1. Details of Module and Its Structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 03 (Class XII, Semester 01)
Module Name/Title	Chemical Kinetics: Part 1
Module Id	lech_10401
Pre-requisites	Chemical Reaction, Thermodynamics of a Reaction, Chemical Equilibrium, Free Energy Change, Concentration Term
Objectives	After studying this module, you will be able to • Define the average and instantaneous rate of a reaction. • Distinguish between elementary and complex reactions. • Express the rate of a reaction in terms of change in concentration of either of the reactants or products with time.
Keywords	Chemical Kinetics, Rate of Reaction, Instantaneous Rate of Reaction, Units of Rate of Reaction.

2. Development Team

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1. General Introduction: Chemistry, by its very nature, is concerned with change. Substances with well defined properties are converted by chemical reactions into other substances with different properties. For any chemical reaction, chemists try to find out

(a) the feasibility of a chemical reaction which can be predicted by thermodynamics (as you know that a reaction with $\Delta G < 0$, at constant temperature and pressure is feasible);
(b) the extent to which a reaction will proceed can be determined from chemical equilibrium;
(c) the speed of a reaction i.e. time taken by a reaction to reach equilibrium.

Along with feasibility and extent, it is equally important to know the rate and the factors controlling the rate of a chemical reaction for its complete understanding. For example, which parameters determine as to how rapidly food gets spoiled? How to design a rapidly setting material for dental filling? Or what controls the rate at which fuel burns in an auto engine? All these questions can be answered by the branch of chemistry, which deals with the study of reaction rates and their mechanisms, called **Chemical Kinetics**. The word kinetics is derived from the Greek word 'kinesis' meaning movement. Chemical Kinetics helps us to understand how a chemical reaction occurs. Thermodynamics tells only about the feasibility of a reaction whereas chemical kinetics tells about the rate of a reaction. For example, thermodynamic data indicate that diamond shall convert to graphite but in reality the conversion rate is so slow that the change is not perceptible at all. Therefore, most people think that diamond is forever. In this module, we shall be dealing with average and instantaneous rate of reaction and the factors affecting these. In order to understand all these, let us first learn about the reaction rate.

2. Rate of a Chemical reaction: In general, various types of reactions can be categorised in depending upon their rates.

(a) Very fast reactions: Some reactions such as ionic reactions occur very fast, for example, precipitation of silver chloride occurs instantaneously by mixing aqueous solution of sodium chloride with aqueous solution of silver nitrate.

$AgNO_3$ (*aq*) + NaCl (*aq*) → AgCl (*s*) + $NaNO_3$ (*aq*)

Also, the reaction between sodium and water takes place instantaneously to form sodium hydroxide. Combustion reactions and explosive reactions also fall in this category. The rate of reaction of such reactions cannot be determined easily.

(b) Very slow reactions: Some reactions are very slow, i.e. they require months or even years for completion. For example, rusting of iron in the presence of air and moisture. Fermentation process of sugar to alcohols and the process of weathering of rocks occur at extremely slow rate. Rate of such reactions do not possess any significance.

(c) Moderately slow reactions: Also there are reactions which proceed with a moderate speed, i.e. their rate of reaction fall in between the two types mentioned above. The rate o for such a reaction can be measured easily. For example, inversion of cane sugar and hydrolysis of starch.

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.

$$R \rightarrow P$$

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,

$$\Delta t = t_2 - t_1$$

$$\Delta[R] = [R]_2 - [R]_1$$

$\Delta[P] = [P]_2 - [P]_1$

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

$$Rate\ of\ disappearance\ of\ R = \frac{Decrease\ in\ concentration\ of\ R}{Time\ taken} = \frac{-\Delta[R]}{\Delta t} \qquad (1)$$

$$Rate\ of\ appearance\ of\ P = \frac{Increase\ in\ concentration\ of\ P}{Time\ taken} = \frac{\Delta[P]}{\Delta t} \qquad (2)$$

The negative sign in equation (1) indicates the decrease in concentration of the reactant with passage of time. 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.

