

I. Introductory Words

All chemical reactions approach to attain equilibrium. But the rate with which they proceed towards equilibrium differs from reactions to reactions. A reaction may be a single step process or may include a number of steps, all having different velocities. Of those the slowest one is called the **rate-determining step**.

Knowing the rate, various aspects regarding mechanism of the reaction is ensured. Hence, chemical kinetics provides an important tool to study the reaction mechanism. Since almost all chemical reactions are path-dependent changes, thermodynamics fails to provide its application in reaction kinetics.

The rate of change of a reaction is studied using a **suitable property of the reaction**, which may be chemical or physical. The change in concentration of the reactants or products may be studied by a simple **acid-base titration** or a **redox titration**, if the characters of the reactants or products demand such method. The change may be estimated **conductometrically**, **potentiometrically** or **pH-metrically** or through observation of **angle of rotation** (like inversion of cane sugar). If there be any change in colour in either of the reactants or products, the rate can well be studied **colorimetrically** or **spectrophotometrically**. Thus there are a good many physical means to study the reactant kinetics.

• Rate of reaction as a function of concentrations

Let us consider the reaction



where g, h, \dots are stichiometric coefficients of the respective substances. Then in a small time interval dt , the rate of concentration changes will be

$$-\frac{1}{g} \frac{d[A]}{dt} = -\frac{1}{h} \frac{d[B]}{dt} = \frac{1}{x} \frac{d[C]}{dt} = \frac{1}{y} \frac{d[D]}{dt}. \quad (2)$$

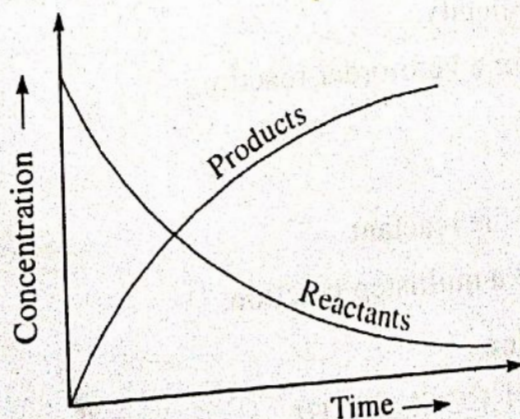


Fig. 8.1

The graphical representation of the concentration changes of the reactants and products will be as follows. The graph shows the fall of concentrations of the reactants and rise of concentrations of the products with the progress of the reaction, i.e., with time.

• Order and molecularity of reactions

Generally, the rate of a reaction at any instant of time is proportional to the concentration of the reactants at that instant. Examples are there, where the rate is somehow proportional to the reciprocal of the concentration of the product (e.g., HBr formation from its elements). But the question is that whether the rate is directly proportional to the concentration of the reactant, i.e., to its first power or to any other exponent of it, say square, square root, etc. The problem is solved experimentally and a kinetic term 'order' is used to express the concentration-dependence of rate of a reaction.

Order of a reaction is defined as the power of the concentration of a reactant with which the rate of the reaction varies and it is ascertained experimentally.

Let it is seen that the rate of the reaction (1) is experimentally found to be

$$r \propto [A]^\alpha [B]^\beta \quad (3)$$

Then the order of the reaction is said to be α with respect to A and β with respect to B, so that the overall order of the reaction will be $(\alpha + \beta)$.

This may also be represented as

$$-\frac{d[A]}{dt} \propto [A]^\alpha \quad \text{and} \quad -\frac{d[B]}{dt} \propto [B]^\beta \quad (4)$$

α or β may be 1, 2, 3, ... or any fractional number and even may be negative. Accordingly the reaction will be said as first order, second order etc. However, the value of α or β will be decided by experiment.

Molecularity is defined as the minimum number of molecules of a reactant which actually takes part in the reaction. The stoichiometry of a reaction cannot tell about the molecularity. It is ascertained from some proposed mechanism of the reaction which satisfies the experimental observation.

