\ = kK_c[\mathrm{A}][\mathrm{A}][\mathrm{B}]$$

$$\therefore Rate = k'[\mathrm{A}]^2[\mathrm{B}]$$

The rate law obeys the termolecular elementary reaction.

Example 2:

The gas phase reaction between $H_2(g)$ and $I_2(g)$ is one example for the above type of reactions.

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

This has a fas*t* pre-equilibrium step in which molecular iodine converts to atoms.

$$I_2(g) \rightleftharpoons 2I(g)$$

Then that atomic iodine reacts with molecular hydrogen to form HI in a slow second step.

$$H_2(g) + 2I\,(g) \rightarrow 2HI(g)$$

The rate of the reaction is governed by the slow step, so the rate equation of the slow step is: $\text{Rate} = k\,[H_2(g)]\,[I(g)]^2$

In the rate law, the concentration of the intermediate, I appears. However, it is known that I is in equilibrium with $I_2(g)$. Therefore the equilibrium constant $\boldsymbol{K_c}$ for the first step is;

$$K_c = \frac{[\mathrm{I(g)}]^2}{[\mathrm{I_2(g)}]}$$

$$\therefore\ [\mathrm{I(g)}]^2 = K_c[\mathrm{I_2(g)}]$$

$$\therefore\ \text{Rate} = kK_c[\mathrm{I_2(g)}][\mathrm{H_2(g)}]$$

$$\therefore \text{Rate} = k'[\mathrm{I_2(g)}][\mathrm{H_2(g)}]$$

Therefore, the rate of reaction depends on the concentrations of both $I_2(g)$ and $H_2(g)$.

Example 3:

In this example in which the first step of the reaction is a *fast* and *reversible*. Consider the oxidation of nitrogen monoxide given below.

$$2NO(g) + O_2(g) \rightarrow 2NO_2(g)$$

The observed rate law is

$$\text{Rate} = k\,[NO(g)]^2\,[O_2(g)]$$

the reaction has the mechanism;

Step 1 : $NO(g) + O_2(g) \rightleftharpoons NO_3(g)$: fast

Step 2 : $NO_3(g) + NO(g) \rightarrow 2NO_2(g)$: slow; rate determining step

The sum of the above two steps gives the overall reaction $2NO(g) + O_2(g) \rightarrow 2NO_2(g)$ and both steps are bimolecular.

Rate law for the slow step is;

$$\text{Rate} = k\,[NO_3(g)]\,[NO(g)]$$

For the step 1, equilibrium constant is,

$$K_c = \frac{[\mathrm{NO_3(g)}]}{[NO(g)][O_2(g)]}$$
$$\therefore [\mathrm{NO_3(g)}] = K_c[\mathrm{NO(g)}][\mathrm{O_2(g)}]$$
$$\therefore \text{Rate} = kK_c[\mathrm{NO(g)}][\mathrm{O_2(g)}][\mathrm{NO}]$$
$$\text{Rate} = k'[\mathrm{NO(g)}]^2[\mathrm{O_2(g)}]$$

This derived rate law is constant with the empirical rate law given earlier. Therefore, the mechanism of the reaction is correct.