Thus,

Rate of reaction = Rate of disappearance of R = Rate of appearance of P = $\frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t}$

3. Units of rate of a reaction: From equations (1) and (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^{-1} s^{-1}. However, in gaseous reactions, when the concentration of gases is expressed in terms of their partial pressures, then the units of rate will be atm s^{-1}.

4. Average rate & Instantaneous rate of reaction: Equations (1) and (2), given above represent the average rate of a reaction, r_{av}. Average rate of reaction is defined as the rate of reaction per unit time. It depends upon the change in concentration of reactants or products and the time taken for that change to occur (Fig. 1).

$$Average\ Rate = \frac{Change\ in\ concentration\ in\ given\ time}{Time\ taken} = \frac{\Delta x}{\Delta t} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \qquad (3)$$

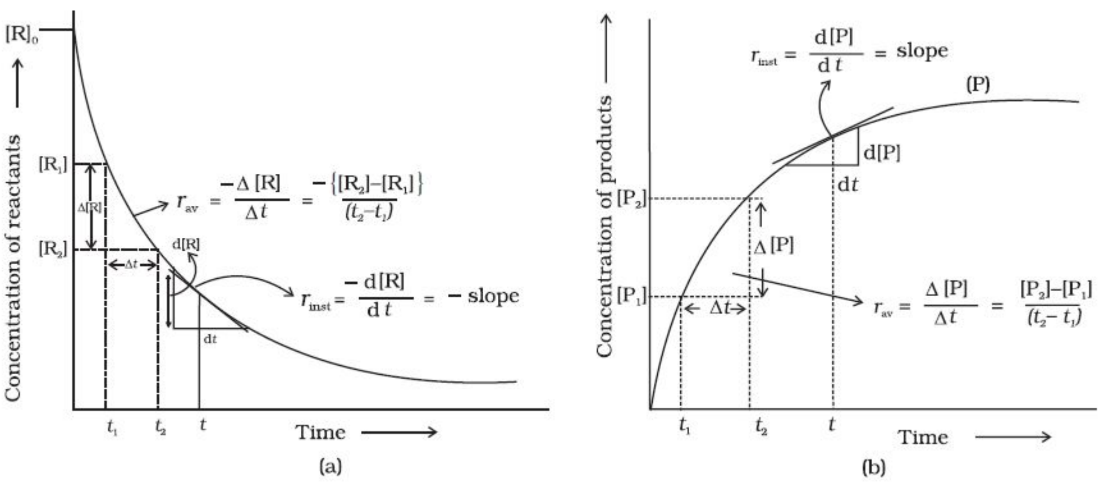

Fig. 1. Average and instantaneous rate of a reaction

(Source: Fig 4.1; Chapter 4 Chemical Kinetics, Page no.95, Class XII Textbook, NCERT)

Example 1. From the concentrations of C_4H_9Cl (butyl chloride) at different times given below, calculate the average rate of the reaction:

$C_4H_9Cl + H_2O \rightarrow C_4H_9OH + HCl$

during different intervals of time.

t/s	0	50	100	150	200	300	400	700	800
$[C_4H_9Cl]$ / mol L^{-1}	0.100	0.0905	0.0820	0.0741	0.0671	0.0549	0.0439	0.0210	0.017

Solution: 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 1).

Table 1 Average rates of hydrolysis of butyl chloride.

$[C_4H_9Cl]_{t_1}$ / mol L^{-1}	$[C_4H_9Cl]_{t_2}$ / mol L^{-1}	t_1 / s	t_2 / s	$r_{av} \times 10^4$ / mol L^{-1} s^{-1} $= \{[C_4H_9Cl]_{t_1} - [C_4H_9Cl]_{t_2} / (t_1 - t_2)\} \times 10^4$
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	0.0210	400	700	1.04
0.0210	0.017	700	800	0.40

It can be seen (Table 1) that the average rate falls from 1.90×10^{-4} mol L^{-1} s^{-1} to 0.4×10^{-4} mol L^{-1} 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, the instantaneous rate of reaction can be defined as the decrease in concentration of any one of the reactant or increase in any one of the product at a particular instant of time. Thus, mathematically for an infinitesimally small time interval, i.e. dt instantaneous rate is given by

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \qquad (4)$$

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

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. 1). So in problem 4.1.1, r_{inst} at 600 seconds 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.2).

