7 REACTION KINETICS

Student Learning Outcomes [C-11-A-01 to C-11-A-25]

After studying this chapter, students will be able to:

- Explain the rate of reaction, and rate constant. **(Understanding)**
- Use experimental data to calculate the rate of a chemical reaction. **(Application)**
- Use the Boltzmann distribution curve to explain the effect of temperature on the rate of a reaction. **(Understanding)**
- Describe the effect of temperature change on the rate constant and rate of reaction. **(Understanding)**
- Explain the concept of activation energy and its role in chemical reactions. **(Understanding)**
- Explain the concept of catalyst and how they increase the rate of a reaction by lowering the activation energy. **(Understanding)**
- Interpret reaction pathway diagrams, including in the presence and absence of catalysts. **(Application)**
- Use rate equations, including orders of reaction and rate constant. **(Application)**
- Calculate the numerical value of a rate constant using the initial rates and half-life method. **(Application)**
- Suggest a reaction mechanism that is consistent with a given rate equation and rate determining step. **(Understanding)**
- Explain the relationship between Gibbs free energy change, $\Delta G°$ and the feasibility of a reaction. **(Understanding)**

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It is a common observation that rates of different chemical reactions differ greatly. For example, the reaction of NaCl with $AgNO_3$ is very fast. The hydrolysis of ester proceeds at a moderate rate. Whereas, rusting of iron is a slow process.

Reaction kinetics is the study of the rates of chemical reactions. It includes a variety of experimental methods for measuring reaction rates, orders and mechanisms of reactions.

An explosion is a swift reaction that happens within a fraction of a second, the rusting of iron is a slow process that may take days or months. The rates of reactions occurring during the explosion are enormous.

The rates of reactions and their control are often important in industry. They might be the deciding factors that determine whether a certain chemical reaction may be used economically or not. Many factors influence the rate of a chemical reaction. It is important to discover the conditions under which the reaction will proceed most economically.

7.1 COLLISION THEORY

Collision theory explains how reactions occur. According to this theory, for a chemical reaction to take place, the particles (atoms, ions or molecules) of reactants must form a homogeneous mixture and collide with one another. These collisions may be effective or ineffective depending upon the energy of the colliding particles. When these collisions are effective, they give rise to the products, otherwise the colliding particles just bounce back. The effective collisions can take place only when the colliding particles possess certain amount of energy and they approach each other with the proper orientation. The minimum amount of energy, required for an effective collision between the reacting species, is called activation energy. Most of the reactions are slow, showing that all the collisions are not equally effective.

Quick Check 7.1

a) What role does the activation energy play in chemical reactions?

b) How does the activation energy affect the rate of a reaction?

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7.2 RATE OF REACTION

During a chemical reaction, reactants are converted into products. So, the concentration of the products increases with the corresponding decrease in the concentration of the reactants as they are being consumed. The rate of a reaction is defined as the change in the concentration of a reactant or a product divided by the time taken for the change.

$$\text{Rate of reaction} = \frac{\text{change in concentration of the substance}}{\text{time taken for the change}}$$

$$\text{Rate of reaction} = \frac{\Delta x}{\Delta t}$$

Where Δx is the change in the concentration of a reactant or a product in a time interval Δt.

It is explained graphically in **Figure 7.1.** For the reactant A which is changing irreversibly to the product B.

$$\mathbf{A} \longrightarrow \mathbf{B}$$

The slope of the graph for the reactant or the product is steepest at the beginning. This shows a rapid decrease in the concentration of the reactant and consequently, a rapid increase in the concentration of the product. As the reaction proceeds, the slope becomes less steep indicating that the reaction is slowing down with time, ultimately both the

curves become parallel. This is the stage of completion of reaction.

The rate of reaction has the units of concentration divided by time. Usually, the concentration is expressed in mol dm^{-3} and the time in second, thus the units for the reaction rate are mol $dm^{-3}s^{-1}$.

$$\text{Rate of reaction} = \frac{\text{mol.dm}^{-3}}{\text{seconds}} = \text{mol.dm}^{-3}\ \text{s}^{-1}$$

However, for a slow reaction the units may be mol dm^{-3} min^{-1} or even mol dm^{-3} h^{-1}. For a gas phase reaction, units of pressure are used in the place of molar concentrations.

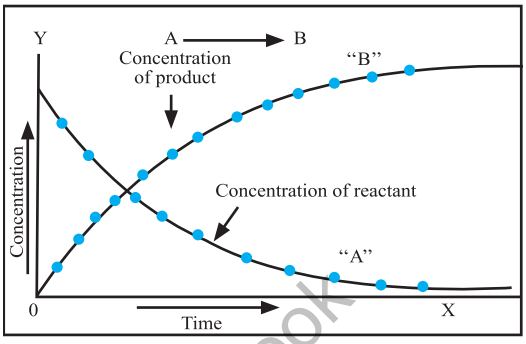

Figure 7.1 Change in the concentration of reactants and products with time for the reaction A → B

The rate of a general reaction, A → B, can be expressed in terms of rate of disappearance of the reactant A or the rate of appearance of the product B mathematically, where [A] and [B] are the concentrations of A and B, respectively.

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} = +\frac{\Delta[B]}{\Delta t}$$

The negative sign with $\frac{\Delta[A]}{\Delta t}$ indicates a decrease in the concentration of the reactant A. Since the concentration of product increases with time, the sign in rate expression involving the change of concentration of product is positive.

7.2.1 Instantaneous and Average Rate

The rate at any one instant during the interval is called the instantaneous rate. Whereas the average rate of reaction is defined as, "The rate of reaction between two specific time intervals or the rate over a time period". The average rate and instantaneous rate are equal for only one instant in any time interval. At first, the instantaneous rate is higher than the average rate. At the end of the interval the instantaneous rate becomes lower than the average rate.

Sample Problem 7.1

The reaction for the formation of ammonia in Haber process is:

$$N_{2(aq)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$

If the concentration of ammonia is 3.5 mol. dm^{-3} after 1.0 min and 6.2 mol.dm^{-3} after 4.0 minutes:

i. Calculate the instantaneous rate after 1.0 min

ii. What is the average rate of production of ammonia for the system, between 1.0 and 4.0 minutes?