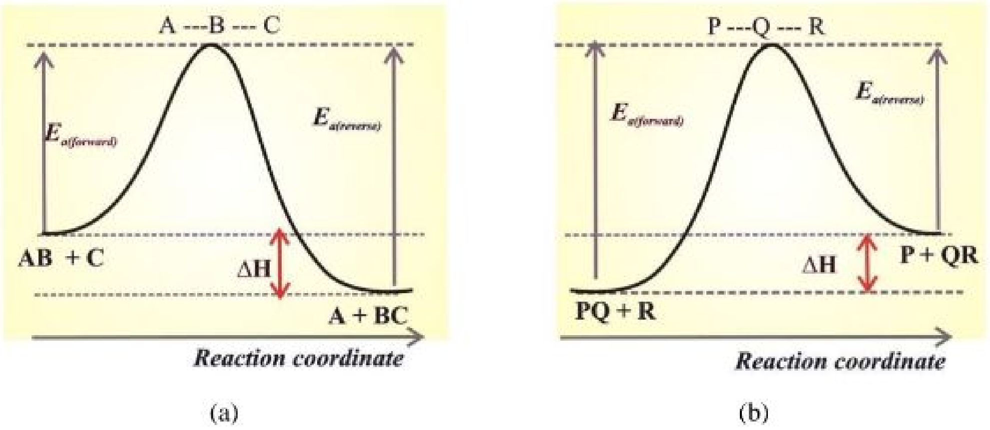
1.11 Energy profiles of reactions

First, consider an elementary reaction which occurs through a single step A → products. As described in earlier sections about the requirements to be satisfied for a chemical reaction to occur when two molecules approach each other, repulsion between their electron clouds continually increase, so they slow down as some of their kinetic energy is converted to potential energy. If they collide, but the energy of the collision is *less* than the activation energy, the molecules bounce off from each other.

According to Maxwell-Boltzmann distribution, however, in a fraction of collisions in which the molecules are moving fast enough, *their kinetic energies push them together with enough force to overcome the repulsions and surmount the activation energy.* Usually in this fraction of sufficiently energetic collisions, the molecules are oriented effectively. In those cases, nuclei in one molecule attract electrons in the other, atomic orbitals overlap, electron densities shift, and some bonds lengthen and weaken while others shorten and strengthen. At some point during this smooth transformation, *a species with partial bonds exists* that is neither a reactant nor a product. This very unstable species, called the **transition state** (or **activated complex**) exists only at the instant of highest potential energy. Thus, *the activation energy of a reaction is used to reach the transition state.* Reaching the transition state does not guarantee that a reaction will proceed to products because *a transition state can change in either direction.* In this case, if the new bond continues to strengthen, products form; but, if the existing bond becomes stronger again, the transition state reverts to reactants.

A useful way to depict these events is with a reaction energy diagram or energy profile which plots how potential energy changes as the reaction proceeds from reactants to products (the *reaction progress or reaction coordinate*). The diagram shows the relative energy levels of reactants, products, and transition state, as well as the forward and reverse activation energies and the enthalpy of reaction. Simply the energy profiles can be depicted for single step exothermic and endothermic reactions as shown in Figure 1.27 considering some hypothetical reactions given below.

AB + C → A + BC: $\Delta H <$ O and PQ + R → P + QR : $\Delta H >$ O.



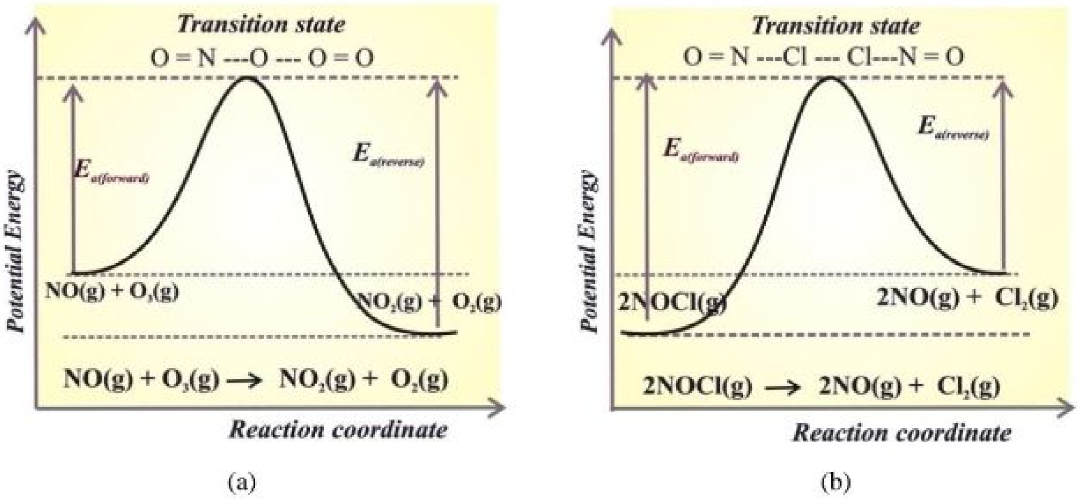
(a) (b)

Figure 1.27 Energy profiles for **(a)** exothermic and **(b)** endothermic reactions going through a single transition state.