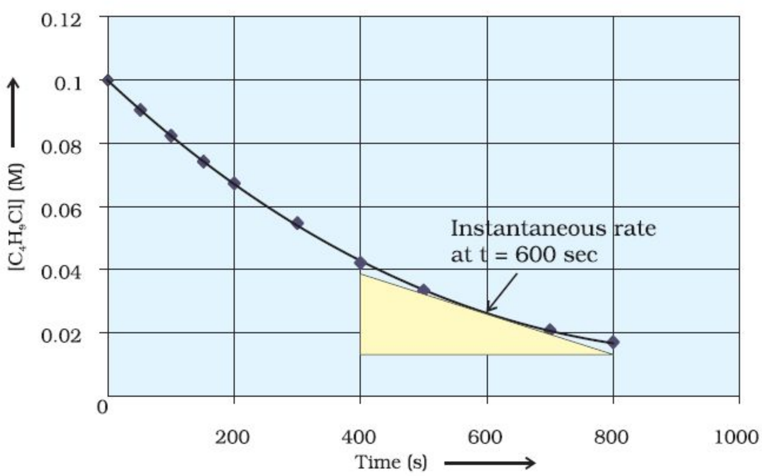

Fig. 2. Instantaneous rate of hydrolysis of butyl chloride (C_4H_9Cl)

(Source: Fig 4.2; Chapter 4, Chemical Kinetics, Page no. 96, Class XII Textbook, NCERT)

The slope of this tangent gives the instantaneous rate.

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

At t = 250 s r_{inst} = 1.22 × 10^{-4} mol L^{-1} s^{-1}

t = 350 s r_{inst} = 1.0 × 10^{-4} mol L^{-1} s^{-1}

t = 450 s r_{inst} = 6.4 × 10^{-5} mol L^{-1} s^{-1}

5. Effect of Stoichiometry on rate of the reaction: Now consider a reaction

$Hg\ (l) + Cl_2\ (g) \rightarrow HgCl_2\ (s)$

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

$$rate\ of\ reaction = \frac{-\Delta[Hg]}{\Delta t} = \frac{-\Delta[Cl_2]}{\Delta t} = \frac{\Delta[HgCl_2]}{\Delta t}$$

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,

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

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 Δ[HI] is divided by 2. The rate of this reaction is given by

$$Rate\ of\ reaction = \frac{-1}{2}\frac{\Delta[HI]}{\Delta t} = \frac{\Delta[H_2]}{\Delta t} = \frac{\Delta[I_2]}{\Delta t}$$

Similarly, for the reaction

$5\ Br\ (aq) + BrO_3^{-1}\ (aq) + 6\ H^+\ (aq) \rightarrow\ 3\ Br_2\ (aq) + 3\ H_2O\ (l)$

$$Rate\ of\ reaction = -\frac{1}{5}\frac{\Delta[Br^-]}{\Delta t} = -\frac{\Delta[BrO_3^-]}{\Delta t} = -\frac{1}{6}\frac{\Delta[H^+]}{\Delta t} = \frac{1}{3}\frac{\Delta[Br_2]}{\Delta t} = \frac{1}{3}\frac{\Delta[H_2O]}{\Delta t}$$

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 2: The decomposition of N_2O_5 in CCl_4 at 318 K 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

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

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: $Average\ Rate\ of\ reaction = \frac{1}{2}\left\{\frac{-\Delta[N_2O_5]}{\Delta t}\right\} = \frac{-1}{2}\left[\frac{(2.08-2.33) mol L^{-1}}{184 min}\right]$