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i) Solution

The instantaneous rate at 1.0 min can be calculated as

$$\text{Instantaneous Rate} = \frac{\Delta C}{\Delta t} = \frac{3.5 \text{ mol dm}^{-3}}{1 \text{ min}} = \mathbf{3.5 \text{ mol dm}^{-3}\text{min}^{-1}}$$

ii) Solution

$\Delta C = \Delta[NH_3] = (6.2\text{-}3.5)$ mol dm^{-3} ; $\Delta c = 2.7$ mol dm^{-3}

$\Delta t = (4.0 - 1.0)$; $\Delta t = 3.0$ min

$$\text{Rate of formation of } NH_3 = \frac{\Delta C}{\Delta t} = \frac{\Delta[NH_3]}{\Delta t} = \frac{2.7 \text{ mol dm}^{-3}}{3 \text{ min}} = \mathbf{0.90 \text{ mol dm}^{-3}\text{min}^{-1}}$$

The rate of production of NH_3 gas over the given time interval is 0.90 mol dm^3 min^1.

Quick Check 7.2

The reaction of hydrogen and iodine to make hydrogen iodide at a particular temperature, $H_2(g) + I_2(g) \rightarrow 2HI(g)$ was studied at various times. At 100.0 s after the start of the reaction, the iodine concentration had fallen from 0.010 mol dm^{-3} to 0.0080 mol dm^{-3}. What is the average rate of reaction during this period?

7.2.2 Measuring the Rate of a Chemical Reaction

The measurement of rate of a chemical reaction involves the determination of the concentration of reactants or products at regular time intervals as the reaction progresses.

Table 7.1 Change in concentration of HI with regular intervals $2HI_{(g)} \rightarrow H_{2(g)} + I_{2(g)}$

Concentration of HI (mol dm^{-3})	Time (s)
0.100	0
0.0716	50
0.0558	100
0.0457	150
0.0387	200
0.0336	250
0.0296	300

To determine the rate of a reaction for a given length of time, a graph is plotted between time on x-axis and concentration of a reactant on y-axis, whereby a curve is obtained. To illustrate it, let us investigate the decomposition of HI to H_2 and I_2 at 50 °C, for which the experimental data is given in **Table 7.1**. By using the data, a graph is plotted as shown in **Figure 7.2**. The graph is plotted between time on x-axis and concentration of HI in mol dm^{-3} on y-axis. Since HI is a reactant, therefore, it is a falling curve. The steepness of the concentration-time curve reflects the progress of the reaction. Greater the slope of the curve near the start of reaction, greater is the rate of reaction.

In order to measure the rate of reaction, draw a tangent say, at 100 seconds, on the curve and measure the slope of that tangent. The slope of the tangent is the rate of reaction at that point i.e., after 100 seconds. A right-angled triangle ABC is completed with a tangent as hypotenuse. **Figure 7.2** shows that in 100 sec, the change in concentration is 0.04 mol dm^{-3}. The rate is then calculated by using the following expression.

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$$\text{Rate of reaction} = \frac{\Delta C}{\Delta t}$$

$$\text{rate} = \frac{0.04 \text{ mol dm}^{-3}}{100 \text{ sec}} = 4\times10^{-4} \text{ mol dm}^{-3} \text{ s}^{-1}$$

This value of rate means that the concentration of HI is decreasing by 2.5 moles per dm^{-3} every second during the given interval.

If we plot a graph between time on x-axis and concentration of any of the products i.e H_2 or I_2, then a rising curve is obtained. The value of the tangent at 100 seconds will give the same value of rate of reaction.

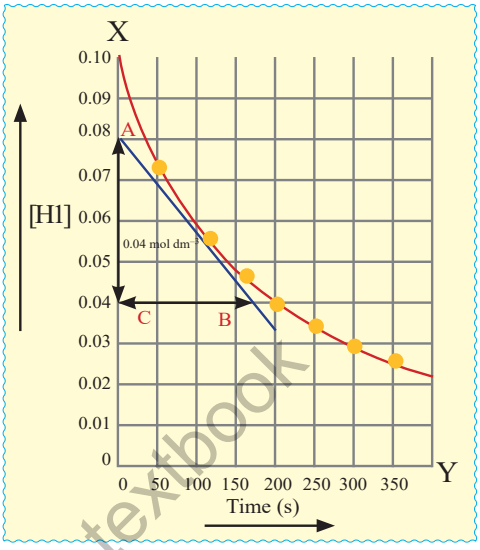

Figure 7.2 The change in the HI concentration with time to the reaction $2HI_{(g)} \longrightarrow H_{2(g)} + I_{2(g)}$ at 508ºC

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Quick Check 7.3

a) Plot the data in Table 7.1 for HI in your note book.

b) Calculate the rate after 300 sec (when the concentration is 0.03 mol dm^{-3}) by drawing a tangent.

c) Use the same method to calculate the rate of reaction at HI concentrations of 0.10 mol dm^{-3}, 0.050 mol dm^{-3} and 0.02 mol dm^{-3}.

d) What do you deduce about the rate of the reaction with time from these calculations?

e) At which concentration, the rate is highest, and lowest?

7.2.3 Measurement of Concentration

The change in concentrations of reactants or products can be determined by both physical and chemical methods depending upon the type of reactants or products involved.

a) Chemical Method

This is particularly suitable for reactions in solution. In this method, we do the chemical analysis of a reactant or a product. The acid hydrolysis of an ester (ethyl acetate) in the presence of a small amount of an acid is one of the best examples.

$$CH_3COO_2H_{5(\ell)} + H_2O_{(\ell)} \xrightarrow{H^+} CH_3COOH_{(aq)} + C_2H_5OH_{(aq)}$$

In the case of hydrolysis of an ester, the solution of ester in water and the acid (acting as a catalyst) are allowed to react. After some time, a sample of reaction mixture is withdrawn by a pipette and run into about four times its volume of ice-cold water. The dilution and chilling stop the reaction.

The acid formed is titrated against a standard alkali, say NaOH, using phenolphthalein as an indicator.

The analysis is repeated at various time intervals after the start of reaction. This would provide an information about the change in concentration of acetic acid formed during the reaction at different time intervals.

b) Physical Methods

Some of the methods used for the measurement of concentration are as follows:

i) Spectrophotometry or colorimetry

This method is applicable if a reactant or a product absorbs ultraviolet, visible or infrared radiation. The rate of a reaction can be measured by measuring the amount of radiation absorbed. For the reaction shown in **Figure 7.3**, the concentration can be measured using the colorimetry.

