

4.1 Rate of a Chemical Reaction

that diamond is forever. Kinetic studies not only help us to determine the speed or rate of a chemical reaction but also describe the conditions by which the reaction rates can be altered. The factors such as concentration, temperature, pressure and catalyst affect the rate of a reaction. At the macroscopic level, we are interested in amounts reacted or formed and the rates of their consumption or formation. At the molecular level, the reaction mechanisms involving orientation and energy of molecules undergoing collisions, are discussed.

In this Unit, we shall be dealing with average and instantaneous rate of reaction and the factors affecting these. Some elementary ideas about the collision theory of reaction rates are also given. However, in order to understand all these, let us first learn about the reaction rate.

Some reactions such as ionic reactions occur very fast, for example, precipitation of silver chloride occurs instantaneously by mixing of aqueous solutions of silver nitrate and sodium chloride. On the other hand, some reactions are very slow, for example, rusting of iron in the presence of air and moisture. Also there are reactions like inversion of cane sugar and hydrolysis of starch, which proceed with a moderate speed. Can you think of more examples from each category?

You must be knowing that speed of an automobile is expressed in terms of change in the position or distance covered by it in a certain period of time. Similarly, the speed of a reaction or the rate of a reaction can be defined as the change in concentration of a reactant or product in unit time. To be more specific, it can be expressed in terms of:

- (i) the rate of decrease in concentration of any one of the reactants, or
- (ii) the rate of increase in concentration of any one of the products.

Consider a hypothetical reaction, assuming that the volume of the system remains constant.



One mole of the reactant R produces one mole of the product P. If $[R]_1$ and $[P]_1$ are the concentrations of R and P respectively at time t_1 and $[R]_2$ and $[P]_2$ are their concentrations at time t_2 then,

$$\begin{aligned}\Delta t &= t_2 - t_1 \\ \Delta[R] &= [R]_2 - [R]_1 \\ \Delta[P] &= [P]_2 - [P]_1\end{aligned}$$

The square brackets in the above expressions are used to express molar concentration.

Rate of disappearance of R

$$= \frac{\text{Decrease in concentration of R}}{\text{Time taken}} = -\frac{\Delta[R]}{\Delta t} \quad (4.1)$$

Rate of appearance of P

$$= \frac{\text{Increase in concentration of P}}{\text{Time taken}} = + \frac{\Delta[P]}{\Delta t} \quad (4.2)$$

Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity.

Equations (4.1) and (4.2) given above represent the **average rate of a reaction**, r_{av} .

Average rate depends upon the change in concentration of reactants or products and the time taken for that change to occur (Fig. 4.1).

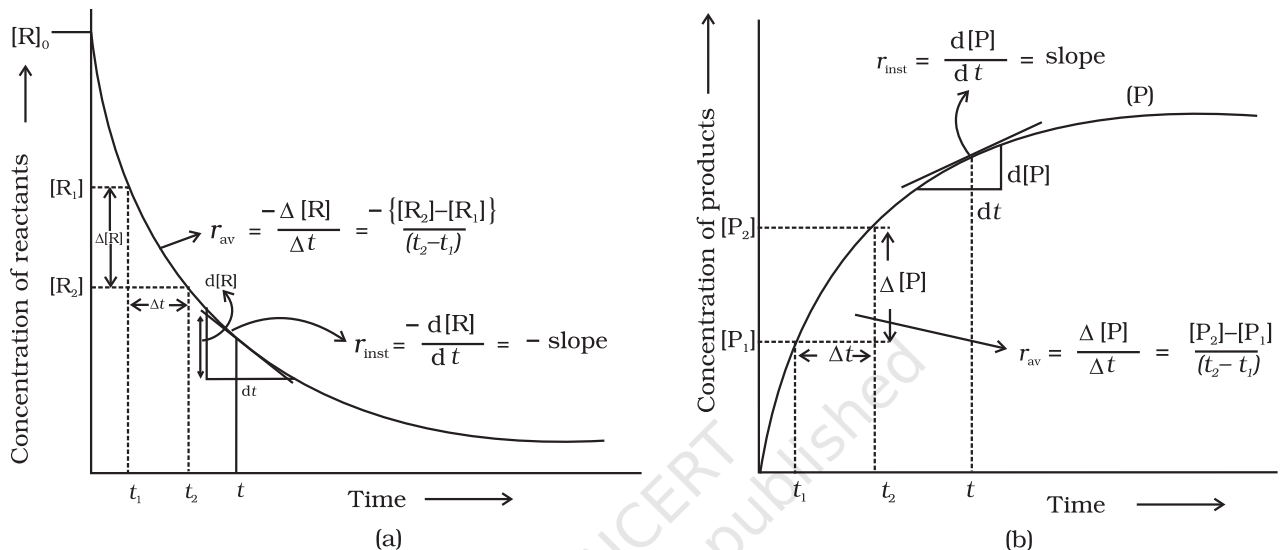
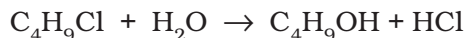