I. Zero order reaction

For the reaction, $A \rightarrow \text{Products}$

$$\text{the rate } r = -\frac{d[A]}{dt} = k_0[A]^0$$

$$\text{or, } \boxed{r = k_0} \quad (5)$$

where $[A]$ is the concentration of A at time t . The **unit of k_0** , the zero order rate constant, is $\text{mol.dm}^{-3}\text{s}^{-1}$.

Equation (5) indicates that the rates of such reactions are independent of the concentration of the reactant and proceed at constant velocity.

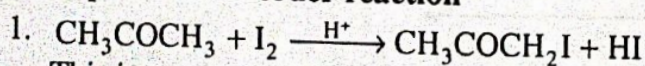
The half-decomposition time for a zero-order reaction,

$$\boxed{t_{\frac{1}{2}} = \frac{a}{2k_0}} \quad (6)$$

a being the initial concentration of the reactant.

A zero order reaction should be a multistep reaction.

Examples of zero-order reaction



This is zero-order with respect to iodine.

2. $2\text{HI (gas)} \xrightarrow{\text{Au}} \text{H}_2 + \text{I}_2$
3. $\text{Substrate} \xrightarrow{\text{Enzyme}} \text{Products}$

II. First order reactions:

For the reaction, $\text{A} \rightarrow \text{Product}$,

$$\text{the rate, } r = -\frac{d[\text{A}]}{dt} = k_1 [\text{A}]$$

The integrated form finally becomes

$$k_1 = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$$

(7)

(8)

where k_1 = 1st order rate constant

a = initial concentration of the reactant

x = concentration of the product in time t .

Unit of k_1 is s^{-1} .

Half-decomposition period of a first order reaction.

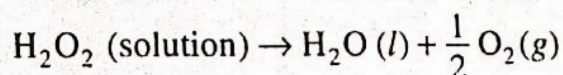
$$t_{\frac{1}{2}} = \frac{0.693}{k_1}$$

(9)

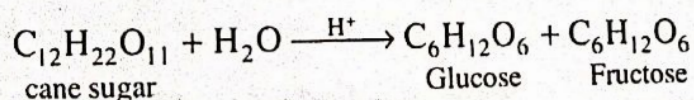
Hence line required to complete half of the amount of the reactant does not depend on its initial concentration. It is a constant quantity.

Examples of 1st order reactions

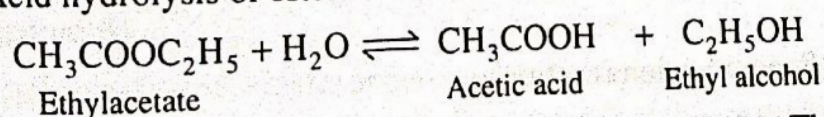
1. Decomposition of H_2O_2 solution:



2. Inversion of cane sugar:

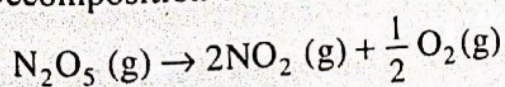


3. Acid hydrolysis of ester:

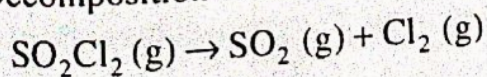


This is an example of a **pseudo first order reaction**. Though water is a reactant, the rate is independent of its concentration, which remains practically constant.

4. Decomposition of dinitrogen pentoxide:



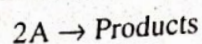
5. Decomposition of thionyl chloride:



6. All radioactive changes.

III. Second order reaction

For the reaction of the type



$$\text{the rate, } r = -\frac{d[A]}{dt} = k_2 (a-x)^2. \quad (10)$$

The integrated form becomes

$$k_2 = \frac{x}{t a(a-x)} \quad (11)$$

where k_2 = second order rate constant a = initial concentration of the reactant x = concentration of the products in time t .Unit of k_2 is $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$.