Figure 1.27(a) shows that, overall, the reaction is exothermic. The products have lower energy than the reactants, so energy is released when the reaction happens. It also shows that the molecules have to possess enough energy (activation energy) to get the reactants over the "activation energy barrier".

For an endothermic reaction, a simple energy profile is shown in Figure 1.27(b).

For example, following two reactions occur through a single step with a single transition state. The reaction; $NO(g) + O_3(g) \rightarrow NO_2(g) + O_2(g)$ is exothermic while the reaction $2NOCl(g) \rightarrow 2NO(g) + Cl_2(g)$ is endorthermic. Their transition states are also shown along with the potential energy in Figure 1.28.



(a) (b)

Figure 1.28 Energy profiles for two gas-phase reactions of **(a)** exothermic and **(b)** endothermic nature. In each case, the structure of the transition state is predicted from the orientations of the reactant atoms that must become bonded in the product.

As another example, the reaction below shows a reaction in which a bromine atom of bromoethane is being replaced by an OH group to produce ethanol.

$$CH_3Br(aq) + OH^-(aq) \rightarrow CH_3OH(aq) + Br^-(aq)$$

In the reaction one of the lone pairs of electrons on the negatively charged oxygen in the OH^- ion is attracted to the carbon atom with the bromine attached.

As the bromine is more electronegative than carbon, and so the electron pair in the C-Br bond is slightly closer to the bromine. The carbon atom becomes slightly positively charged and the bromine slightly negative. As the hydroxide ion approaches the slightly positive carbon, a new bond starts to be set up between the oxygen and the carbon. At the same time, the bond between the carbon and bromine starts to break as the electrons in the bond are repelled towards the bromine.

At some point, the process is exactly half complete. The carbon atom now has the oxygen half-attached, the bromine half-attached, with three other groups still there and then the process undergo completion. The structure in which the bonds are half-made and half-broken is the **transition state**, and is at the maximum potential energy.

It has to be noted that the transition state is entirely unstable. Any tiny change in either direction will send it either forward to make the products or back to the reactants again. There is no anything special about a transition state except that it has this maximum energy.

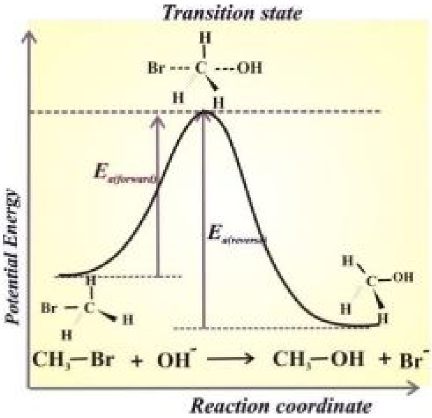


Figure 1.29 Energy profile for the reaction $CH_3Br + OH^- \rightarrow CH_3OH + Br^-$

Example 1.15

The reaction, $O_3(g) + O(g) \rightarrow 2O_2(g)$ has the activation energy of 19 kJ mol^{-1} for the forward reaction and the ΔH for the reaction is -392 kJ mol^{-1}. Draw an energy profile for the reaction with approximate relative positions of the species. Estimate the activation energy for the backward reaction.