Fig. 4.1: Instantaneous and average rate of a reaction

Units of rate of a reaction

From equations (4.1) and (4.2), it is clear that units of rate are concentration time⁻¹. For example, if concentration is in mol L⁻¹ and time is in seconds then the units will be mol L⁻¹s⁻¹. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of the rate equation will be atm s⁻¹.

From the concentrations of C₄H₉Cl (butyl chloride) at different times given below, calculate the average rate of the reaction: **Example 4.1**



during different intervals of time.

t/s	0	50	100	150	200	300	400	700	800
$[\text{C}_4\text{H}_9\text{Cl}]/\text{mol L}^{-1}$	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

We can determine the difference in concentration over different intervals of time and thus determine the average rate by dividing $\Delta[R]$ by Δt (Table 4.1). **Solution**

Table 4.1: Average rates of hydrolysis of butyl chloride

$[\text{C}_4\text{H}_9\text{Cl}]_{t_1} / \text{mol L}^{-1}$	$[\text{C}_4\text{H}_9\text{Cl}]_{t_2} / \text{mol L}^{-1}$	t_1/s	t_2/s	$r_{\text{av}} \times 10^4 / \text{mol L}^{-1}\text{s}^{-1}$ $= -\{[\text{C}_4\text{H}_9\text{Cl}]_{t_2} - [\text{C}_4\text{H}_9\text{Cl}]_{t_1} / (t_2 - t_1)\} \times 10^4$
0.100	0.0905	0	50	1.90
0.0905	0.0820	50	100	1.70
0.0820	0.0741	100	150	1.58
0.0741	0.0671	150	200	1.40
0.0671	0.0549	200	300	1.22
0.0549	0.0439	300	400	1.10
0.0439	0.0335	400	500	1.04
0.0210	0.017	700	800	0.4

It can be seen (Table 4.1) that the average rate falls from $1.90 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$ to $0.4 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$. However, average rate cannot be used to predict the rate of a reaction at a particular instant as it would be constant for the time interval for which it is calculated. So, to express the rate at a particular moment of time we determine the **instantaneous rate**. It is obtained when we consider the average rate at the smallest time interval say dt (i.e. when Δt approaches zero). Hence, mathematically for an infinitesimally small dt instantaneous rate is given by

$$r_{\text{av}} = \frac{-\Delta[\text{R}]}{\Delta t} = \frac{\Delta[\text{P}]}{\Delta t} \quad (4.3)$$

As $\Delta t \rightarrow 0$ or $r_{\text{inst}} = \frac{-d[\text{R}]}{dt} = \frac{d[\text{P}]}{dt}$