Figure 7.3 The concentration change for this reaction can be determined using colorimetry.

ii) Electrical conductivity method

The rate of a reaction involving ions can be studied by electrical conductivity method. The conductivity of such a solution depends upon the rate of change of concentration of the reacting ions or the ions formed during the reaction. The conductivity will be proportional to the rate of change in the concentration of such ions.

iii) Volume change method

This method is useful for those reactions which involve changes in volumes of gases as shown in **Figure 7.4.** The volume change is directly proportional to the extent of reaction and changes in concentration.

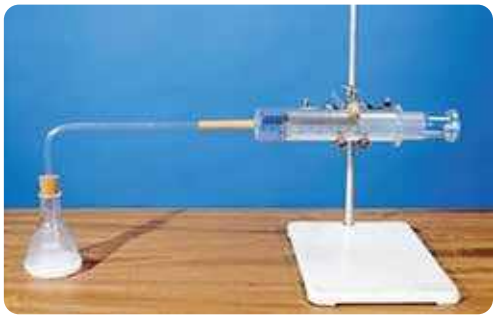

Figure 7.4 Rate of reaction can be followed by measuring the change in volume of a gas given off in a reaction.

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Interesting Information

The rates of some very fast reactions can be monitored using stopped-flow spectrophotometry. In this technique, very small volumes of reactants are driven at high speed into a mixing chamber. From here they go to an observation cell, where the progress of the reaction is monitored (usually by measuring the transmission of ultraviolet radiation through the sample). A graph of rate of reaction against time can be generated automatically.

7.3 FACTORS AFFECTING RATE OF A CHEMICAL REACTION

In general, the rates at which reactants are consumed and products are formed during chemical reactions vary greatly. Even a chemical reaction involving the same reactants may have different rates under different conditions. The factors affecting the rate of a reaction are:

i. Concentrations of the reactants
ii. Temperature of the system
iii. Surface area
iv. Catalyst

Did You Know?

In the case of reactions that involve gaseous reactants, an increase in pressure increases the concentration of the gases which leads to an increase in the rate of reaction. However, pressure change has no effect on the rate of reaction if the reactants are either solids or liquids.

7.3.1 Concentration

According to the law of mass action, the greater the concentration of the reactants, the more rapidly the reaction proceeds. When the concentration of one or more reactants increases, the rate of reaction increases. This is because increasing the concentration results in more collisions between the reacting particles, which speeds up the reaction.

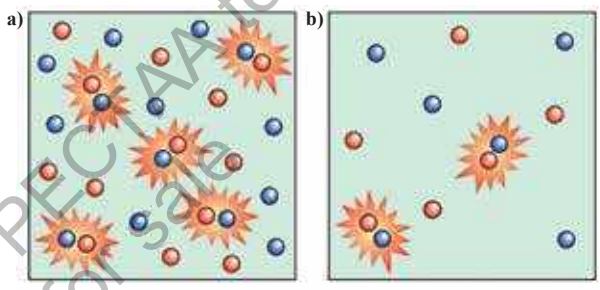

Figure 7.5 The reaction in box **a)** will occur faster than that in, **b)** due to the higher concentration.

7.3.2 Temperature

(Maxwell-Boltzmann distribution curve)

Increase in temperature increases the reaction rate. It has been observed that rate either doubles or triples for every 10 °C rise in temperature. Temperature usually has a major effect on the rate of reaction. Molecules at higher temperatures have more thermal energy. So, they collide more frequently and with greater energy.

The Boltzmann distribution curve is a graph that shows the distribution of energies at certain temperature. In a reaction, a few particles will have very low energy, a few particles will have very high energy, and many particles will have energy in between. The distribution of energies at a given temperature can be shown on a graph as shown in **Figure 7.6,** this is called the **Boltzmann distribution curve**. As you know that the activation energy is the minimum energy required for colliding particles fruitfully to convert into the product. The shaded area under the graph as shown in **Figure 7.6** represents the proportion of molecules that have enough energy to cause a chemical change when they collide. The area under the curve represents the number of particles. The shaded area shows the number of particles with energy greater than the activation energy, E_a.

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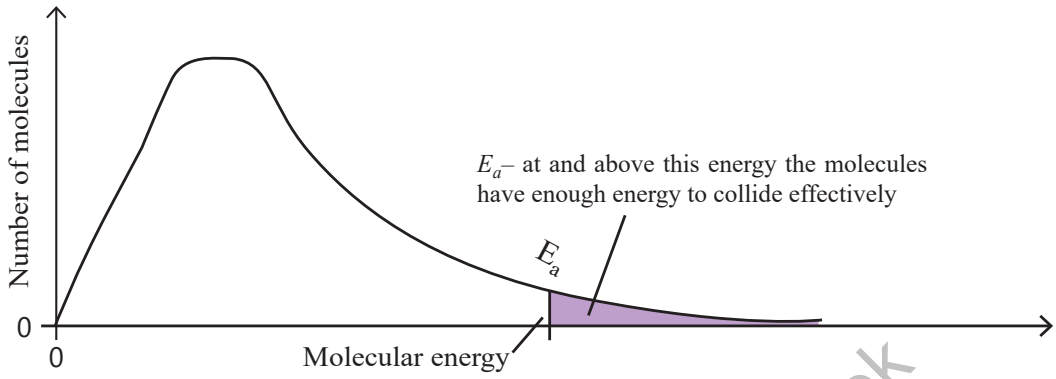

Figure 7.6 The Boltzmann distribution curve showing molecular energies and activation energy

As the temperature of a reaction mixture is raised, the average kinetic energy of the particles increases. The reacting particles move around more quickly at a higher temperature, resulting in more frequent collisions. Therefore, the proportion of successful collisions also increases greatly as shown in **Figure 7.7**. The curve showing the Boltzmann distribution at the higher temperature flattens and the peak shifts to the right. For 10 °C rise in temperature, the shaded area under the curve approximately doubles. In conclusion, increasing the temperature increases the rate of a reaction.