$= 6.79 \times 10^{-4}$ mol L^{-1} / min

$= (6.79 \times 10^{-4}$ mol L^{-1} / min) $\times$ (60 min / hr) $= 4.07 \times 10^{-2}$ mol L^{-1} / h

$= (6.79 \times 10^{-4}$ mol L^{-1} / min) $\times$ (1min / 60 sec) $= 1.13 \times 10^{-5}$ mol L^{-1} s^{-1}

Also,

$$Average\ Rate\ of\ reaction = \frac{1}{2}\left\{\frac{-\Delta[N_2O_5]}{\Delta t}\right\} = \frac{1}{4}\left\{\frac{\Delta[NO_2]}{\Delta t}\right\}$$

$= \quad 6.79 \times 10^{-4}$ mol L^{-1} / min

Hence, Rate of production of $NO_2 = \frac{\Delta[NO_2]}{\Delta t} = (6.79 \times 10^{-4} \times 4)$ mol L^{-1} min^{-1})

$= \quad 2.72 \times 10^{-3}$ mol L^{-1} min^{-1}

Example 3: For the reaction R → 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.

Solution: Average rate of the reaction R → P will be

$$= \frac{-\Delta[R]}{\Delta t} = \frac{-[R]_2-[R]_1}{t_2-t_1}$$

Now, $[R]_2 = 0.02$ M, $[R]_1 = 0.03$ M and $\Delta t = 25$ min

Therefore, Average rate $= -\left(\frac{0.02-0.03}{25}\right)$ M min^{-1} $= -\left(\frac{-0.01}{25}\right)$ M min^{-1}

$= 4 \times 10^{-4}$ M min^{-1}

$= -\left(\frac{-0.01}{25\times60}\right)$ M s^{-1} $= 6.66 \times 10^{-6}$ M s^{-1}

Example 4: In a reaction, 2A → 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?

Solution: Average rate of the reaction 2A → P will be

$$= \frac{-1}{2}\frac{\Delta[A]}{\Delta t} = \frac{-1}{2}\frac{[A]_2-[A]_1}{t_2-t_1}$$

Now, $[A]_2 = 0.4$ mol L^{-1}, $[A]_1 = 0.5$ mol L^{-1} and $\Delta t = 10$ min

Therefore, Average rate $= \frac{-1}{2}\left(\frac{0.4-0.5}{10}\right)$ mol L^{-1} min^{-1} $= \frac{-1}{2}\left(\frac{-0.1}{10}\right)$ mol L^{-1} min^{-1}

$= 5 \times 10^{-3}$ mol L^{-1} min^{-1}

Example 5: In a hypothetical chemical reaction, 2A → 4B + C, the concentration of B is found to increase by 4×10^{-4} mol L^{-1} in 10 seconds. Calculate (a) rate of appearance of B, (b) rate of the reaction, and (c) rate of disappearance of A.

Solution: For the reaction, 2A → 4B + C

Average rate of reaction $= \frac{1}{4} \times$ Rate of appearance of B $= \frac{1}{4}\frac{\Delta[B]}{\Delta t}$

$= \frac{1}{2} \times$ Rate of disappearance of A $= \frac{-1}{2}\frac{\Delta[A]}{\Delta t}$

(a) Rate of appearance of B $= \frac{\textit{Increase in concentration of B}}{\textit{Time taken}}$

$= \frac{4\times10^{-4}}{10}$ mol L^{-1} s^{-1}

$= 4 \times 10^{-5}$ mol L^{-1} s^{-1}

(b) Rate of reaction $= \frac{1}{4} \times$ Rate of appearance of B

$= \frac{4\times10^{-4}}{4}$ mol L^{-1} s^{-1}

$= 1 \times 10^{-4}$ mol L^{-1} s^{-1}

(c) Rate of disappearance of A = 2 × rate of reaction

$= 2 \times (1 \times 10^{-4})$ mol L^{-1} s^{-1}

$= 2 \times 10^{-4}$ mol L^{-1} s^{-1}

Example 6: In a chemical reaction, the iodide ions are oxidised by peroxydisulphate ions.