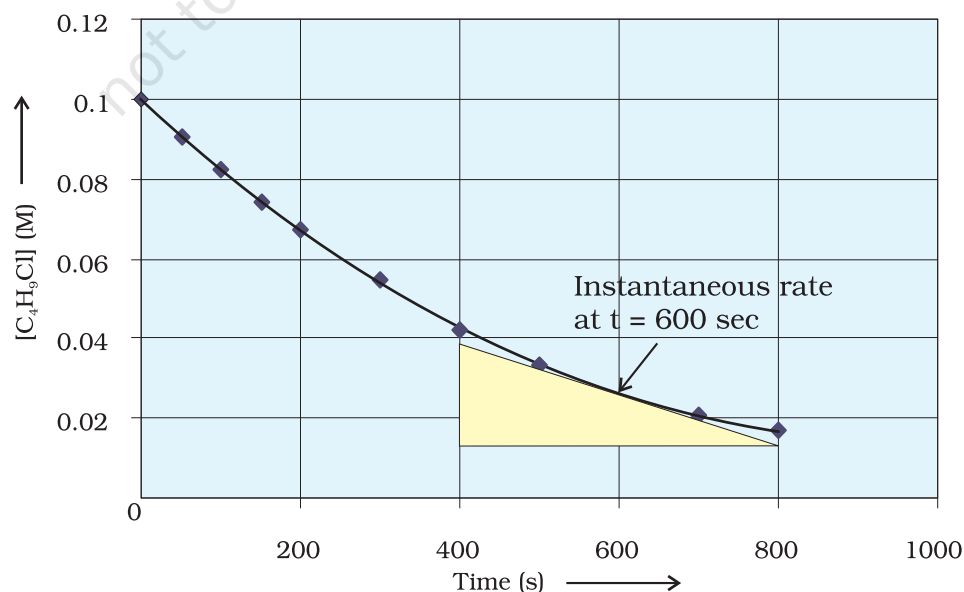


Fig 4.2
Instantaneous rate of hydrolysis of butyl chloride ($\text{C}_4\text{H}_9\text{Cl}$)

It can be determined graphically by drawing a tangent at time t on either of the curves for concentration of R and P vs time t and calculating its slope (Fig. 4.1). So in problem 4.1, r_{inst} at 600s for example, can be calculated by plotting concentration of butyl chloride as a function of time. A tangent is drawn that touches the curve at $t = 600$ s (Fig. 4.2).

The slope of this tangent gives the instantaneous rate.

$$\text{So, } r_{\text{inst}} \text{ at } 600 \text{ s} = - \left(\frac{0.0165 - 0.037}{(800 - 400)\text{s}} \right) \text{ mol L}^{-1} = 5.12 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

$$\text{At } t = 250 \text{ s } \quad r_{\text{inst}} = 1.22 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$$

$$t = 350 \text{ s } \quad r_{\text{inst}} = 1.0 \times 10^{-4} \text{ mol L}^{-1}\text{s}^{-1}$$

$$t = 450 \text{ s } \quad r_{\text{inst}} = 6.4 \times 10^{-5} \text{ mol L}^{-1}\text{s}^{-1}$$

Now consider a reaction



Where stoichiometric coefficients of the reactants and products are same, then rate of the reaction is given as

$$\text{Rate of reaction} = - \frac{\Delta[\text{Hg}]}{\Delta t} = - \frac{\Delta[\text{Cl}_2]}{\Delta t} = \frac{\Delta[\text{HgCl}_2]}{\Delta t}$$

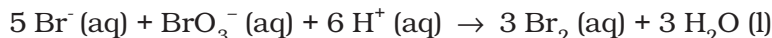
i.e., rate of disappearance of any of the reactants is same as the rate of appearance of the products. But in the following reaction, two moles of HI decompose to produce one mole each of H_2 and I_2 .