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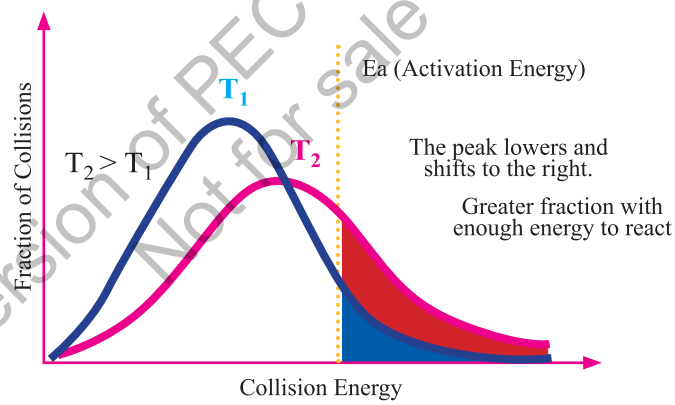

Figure 7.7 The Boltzmann distribution of molecular energies at temperatures T_1 and T_2

Quick Check 7.4

a) What is the Boltzmann distribution curve?

b) Explain why a 10 °C rise in temperature approximately doubles the rate of a reaction.

7.3.3 Catalyst

A catalyst is defined as a substance which alters the rate of a chemical reaction, but remains chemically unchanged at the end of the reaction. A catalyst is often present in a very small amount. For example, the reaction between H_2 and O_2 to form water is very slow at ordinary temperature, but proceeds more rapidly in the presence of platinum. Platinum acts as a catalyst. Similarly, $KClO_3$ decomposes much more rapidly in the presence of a small

amount of MnO_2. HCl is oxidized to Cl_2 in the presence of $CuCl_2$.

$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

The process, which takes place in the presence of a catalyst, is called catalysis. A catalyst provides a new reaction path with a low activation energy barrier, as shown in **Figure 7.8**. A greater number of molecules are now able to get over the new energy barrier and reaction rate increases.

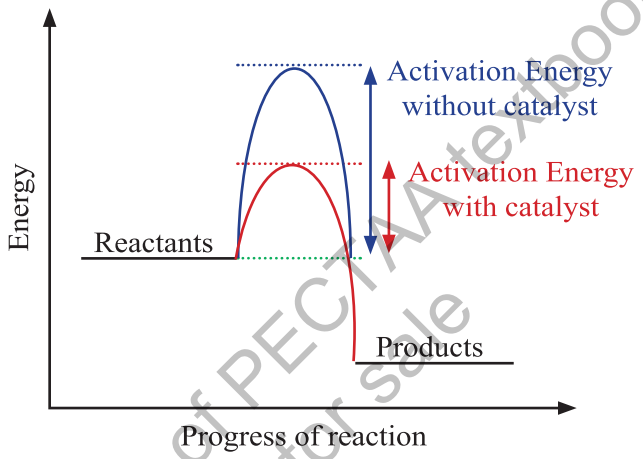

Figure 7.8 The energy path diagram for an uncatalyzed and a catalyzed reaction

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Types of Catalysis

i) Homogeneous Catalysis

In this process, the catalyst and the reactants are in the same phase and the reacting system is homogeneous throughout. The catalyst is distributed uniformly throughout the system.

For example:

i. The formation of $SO_{3(g)}$ from $SO_{2(g)}$ and $O_{2(g)}$ in the contact process for the manufacture of sulphuric acid, needs $NO_{(g)}$ as a catalyst. Both the reactants and the catalyst are gases.

$$2SO_{2\,(g)} + O_{2\,(g)} \xrightarrow{NO_{(g)}} 2SO_{3(g)}$$

ii. Esters are hydrolyzed in the presence of H_2SO_4. Both the reactants and the catalyst are in the solution state.

$$\underset{\text{Ethyl ethanoate}}{CH_3COOCH_2CH_{3(\ell)}} + H_2O_{(\ell)} \xrightarrow{H^+} \underset{\text{Ethanoic acid}}{CH_3COOH_{(aq)}} + \underset{\text{Ethanol}}{CH_3CH_2OH_{(aq)}}$$

Did you Know!

Biochemical catalysts, commonly known as enzymes (nature's catalyst) are essential molecules in living organisms' functions by lowering the activation energy required for a chemical reaction to proceed, thereby increasing the reaction rate. Enzymes are typically proteins. Factors such as pH, temperature, and the concentration of substrate molecules can influence enzyme activity.

ii) Heterogeneous Catalysis

In such systems, the catalyst and the reactants are in different phases. Mostly, the catalysts are in the solid phase, while the reactants are in the gaseous or liquid phase. For example, the oxidation of ammonia to NO in the presence of platinum gauze to produce HNO_3 industrially through the hetrogeneous catalysis.

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{\text{Pt, 800 ºC}} 4NO_{(g)} + 6H_2O_{(g)}$$

Hydrogenation of unsaturated organic compounds is catalysed by finely divided Ni, Pd or Pt.

$$C_2H_{4(g)} + H_{2(g)} \xrightarrow{\text{Ni, 150 ºC}} C_2H_{6(g)}$$

Interesting Information

Vitamins are organic compounds that act as catalysts in biochemical reactions, especially when they function as coenzymes. Coenzymes are organic molecules that help enzymes catalyze reactions more efficiently. For example, Vitamin K, is necessary for blood clotting. Low levels of vitamin K can cause bleeding diathesis. A lack of vitamins can disrupt metabolic balance in cells and organisms. Vitamin deficiency is an example of a cofactor deficiency.

Quick Check 7.5

a) Can a catalyst be consumed in a chemical reaction? Why or why not?

b) Explain whether the reaction below is an example of heterogeneous or homogeneous catalysis:

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_5\ (solid)} 2SO_{3(g)}$$

c) Draw an energy profile diagram to show a typical uncatalysed reaction and an enzyme-catalysed reaction.

On your diagram show the activation energy for:

i) Catalysed reaction

ii) Uncatalysed reaction

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7.4 RATE LAW, RATE CONSTANT AND ORDER OF REACTION

7.4.1 Rate Law and Rate Constant

The rate of a chemical reaction at a given temperature may depend on the concentration of one or more reactants and products. The representation of rate of a reaction in terms of concentration of the reactants is known as **rate law**. A rate law is an equation that relates the rate of a reaction to the concentrations of reactants raised to various powers according to the experimental data.