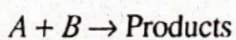
Half decomposition-period of a first order reaction.

$$t_{1/2} = \frac{1}{k_2 a} \quad (12)$$

$$\text{i.e., } t_{1/2} \propto \frac{1}{a} \quad (13)$$

Hence larger the initial concentration of the reactant, shorter will be the time for decomposition of half-amount of the reactant.

For two different reactants with different initial concentrations of the type



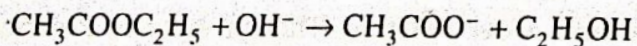
$$r = \frac{dx}{dt} = k_2 (a-x)(b-x) \quad (14)$$

which on integration becomes

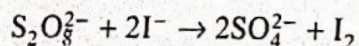
$$k_2 = \frac{2.303}{b-a} \log_{10} \frac{b-x}{a-x} \quad (15)$$

 $t_{1/2}$ cannot be calculated from this equation.**Examples of 1st order reactions**

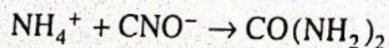
1. Alkali hydrolysis of an ester (Saponification reaction):



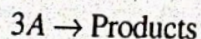
2. Reaction of persulphate with iodide ions



3. Formation of urea from ammonium cyanate:

**IV. Third order reactions**

For the simple third order reactions of the type



$$r = -\frac{d[A]}{dt} = k_3 (a-x)^3$$

The integrated form is

$$k_3 = \frac{1}{2t} \left[\frac{1}{(a-x)^2} - \frac{1}{a^2} \right]$$

(16)

(17)

Unit of k_3 is $\text{mol}^{-2} \text{dm}^6 \text{s}^{-1}$.

$$t_{1/2} = \frac{3}{2k_3 a^2}$$

(18)

Examples of 1st order reactions

1. $2\text{NO} + \text{O}_2 \rightarrow 2\text{NO}_2$
2. $2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}$
3. $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$
4. $2\text{NO} + \text{Br}_2 \rightarrow 2\text{NOBr}$
5. $2\text{NO} + \text{D}_2 \rightarrow \text{N}_2\text{O} + \text{D}_2\text{O}$

IV. n -th order reactions

$$r = -\frac{d[A]}{dt} = k (a-x)^n$$

(19)

The integrated form is

$$k_n = \frac{1}{t(n-1)} \left[\frac{1}{(a-x)^{n-1}} - \frac{1}{a^{n-1}} \right]$$

(20)

(except for 1st order reaction)

$$\text{and } t_{1/2} = \frac{k'}{a^{n-1}}$$

(21)

General unit of k_n : $(\text{dm}^3)^{n-1} \text{mol}^{1-n} \text{s}^{-1}$

• Instruments

As already mentioned, kinetic experiment find its use in a number of instruments including **mechanical titration**, i.e., pipette-burette-indicator. **Polarimeter** (angle of rotation measured), **Spectrophotometer** (for optical density measurement of both colour and colourless solutions), **Conductometer**, **pH-meter**, **Potentiometer** and even **Stalagmometer** are in use.

Different experiments in relevant chapters of this book have been discussed with the above instruments.

For better result, it is suggested to use a **thermostat**, as rate of reaction is highly influenced even by a small variation of temperature.

As the term involves, all the kinetic experiments require a **stopwatch**.

Experiment 3

Kinetic study of the decomposition of hydrogen peroxide in presence of ferric chloride solution and effect of catalyst on the rate constant.

Theory: Hydrogen peroxide undergoes decomposition in accordance with the equation

$\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \frac{1}{2}\text{O}_2$ and the rate of decomposition is markedly accelerated by the presence of various catalysts. In this experiment we will study the above decomposition reaction in presence of FeCl_3 solution which acts as a positive catalyst and whose concentration remains unchanged during the course of the reaction. The course of the reaction may be followed by titrating the hydrogen peroxide with potassium permanganate in acid medium, the volume of permanganate solution required at any time being proportional to the concentration of hydrogen peroxide remaining at that time.