For expressing the rate of such a reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or the rate of appearance of products is divided by their respective stoichiometric coefficients. Since rate of consumption of HI is twice the rate of formation of H_2 or I_2 , to make them equal, the term $\Delta[\text{HI}]$ is divided by 2. The rate of this reaction is given by

$$\text{Rate of reaction} = - \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t} = \frac{\Delta[\text{H}_2]}{\Delta t} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

Similarly, for the reaction



$$\text{Rate} = - \frac{1}{5} \frac{\Delta[\text{Br}^-]}{\Delta t} = - \frac{\Delta[\text{BrO}_3^-]}{\Delta t} = - \frac{1}{6} \frac{\Delta[\text{H}^+]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{Br}_2]}{\Delta t} = \frac{1}{3} \frac{\Delta[\text{H}_2\text{O}]}{\Delta t}$$

For a gaseous reaction at constant temperature, concentration is directly proportional to the partial pressure of a species and hence, rate can also be expressed as rate of change in partial pressure of the reactant or the product.

Example 4.2 The decomposition of N_2O_5 in CCl_4 at 318K has been studied by monitoring the concentration of N_2O_5 in the solution. Initially the concentration of N_2O_5 is 2.33 mol L^{-1} and after 184 minutes, it is reduced to 2.08 mol L^{-1} . The reaction takes place according to the equation



Calculate the average rate of this reaction in terms of hours, minutes and seconds. What is the rate of production of NO_2 during this period?

Solution

$$\begin{aligned} \text{Average Rate} &= \frac{1}{2} \left\{ -\frac{\Delta[\text{N}_2\text{O}_5]}{\Delta t} \right\} = -\frac{1}{2} \left[\frac{(2.08 - 2.33) \text{ mol L}^{-1}}{184 \text{ min}} \right] \\ &= 6.79 \times 10^{-4} \text{ mol L}^{-1} / \text{min} = (6.79 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}) \times (60 \text{ min} / 1\text{h}) \\ &= 4.07 \times 10^{-2} \text{ mol L}^{-1} / \text{h} \\ &= 6.79 \times 10^{-4} \text{ mol L}^{-1} \times 1 \text{min} / 60\text{s} \\ &= 1.13 \times 10^{-5} \text{ mol L}^{-1} \text{s}^{-1} \end{aligned}$$

It may be remembered that

$$\text{Rate} = \frac{1}{4} \left\{ \frac{\Delta[\text{NO}_2]}{\Delta t} \right\}$$

$$\frac{\Delta[\text{NO}_2]}{\Delta t} = 6.79 \times 10^{-4} \times 4 \text{ mol L}^{-1} \text{ min}^{-1} = 2.72 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}$$

Intext Questions

- 4.1** For the reaction $\text{R} \rightarrow \text{P}$, the concentration of a reactant changes from 0.03M to 0.02M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.
- 4.2** In a reaction, $2\text{A} \rightarrow \text{Products}$, the concentration of A decreases from 0.5 mol L^{-1} to 0.4 mol L^{-1} in 10 minutes. Calculate the rate during this interval?

4.2 Factors Influencing Rate of a Reaction

Rate of reaction depends upon the experimental conditions such as concentration of reactants (pressure in case of gases), temperature and catalyst.

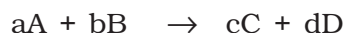
4.2.1 Dependence of Rate on Concentration

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 reaction in terms of concentration of the reactants is known as **rate law**. It is also called as rate equation or rate expression.

4.2.2 Rate Expression and Rate Constant

The results in Table 4.1 clearly show that rate of a reaction decreases with the passage of time as the concentration of reactants decrease. Conversely, rates generally increase when reactant concentrations increase. So, rate of a reaction depends upon the concentration of reactants.

Consider a general reaction



where a, b, c and d are the stoichiometric coefficients of reactants and products.