For a general reaction between A and B where 'a' moles of A and 'b' moles of B react to form 'c' moles of C and 'd' moles of D.

$$aA + bB \longrightarrow cC + dD$$

We can write the rate equation as:

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

Where x and y are the experimentally determined values that may or may not be equal to the coefficient of reactants in the balanced chemical equation, as 'a' and 'b' in the above equation. This expression is called rate equation. The brackets [ ] represent the molar concentrations and the proportionality constant k is called rate constant for the reaction.

If $[A] = 1 \text{ mol dm}^{-3}$ and $[B] = 1 \text{ mol dm}^{-3}$

$$\text{Rate of reaction} = k \times 1^x \times 1^y = k \text{ (rate constant)}$$

The rate constant can be defined as "The specific rate constant of a chemical reaction is the rate of reaction when the concentrations of the reactants are unity". Under the given conditions, k remains constant, but it changes with temperature.

7.4.2 Reaction Order

The exponents 'x' or 'y' in the above equation give the order of reaction with respect to the individual reactants. "The order of a reaction with respect to a specific reactant is the exponent applied to that reactant's concentration within the rate equation". Thus, the reaction is of order 'x' with respect to A and of order 'y' with respect to B. The overall order of reaction is (x+y). The order of a reaction defines how the reactant concentration influences its rate. For a single-reactant, the order is simply the concentration's power in the rate equation.

The chemical reactions are classified as zero, first, second and third order reactions. The order of reaction provides valuable information about the mechanism of a reaction.

It is crucial to differentiate between the order concerning a single reactant and the overall reaction order.

Take equation for the reaction of nitrogen (II) oxide (NO) with H_2:

$$2H_{2(g)} + 2NO_{(g)} \longrightarrow N_{2(g)} + H_2O_{(g)}$$

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The experimentally determined rate expression for this is,

$$\text{rate} = k[H_2][NO]^2$$

The expression shows that this reaction is:

i. first-order with respect to H_2
ii. second-order with respect to NO
iii. third-order overall (1 + 2 = 3)

Keep in Mind

The order of a reaction is given by the sum of all the exponents to which the concentrations in the rate equation are raised. It is important to note that the order of a reaction is an experimentally determined quantity and cannot be inferred simply by looking at the reaction equation. The sum of the exponents in the rate equation may or may not be the same as in a balanced chemical equation.

Quick Check 7.6

a) How order of reaction is derived from the rate law?

b) Explain what is meant by the specific rate (rate constant) of a reaction and how it is represented in rate equation.

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7.4.3 Types of Reaction Order

Zero Order Reaction

The rate of a zero order reaction is independent of the concentration of the reactants. A change in the concentration has no effect on the speed of the reaction.

For the general reaction:

$$A \rightarrow \text{Product}$$

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

Examples:

i) $H_{2(g)} + Cl_{2\,(g)} \xrightleftharpoons{\text{sunlight}} 2HCl_{(g)}$

$$\text{Rate} = k\,[H_2]^0[Cl_2]^0 = k$$

ii) $2NH_{3\,(g)} \underset{\text{catalyst}}{\overset{\text{high T}}{\rightleftharpoons}} N_{2\,(g)} + 3H_{2\,(g)}$

$$\text{Rate} = k\,[NH_3]^0 = k$$

Photochemical reactions are usually zero order.

First Order Reaction

A reaction for which the some of the exponents of the concentrations in the rates equations is 1. In these reactions, there may be multiple reactants present, but concentration of only

one reactant will change during the reaction. Examples of a first order reaction is the decomposition of nitrogen pentaoxide, which involves the following equation.

$$2N_2O_{5(g)} \longrightarrow 2N_2O_{4(g)} + O_{2(g)}$$

The experimentally determined rate equation for this reaction is as follows:

$$\text{Rate} = k[N_2O_5]^1 \quad (n = 1)$$

This equation suggests that the reaction is first order with respect to the concentration of N_2O_5.

Second Order Reaction

A reaction for which sum of the exponents of the concentrations in the rate equation is 2. A second order reaction is a reaction whose rate depends either on the concentration of one reactant raised to the second power or on the concentrations of two different reactants, each raised to the first power. The simpler type of reaction involves one kind of reactant molecule. Hypothetically, it can be expressed as:

$$\text{Rate} = k[A]^2 \quad (n = 2)$$

$$\text{Rate} = k\,[A]^1[B]^1 \quad (n = 1+1 = 2)$$

Oxidation of nitric oxide with ozone is first order with respect to NO and first order with respect to O_3. The sum of the individual orders gives the overall order of reaction as two.

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)} \qquad \text{Rate} = k[NO]^1[O_3]^1$$

Third Order Reaction

A third order reaction is the reaction for which sum of the exponents of the concentrations in the rate equation is three.

$$\text{Rate} = k[A]^3 \quad (n = 3)$$

$$\text{or Rate} = k\,[A]^2[B]^1 \quad (n = 2+1 = 3)$$

$$\text{or Rate} = k\,[A]^1[B]^1[C]^1 \quad (n = 1+1+1 = 3)$$

$$2FeCl_{3(aq)} + 6KI_{(aq)} \longrightarrow 2FeI_{2\,(aq)} + 6KCI_{(aq)} + I_2$$

This reaction involves eight reactant molecules but experimentally it has been found to be a third order reaction.

$$\text{Rate} = k[FeCl_3][KI]^2$$

also, the following reaction is third order

$$2NO_{(g)} + O_{2(g)} \longrightarrow 2NO_{2(g)} \qquad \text{Rate} = k[NO]^2[O_2]^1$$

$$\text{order} = 1 + 1 = 2$$

Fractional Order Reaction

A reaction in which the sum of exponents of rate equation is in fraction, is called the **fractional order reaction**. For example, consider the formation of carbon tetrachloride from chloroform.

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$$CHCl_{3(l)} + Cl_{2(g)} \longrightarrow CCl_{4(\ell)} + HCl_{(g)}$$

$$\text{Rate} = k[CHCl_3]\,[Cl_2]^{1/2} \qquad n = 1 + \frac{1}{2} = 1.5$$

Reactions involving free radicals frequently exhibit fractional orders.