Answer

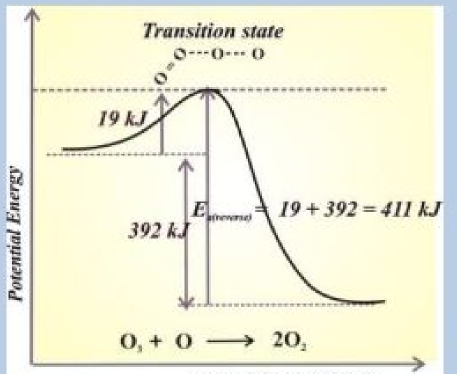


Figure 1.30 Energy profile for the reaction $O_3(g) + O(g) \rightarrow 2O_2(g)$.

Calculation of the activation energy of the backward reaction is indicated in the figure and the postulated structure of the transition state is also drawn.

Energy profiles for reactions which go via an intermediate

In this case, consider the following reaction which goes through an intermediate.

$$(CH_3)_3CBr + OH^- \rightarrow (CH_3)_3COH + Br^-$$

In the overall reaction the bromine atom is replaced by an OH group.

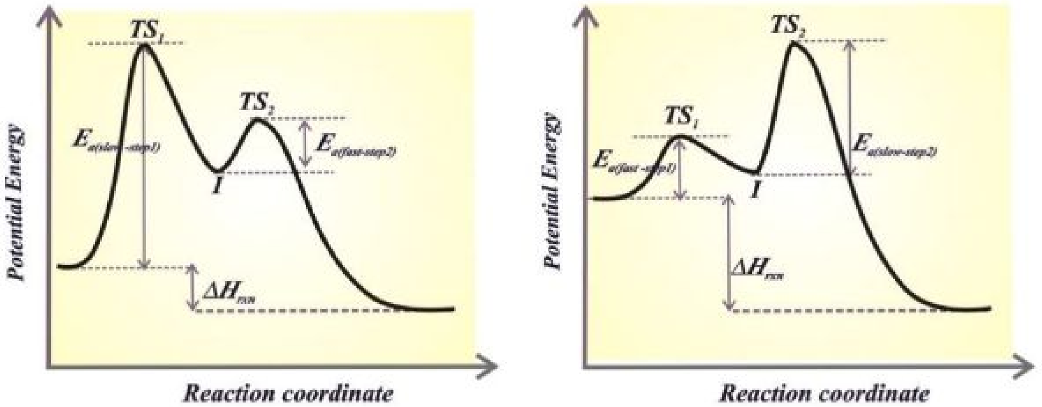
As mentioned earlier the reaction occurs via two steps as follows.

$$(CH_3)_3CBr \rightleftharpoons (CH_3)_3C^+ + :Br^- \quad : \text{slow}$$

$$(CH_3)_3C^+ + :OH^- \rightleftharpoons (CH_3)_3COH \quad : \text{fast}$$

The main difference in this case is that the positively charged ion can actually be detected in the mixture. It is very unstable, short-lived and soon reacts with a hydroxide ion (or picks up its bromide ion again). But, it does have a real presence in the system. The stability (however temporary and slight) of the intermediate is shown by the fact that there are small activation barriers to its conversion either into the products or back into the reactants again.

Notice that the barrier on the product side of the intermediate is lower than that on the reactant side meaning the fast second step as shown in Figure 1.30(a). That means, there is a greater chance of it to find the extra bit of energy to convert into products. It would need a greater amount of energy to convert back to the reactants again. The "TS$_1$" and "TS$_2$" both represent transition states between the intermediate and either the reactants or the products. During either conversion, there will be some arrangement of the atoms which causes an energy maximum.



(a) (b)

Figure 1.31 Energy profiles for two reactions, each of which has a two-step mechanism. **(a)** The reaction starts with a slow step, and **(b)** The reaction starts with a fast step. Both overall reactions are exothermic. Note these key points: Each step in the mechanism has its own peak with the transition state at the top. The intermediates are reactive, unstable species, so they are higher in energy than the reactants or product. The slow (rate-determining) step (step 1 in **(a)** and step 2 in **(b)** has a larger E_a than the other step.