Let V_0 be the volume of potassium permanganate solution required corresponding to the initial concentration of hydrogen peroxide a at time $t = 0$, and V_t be the volume of potassium permanganate solution required corresponding to the concentration of hydrogen peroxide remaining $(a - x)$ at time t . Since the reaction follows first order kinetics, the expression of rate constant at laboratory temperature is given by

$$K = \frac{2.303}{t} \log \frac{a}{a-x} \quad \text{or, i.e., } K = \frac{2.303}{t} \log \frac{V_0}{V_t}.$$

It is difficult to measure V_0 as the decomposition starts as soon the catalyst is mixed with hydrogen peroxide and it can be eliminated by taking the difference in time $\Delta t_n = t_n - t_1$ such that

$$K = \frac{2.303}{\Delta t_n} \log \frac{V_1}{V_n} \quad [n = 2, 3, 4, \dots]$$

$$\text{or, } \log \frac{V_1}{V_n} = \frac{K}{2.303} \Delta t_n, \quad (1)$$

where V_1 is the volume of permanganate solution required for a particular volume (say, 5 ml) of reaction mixture at time t_1 after the initiation of the reaction and V_n is that at time t_2, t_3, \dots after the initiation of the reaction. If $\log \frac{V_1}{V_n}$ is plotted against Δt_n , a straight line passing through the origin will be obtained from the slope of which K can be determined. The reaction is studied using two different concentrations of FeCl_3 solution, K_1 and K_2 are determined and the result is interpreted from ratio $\frac{K_1}{K_2}$.

Materials: (i) 2(V) hydrogen peroxide, (ii) 1.0% and 0.5% FeCl_3 solution, (iii) 1(N) H_2SO_4 , (iv) $\frac{N}{50}$ KMnO_4 solution, (v) Ice, (vi) Pipettes, burettes, conical flasks, etc.

Procedure

1. In the laboratory, the hydrogen peroxide which is available is labelled as 30% (100 volumes). Prepare 250 ml 2(V) H_2O_2 from this concentrated H_2O_2 (5 ml is diluted to 250 ml with distilled water).
2. Prepare 100 ml 1% anhydrous FeCl_3 solution (1 gm is dissolved in 100 ml water) and then from this solution prepare 50 ml 0.5% FeCl_3 solution by exact dilution (25 ml FeCl_3 solution 1% + 25 distilled water).
3. Prepare 250 ml 1(N) H_2SO_4 from concentrated H_2SO_4 [36 (N)]. Dilute ≈ 7 ml concentrated H_2SO_4 to 250 ml carefully.
4. Prepare 500 ml $\frac{N}{50}$ KMnO_4 solution (dissolved ≈ 0.3 ml KMnO_4 in 500 ml water).
5. Take 50 ml of 2(V) H_2O_2 in a 250 ml stoppered bottle and add 10 ml of 1% FeCl_3 solution starting the stop-watch when the pipette is half-emptied. Shake the reaction mixture well and withdraw 5 ml portions of the reaction mixture at intervals of 3 minutes and then run it into 10 ml ice-cold (IN) H_2SO_4 , noting the time of the half-discharge of the reaction mixture. Immediately titrate it against $\frac{N}{50}$ KMnO_4 solution. Note the burette readings when just pink colour appears in each case. Take at least seven readings.
6. Repeat the same using 0.5% FeCl_3 solution.