7.4.4 Units of Rate Constant

The rate constant is specific for a particular reaction at a certain temperature. Since concentrations are in mol dm^{-3} and the reaction rate is in units of mol dm^{-3} s^{-1}. The units for k depend on the order of the reaction and the units of time.

$$\text{Rate} = k[\text{Reactants}]^n \qquad \text{where } n = \text{order of reaction}$$

$$k_n = \frac{\text{Rate}}{(\text{Rectants})^n} = \frac{(\text{mol dm}^{-3})\ s^{-1}}{(\text{mol dm}^{-3})^n}$$

$$\text{or } k_n = (\text{mol dm}^{-3})^{1-n}\ s^{-1}$$

$$\text{or } k_n = (\text{concentration})^{1-n}\ s^{-1}$$

This equation can be used to determine units of any order of reaction.

For a **zero order reaction** (n = 0),

$$k_0 = (\text{mol dm}^{-3})^{1-0}\ s^{-1}$$

$$k_0 = \text{mol dm}^{-3}\ s^{-1}$$

For a first order reaction (n = 1), the rate is directly proportional to the concentration of one reactant.

$$k_1 = (\text{mol dm}^{-3})^{1-1}\ s^{-1}$$

$$k_1 = (\text{mol dm}^{-3})^{0}\ s^{-1}$$

$$k_1 = s^{-1}$$

Therefore, the units of k for a first order rate constant are s^{-1}.

For a second order reaction (n = 2),

$$k_2 = (\text{mol dm}^{-3})^{1-2}\ s^{-1}$$

$$k_2 = \text{mol}^{-1}\ \text{dm}^3\ s^{-1}$$

$$k_2 = \text{dm}^3\ \text{mol}^{-1}\ s^{-1}$$

The units of k for a second order rate constant are dm^3 mol^{-1} s^{-1}.

For a third order reaction (n = 3),

$$k_3 = (\text{mol dm}^{-3})^{1-3}\ s^{-1}$$

$$k_3 = \text{mol}^{-2}\ \text{dm}^6\ s^{-1}$$

$$k_3 = \text{dm}^6\ \text{mol}^{-2}\ s^{-1}$$

Therefore, the units of k for a third order rate constant are dm^6 mol^{-2} s^{-1}.

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Quick Check 7.7

a) Consider the following rate expression:

rate = $k[NO]^2\ [NH_3]^0$

rate = $k[BrO_3][Br^-][H^+]^2$

i) Calculate the overall order of reactions.

ii) What are the orders with respect to each reactant in the expression.

c) Why the sum of the coefficients of a balanced chemical equation is not necessarily important to give the order of a reaction?

7.5 DETERMINATION OF RATE CONSTANT

The rate constant (k) of a reaction can be calculated using the following two methods:

7.5.1 Initial Concentration Method

In the presence of hydrogen ions, hydrogen peroxide, H_2O_2, reacts with iodide ions to form water and iodine:

$$H_2O_{2(aq)} + 2I^-_{(aq)} + 2H^+_{(aq)} \longrightarrow 2H_2O_{(l)} + I_{2(aq)}$$

The rate equation for this reaction is:

$$\text{rate of reaction} = \frac{k[H_2O_2]}{[I^-]}$$

The progress of the reaction can be followed by measuring the initial rate of formation of iodine. **Table 7.2** shows the rates of the reaction obtained using various initial concentrations of each reactant.

The procedure for calculating k is shown below, using the data for experiment 1 in **Table 7.2**.

Step 1 Write out the rate equation.

$$\text{rate of reaction} = \frac{k[H_2O_2]}{[I^-]}$$

Step 2 Rearrange the equation in terms of k

$$k = \frac{\text{rate} \times [I^-]}{[H_2O_2]}$$

Step 3 Substitute the values

$$k = \frac{3.50 \times 10^{-6} \times (0.0100)}{(0.0200)}$$

$$k = 1.75 \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$$

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Table 7.2 Effect of change in concentrations of reactants on the rate of reaction

Experiment	$[H_2O_2]$ mol dm^{-3}	$[I^-]$ mol dm^{-3}	$[H^+]$ mol dm^{-3}	Initial rate of reaction mol dm^{-3} s^{-1}
1	0.0200	0.0100	0.0100	3.5×10^{-6}
2	0.0300	0.0100	0.0100	5.3×10^{-6}
3	0.0050	0.0200	0.0200	1.75×10^{-6}

The concentration of hydrogen ions is ignored because $[H^+]$ does not appear in the rate equation. The reaction is zero order with respect to $[H^+]$.

7.5.2 Half-Life Method

"Half-life, $t_{1/2}$, is the time taken for the concentration of a reactant to fall to half of its original value". Calculating the rate constant (k) using the half-life method involves measuring the time it takes for the concentration of a reactant to decrease by half.

If the reaction is first-order, then the rate constant and the half-life of the reaction are related in the following way:

$$k = \frac{0.693}{t_{1/2}}$$

Here is an example to help you understand how the process is done. A sample of hydrogen peroxide has a half-life of 2 hours. It decomposes in a first-order reaction. Calculate the rate constant, k, for this reaction.

To calculate k, we first need to convert the half-life into seconds:

$$2 \times 60 \times 60 = 7200 \text{ s}$$

We then simply substitute this value into the equation:

$$k = \frac{0.693}{7200 \text{ s}}$$

$$k = 9.6 \times 10^{-5} \text{ s}^{-1}$$

Sample Problem 7.2

The conversion of cyclopropane to propene is a first order raections. The half-life is 17.0 min, Calculate the rate constant of this reaction.

Solution:

Step 1 convert minutes to seconds

Step 2 substitute the half-life into the expression:

$$k = \frac{0.693}{t_{1/2}}$$

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$$k = \frac{0.693}{17 \times 60 \text{ s}}$$

$$k = 6.79 \times 10^{-4} \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$$

Quick Check 7.8

Consider a first-order reaction with a half-life of 15 minutes. If the initial concentration of the reactant is 0.100 mol dm^{-3}, calculate the rate constant (k) for the reaction.