$3I^- + S_2o_8^{2-} \longrightarrow I^-_3 + 2\ So_4^{2-}$

If the rate of disappearance of peroxydisulphate ions is 3.5×10^{-4} mol L^{-1} s^{-1} for a given interval of time, then calculate the rate of disappearance of iodide ions for the same time interval. Also calculate the rate of formation of sulphate ions (So) for the same time period.

Solution: For the given reaction:

$$Average\ Rate\ of\ reaction = -\frac{1}{3}\frac{\Delta[I^-]}{\Delta t} = -\frac{\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{\Delta[I_3^-]}{\Delta t} = \frac{1}{2}\frac{\Delta[SO_4^{2-}]}{\Delta t}$$

Given: Rate of disappearance of peroxydisulphate ions, $\left(-\frac{\Delta[S_2O_8^{2-}]}{\Delta t}\right) = 3.5 \times 10^{-4}$ mol L^{-1} s^{-1}

Therefore, rate of disappearance of iodide ions, , $\left(-\frac{\Delta[I^-]}{\Delta t}\right) = 3 \times \left[-\frac{\Delta[S_2O_8^{2-}]}{\Delta t}\right]$

$= 3 \times 3.5 \times 10^{-4}$ mol L^{-1} s^{-1}

$= 10.5 \times 10^{-4}$ mol L^{-1} s^{-1}

Also, rate of formation of sulphate ions, $\left(\frac{\Delta[SO_4^{2-}]}{\Delta t}\right) = 2 \times \left[-\frac{\Delta[S_2O_8^{2-}]}{\Delta t}\right]$

$= 2 \times 3.5 \times 10^{-4}$ mol L^{-1} s^{-1}

$= 7.0 \times 10^{-4}$ mol L^{-1} s^{-1}

Example 7: For the chemical reaction:

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

if the concentration of NO_2 increases by 7.0×10^{-4} mol L^{-1} in 15 seconds, then what is rate of reaction?

Solution: For the given reaction:

$$Average\ Rate\ of\ reaction = \frac{1}{2}\left\{\frac{-\Delta[N_2O_5]}{\Delta t}\right\} = \frac{1}{4}\left\{\frac{\Delta[NO_2]}{\Delta t}\right\} = \left\{\frac{\Delta[O_2]}{\Delta t}\right\}$$

Given: $\Delta\left[NO_2\right] = 7.0 \times 10^{-4}$ mol L^{-1} and $\Delta t = 15$ sec

$$Average\ Rate\ of\ reaction = \frac{1}{4}\left\{\frac{\Delta[NO_2]}{\Delta t}\right\}$$

$$= \frac{1}{4}\left\{\frac{7.0\times10^{-4} molL^{-1}}{15 sec}\right\}$$

$$= 1.17 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}$$

6. Summary: Chemical kinetics is the study of chemical reactions with respect to reaction rates. This module described various chemical reactions associated with different types of reaction rates. The rate of a reaction is concerned with decrease in concentration of reactants or increase in the concentration of products per unit time. The rate of the reaction can be expressed as either instantaneous rate (r_{inst}) or average rate (r_{av}). Average rate of the reaction is defined as the either decrease in concentration of any one of the reactants or increase in any one of products over a large interval of time. On the other hand, the instantaneous rate of the reaction is expressed as either decrease in concentration of any one of the reactants or increase in any one of products at a particular instant of time.

$$r_{av} = \frac{-\Delta[R]}{\Delta t} = \frac{\Delta[P]}{\Delta t} \quad \text{and} \quad r_{inst} = \frac{-d[R]}{dt} = \frac{d[P]}{dt}$$

The rate of the reaction is generally expressed in concentration $time^{-1}$ (for example, mol L^{-1} s^{-1} or mol L^{-1} min^{-1} or mol L^{-1} h^{-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 at s^{-1}. There are number of factors that affect the rate of the reaction which will be discussed in the next module.