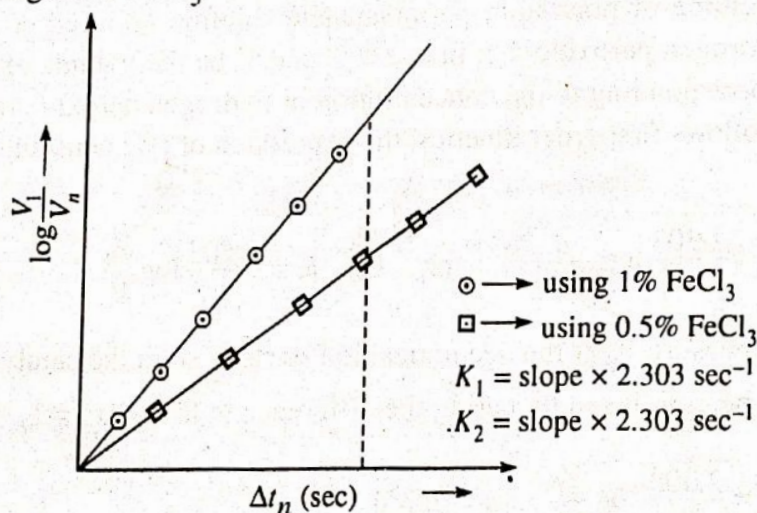


Fig. 8.5: Plot of $\log \frac{V_1}{V_n}$ vs. Δt_n

- vii. Plot $\log \frac{V_1}{V_n}$ vs. Δt_n for the two sets of data on the same graph paper and determine K_1 and K_2 for two sets. The expected nature of graph will be as follows.
- viii. Interpret the result.

N.B.:

- a. Before starting the experiment a blank titration of H_2O_2 is necessary. For this purpose take 50 ml of 2(V) H_2O_2 (prepared) and add 10 ml of distilled water instead of FeCl_3 solution. Withdraw 5 ml of that H_2O_2 and then run into 10 ml of 1(N) H_2SO_4 . Titrate it against $\frac{N}{50}$ thio and note the burette reading. If the burette reading lies in the range 20 ml to 30 ml, then start the experiment. Otherwise adjust the strength of H_2O_2 so that the burette reading lies approximately on the above range. The blank titration of H_2O_2 is necessary because the strength of H_2O_2 , which is available in the laboratory, is not correctly known, some of it may decompose and its strength may change from 30% i.e., 100 volumes.

- b. During performing the experiment there may always some bubbling at the time of pipetting. Minimize the rate of bubbling by adjusting the strength of FeCl_3 solution. Whatever may be the strength of FeCl_3 solution adjusted, the strength of one should be just half of the other.]

Results and Calculations

1. Recording of laboratory temperature

Temperature →	Before experiment	After experiment	Mean
	$^{\circ}\text{C}$	$^{\circ}\text{C}$	$^{\circ}\text{C}$

2. Titration results of set 1 (using 1% FeCl_3 solution)

Time (sec)	Δt_n (sec)	Volume of KMnO_4 required (ml)	$\log \frac{V_1}{V_n}$ [$n = 2, 3, 4, \dots$]
t_1	—	V_1	—
t_2	$t_2 - t_1$	V_2	...
t_3	$t_3 - t_1$	V_3	...
t_4	$t_4 - t_1$	V_4	...
t_5	$t_5 - t_1$	V_5	...
t_6	$t_6 - t_1$	V_6	...

3. Titration results for set 2 (using 0.5% FeCl_3 solution)

Time (sec)	Δt_n (sec)	Volume of KMnO_4 required (ml)	$\log \frac{V_1}{V_n}$ [$n = 2, 3, 4, \dots$]
t_1	—	V_1	—
t_2	$t_2 - t_1$	V_2	...
t_3	$t_3 - t_1$	V_3	...
t_4	$t_4 - t_1$	V_4	...
t_5	$t_5 - t_1$	V_5	...
t_6	$t_6 - t_1$	V_6	...

4. Calculations and Conclusion

From the plot of $\log \frac{V_1}{V_n}$ vs. Δt_n .

For set 1 $K_1 = \text{slope} \times 2.303 \text{ sec}^{-1}$

For set 2 $K_2 = \text{slope} \times 2.303 \text{ sec}^{-1}$

\therefore the ratio $\frac{K_1}{K_2} = \dots$

[It has been found that $\frac{K_1}{K_2} \neq 2$. The expected value of the ratio is nearly 1.5.]

If it is, we can conclude that FeCl_3 does not act as a homogenous catalyst. In case of a homogeneous catalyst the expected value of the ratio is 2].