7.6 REACTION MECHANISM

A reaction mechanism is a detailed, step by step description of how a chemical reaction occurs at the molecular level to yield the product(s). Unlike the overall balanced chemical equation, which only shows the reactants and products, the reaction mechanism reveals the actually happening individual steps (called elementary steps) that lead to the formation of products. Each of these steps represents a single molecular event, such as the breaking or forming of bonds.

Many reactions do not occur in a single step, but rather proceed through a series of steps. Each step is called an elementary reaction and is directly caused by the collision of atoms, ions or molecules. The number of reactant molecules involved in an elementary step is called its molecularity.

A unimolecular elementary reaction involves only a single reactant molecule. The example of a unimolecular reactions is the decomposition of N_2O_5.

$$N_2O_{5(g)} \longrightarrow NO_{2(g)} + NO_{3(g)}$$

An elementary reaction that involves two atoms, ions or molecules and is called **bimolecular**. For example;

$$CO_{(g)} + NO_{3(g)} \longrightarrow NO_{2(g)} + CO_{2(g)}$$

$$NO_{(g)} + O_{3(g)} \longrightarrow NO_{2(g)} + O_{2(g)}$$

A **termolecular** reaction step involves the simultaneous reaction of three molecules. Such reactions are rare. An example is the reaction between oxygen molecules and atomic oxygen to form ozone in the stratosphere or during smog formation.

$$2O_{2(g)} + O_{(g)} \longrightarrow O_{3(g)} + O_{2(g)}$$

Intermediates are short lived species (ions or free radicals) that are produced in one step of the mechanism and consumed in a subsequent step. They do not appear in the overall balanced equation because they are not stable products.

Rate Determining Step

In many reaction mechanisms, one step is significantly slower than all the others. This step is called the rate-determining step. This step controls the overall rate of the reaction because it limits the speed at which the reaction can proceed. The balanced equation for the overall reaction is equal to the net result of all the individual steps. In a chemical

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reaction, any step that occurs after the rate-determining step will not affect the rate. So the atoms, ions or molecules taking part in the mechanism after the rate-determining step do not appear in the rate expression. All reactants that appear in the rate-determining step will also appear in the **rate equation**. As the rate-determining step limits the rate of the overall reaction, the order of a reaction can be deduced from the rate determining step.

Lets consider the following reaction:

$$2NO_{(g)} + 2H_{2(g)} \longrightarrow 2H_2O_{(g)} + N_{2(g)}$$

Table 7.3 shows the results of six experiments. In the first three experiments, the concentration of H_2 is increased by keeping the concentration of NO constant. By doubling the concentration of H_2, the rate is doubled and by tripling the concentration of H_2, the rate is tripled. So, the rate of the reaction is directly proportional to the first power of concentration of H_2.

$$\text{Rate} \propto [H_2]^1$$

In the next three experiments, the concentration of H_2 is kept constant. By doubling the concentration of NO, the rate increases four times and by tripling the concentration of NO the rate is increased nine times. So, the rate is proportional to the square of concentration of NO.

$$\text{Rate} \propto [NO]^2$$

Table 7.3 Effect of change in concentrations of reactants on the rate of reaction

[NO] in (mol dm^{-3})	[H_2] in (mol dm^{-3})	Initial rate (atm min^{-1})
0.006	0.001	0.025
0.006	0.002	0.050
0.006	0.003	0.0075
0.001	0.009	0.0063
0.002	0.009	0.025
0.003	0.009	0.056

The overall rate equation of reaction is,

$$\text{Rate} \propto [H_2][NO]^2$$

$$\text{or Rate} = k[H_2]^1[NO]^2$$

$$\text{Order} = 1 + 2 = 3$$

Hence, the reaction is a third order one. This final equation is the rate law for this reaction. It should be kept in mind that rate law cannot be predicted from the balanced chemical equation. The possible mechanism consisting of two steps for the reaction is as follows.

$$\text{Step 1: } 2NO_{(g)} + H_{2(g)} \xrightarrow{\text{Slow}} N_{2(g)} + H_2O_{2(g)} \text{ (rate determining step)}$$

$$\text{Step 2: } H_2O_{2\,(g)} + H_{2(g)} \xrightarrow{\text{Fast}} 2H_2O_{(g)}$$

The step 1 is slow and rate determining.

Another example is the reaction between nitrogen dioxide and fluorine gas:

$$2NO_{2(g)} + F_{2(g)} \longrightarrow 2NO_2F_{(g)}$$

This reaction is first order in NO_2, first order in F_2 and second order overall. The experimental rate law is first order in NO_2 and in F_2:

$$\text{Rate} = k\,[NO_2][F_2] \qquad \text{(Observed)}$$

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The accepted mechanism for the reaction is:

Step 1: $NO_{2(g)} + F_{2(g)} \xrightarrow{\text{Slow}} NO_2F_{(g)} + F^{\cdot}_{(g)}$ Rate = $k_1[NO_2][F_2]$

Step 2: $NO_{2(g)} + F^{\cdot}_{(g)} \xrightarrow{\text{Fast}} NO_2F_{(g)}$ Rate = $k_2[NO_2][F^{\cdot}]$

The first step is slow and determines the rate, in agreement with the observed rate expression. The second and fast step does not affect the reaction rate because fluorine atoms react with NO_2 as soon as they are produced.

Quick Check 7.9

An acidified solution of hydrogen peroxide reacts with iodide ions.

$$H_2O_{2(aq)} + 2H^+_{(aq)} + 2I^-_{(aq)} \longrightarrow 2H_2O_{(l)} + I_{2(aq)}$$

The rate equation for this reaction is

$$\text{rate} = k\,[H_2O_2]\,[I^-]$$

The mechanism below has been proposed for this reaction.

$H_2O_2 + I^- \xrightarrow{\text{Slow}} H_2O + IO^-$

$H^+ + IO^- \xrightarrow{\text{Fast}} HIO$

$HIO + H^+ + I^- \xrightarrow{\text{Fast}} I_2 + H_2O$

Explain why this mechanism is consistent with the rate equation.

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EXERCISE

MULTIPLE CHOICE QUESTIONS

Q.1 Four choices are given for each question. Select the correct choice.