The rate expression for this reaction is

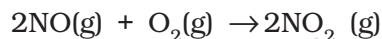
$$\text{Rate} \propto [A]^x [B]^y \quad (4.4)$$

where exponents x and y may or may not be equal to the stoichiometric coefficients (a and b) of the reactants. Above equation can also be written as

$$\text{Rate} = k [A]^x [B]^y \quad (4.4a)$$

$$-\frac{d[R]}{dt} = k[A]^x [B]^y \quad (4.4b)$$

This form of equation (4.4 b) is known as differential rate equation, where *k* is a proportionality constant called **rate constant**. The equation like (4.4), which relates the rate of a reaction to concentration of reactants is called rate law or rate expression. Thus, **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.** For example:



We can measure the rate of this reaction as a function of initial concentrations either by keeping the concentration of one of the reactants constant and changing the concentration of the other reactant or by changing the concentration of both the reactants. The following results are obtained (Table 4.2).

Table 4.2: Initial rate of formation of NO₂

Experiment	Initial [NO]/ mol L ⁻¹	Initial [O ₂]/ mol L ⁻¹	Initial rate of formation of NO ₂ / mol L ⁻¹ s ⁻¹
1.	0.30	0.30	0.096
2.	0.60	0.30	0.384
3.	0.30	0.60	0.192
4.	0.60	0.60	0.768

It is obvious, after looking at the results, that when the concentration of NO is doubled and that of O₂ is kept constant then the initial rate increases by a factor of four from 0.096 to 0.384 mol L⁻¹s⁻¹. This indicates that the rate depends upon the square of the concentration of NO. When concentration of NO is kept constant and concentration of O₂ is doubled the rate also gets doubled indicating that rate depends on concentration of O₂ to the first power. Hence, the rate equation for this reaction will be

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

The differential form of this rate expression is given as

$$-\frac{d[R]}{dt} = k[\text{NO}]^2 [\text{O}_2]$$

Now, we observe that for this reaction in the rate equation derived from the experimental data, the exponents of the concentration terms are the same as their stoichiometric coefficients in the balanced chemical equation.

Some other examples are given below:

Reaction	Experimental rate expression
1. $\text{CHCl}_3 + \text{Cl}_2 \rightarrow \text{CCl}_4 + \text{HCl}$	$\text{Rate} = k [\text{CHCl}_3] [\text{Cl}_2]^{1/2}$
2. $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$	$\text{Rate} = k [\text{CH}_3\text{COOC}_2\text{H}_5]^1 [\text{H}_2\text{O}]^0$

In these reactions, the exponents of the concentration terms are not the same as their stoichiometric coefficients. Thus, we can say that:

Rate law for any reaction cannot be predicted by merely looking at the balanced chemical equation, i.e., theoretically but must be determined experimentally.

4.2.3 Order of a Reaction

In the rate equation (4.4)

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

x and y indicate how sensitive the rate is to the change in concentration of A and B. Sum of these exponents, i.e., x + y in (4.4) gives the overall order of a reaction whereas x and y represent the order with respect to the reactants A and B respectively.

Hence, **the sum of powers of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.**

Order of a reaction can be 0, 1, 2, 3 and even a fraction. A zero order reaction means that the rate of reaction is independent of the concentration of reactants.

Example 4.3

Calculate the overall order of a reaction which has the rate expression

(a) $\text{Rate} = k [\text{A}]^{1/2} [\text{B}]^{3/2}$

(b) $\text{Rate} = k [\text{A}]^{3/2} [\text{B}]^{-1}$

Solution

(a) $\text{Rate} = k [\text{A}]^x [\text{B}]^y$

$$\text{order} = x + y$$

$$\text{So order} = 1/2 + 3/2 = 2, \text{ i.e., second order}$$

(b) $\text{order} = 3/2 + (-1) = 1/2, \text{ i.e., half order.}$

A balanced chemical equation never gives us a true picture of how a reaction takes place since rarely a reaction gets completed in one step. The reactions taking place in one step are called **elementary reactions**. When a sequence of elementary reactions (called mechanism) gives us the products, the reactions are called **complex reactions**.