I. The rate of reaction:

a) Increases as the reaction proceeds

b) Decreases as the reaction proceeds

c) Remains the same as the reaction proceeds

d) May decrease or increase as the reaction proceeds

II. Increasing the temperature of a chemical reaction increases the rate of a reaction because:

a) Both the collision frequency and collision energies of reactant molecules increase

b) Collision frequency of reactant molecules increases

c) Activation energy increase

d) Activation energy decrease

III. Consider two reactions with different activation energies at the same temperature. The reaction with the lower activation energy will have:

a) A smaller rate constant
b) A larger rate constant
c) The same rate constant
d) A rate constant that depends on the enthalpy change

IV. The order of a chemical reaction, that is independent of concentration is:

a) Second order reaction
b) First order reaction
c) Zero order reaction
d) Pseudo first order reaction

V. On a Boltzmann distribution curve, the area under the curve represents:

a) Activation energy of the reaction.
b) Total number of molecules in the sample.
c) Average kinetic energy of the molecules.
d) Rate constant of the reaction.

VI. On a Boltzmann distribution curve, the activation energy (E_a) is represented by:

a) The height of the peak
b) The area under the entire curve
c) A vertical line drawn at a specific kinetic energy value
d) The difference between the peak and the X-axis

VII. If we double the concentration of a reactant, the rate increases by four times, the reaction is:

a) Second order
b) First order
c) Third order
d) Zero order

VIII. The rate determining step in a multi-step reaction is:

a) Always the first step
b) Always the last step
c) The slowest step
d) The fastest step

IX. The reaction $NO_{2(g)} + CO_{(g)} \rightarrow NO_{(g)} + CO_{2(g)}$ occurs in two steps. What is the rate law equation for this reaction?

$2NO_2 \rightarrow NO + NO_3$ (k_1) slow

$NO_3 + CO \rightarrow CO_2 + NO_2$ (k_2) fast

a) $R = k_1 [NO_2]^3$
b) $R = k_2 [NO_3][CO]$
c) $R = k_1 [NO_2]$
d) $R = k_1 [NO_2]^2$

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X. How does the presence of a catalyst affect the rate of a chemical reaction?

a) It always decreases the rate of the reaction.

b) It always increases the rate of the reaction.

c) It increases the rate of the forward and decreases the rate of the reverse reaction.

d) It increases the rate of both the forward and reverse reactions.

XI. On an energy profile diagram, the presence of a catalyst is represented by:

a) A higher peak representing the activation energy.

b) A lower peak representing the activation energy.

c) A change in the energy level of the reactants or products.

d) A shift in the equilibrium position.

XII. The units of the rate constant (k) for a reaction depend on the:

a) Activation energy of the reaction

b) Temperature of the reaction

c) Overall order of the reaction

d) Stoichiometry of the balanced chemical equation

XIII. A first-order reaction has a half-life ($t_{1/2}$) of 20 minutes. What is the value of its rate constant (k)?

a) 0.05 min^{-1}

b) 0.693 min^{-1}

c) 0.0347 min^{-1}

d) 13.86 min^{-1}

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SHORT ANSWER QUESTIONS

Q.2 Attempt the following short-answer questions:

a) What do you understand by the rate of a reaction?

b) Give the difference between enthalpy change of reaction and energy of activation of reaction

c) Differentiate clearly between order and molecularity of a reaction.

d) Why the instantaneous rate changes during a reaction?

e) Briefly summarize the effects of temperature and surface area on the rates of reactions.

f) Justify that the radioactive decay is always a first order reaction.

g) A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration is doubled and reduced to half?

h) What is meant by half-life and what is it used for?

i) Why does wood burn more rapidly in pure oxygen than in air?

j) A catalyst lowers the activation energy of a chemical reaction. Illustrate it.

k) The rate constant for a certain reaction is 3.5×10^{-4} s^{-1} at 25°C. What is the order of the reaction.? Explain based on the units of the rate constant.

l) If the initial concentration of the reactant is 0.50 mol dm^{-3}, calculate the initial rate of the reaction.

m) How would the rate of this reaction change if the concentration of the reactant were doubled?

n) A certain first-order reaction has a rate constant of 2.5×10^{-3} s^{-1}. Calculate the half-life of the reaction in minutes.

o) A radioactive isotope decays by a first-order process with a half-life of 12 hours. Calculate the rate constant for the decay in s^{-1}.

DESCRIPTIVE QUESTIONS

Q.3 Relate the order of a reaction to the rate law for the reaction. How do you distinguish between zero order, first order and second order reaction?

Q.4 How do you find the numerical value of a rate constant by initial and half-life methods?

Q.5 How does the activation energy profile of an uncatalyzed reaction compare with that of the catalyzed reaction?

Q. 6 The reaction between hydrogen peroxide (H_2O_2) and iodide ions (I^-) in acidic solution is believed to occur via the following mechanism:

Step 1: $H_2O_2 + I^- \longrightarrow H_2O + OI^-$ (slow)

Step 2: $OI^- + H^+ \longrightarrow HOI$ (fast)

Step 3: $HOI + I^- + H^+ \longrightarrow H_2O + I_2$ (fast)

i) Write the overall balanced equation for the reaction.

ii) Identify any intermediates and catalysts in this mechanism.

iii) What is the rate-determining step?

iv) Write the rate equation for the reaction, expressing it in terms of the reactants in the overall reaction.

NUMERICAL PROBLEMS

Q.6 Calculate the reaction rate if the concentration of A is 0.5 M, the concentration of B is 0.2 and the rate constant k is $4.0M^{-2}s^{-1}$. Given the rate law for a reaction: Rate = $k[A][B]^2$.

Q.7 A first order reaction is found to have a rate constant, $k = 5.5 \times 10^{-14}$ s^{-1}. Find the half-life of the reaction.

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Temp. (K)	Rate constant ($cm^3\ mol^{-1}S^{-1}$) (K)
500	6.814×10^{-4}
550	2.64×10^{-2}
600	0.56×10^{0}
650	7.31×10^{0}
700	66.67×10^{0}

Q.8 Three experiments that have identical conditions were performed to measure the initial rate of the reaction. $2HI(g) \rightarrow H_2(g) + I_2(g)$

Experiment	[HI] (M)	Rate (M/s)
1	**0.015**	**1.1×10^{-3}**
2	**0.030**	**4.4×10^{-3}**
3	**0.045**	**9.9×10^{-3}**

Write the rate law for the reaction. Find the value and units of the specific rate constant, k.

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