Chemical Kinetics and Reaction Dynamics

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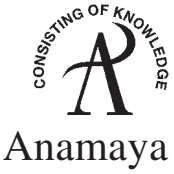

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To

My Mother

Preface

Reaction dynamics is the part of chemical kinetics which is concerned with the microscopic-molecular dynamic behavior of reacting systems. Molecular reaction dynamics is coming of age and much more refined state-to-state information is becoming available on the fundamental reactions. The contribution of molecular beam experiments and laser techniques to chemical dynamics has become very useful in the study of isolated molecules and their mutual interactions not only in gas surface systems, but also in solute-solution systems.

This book presents the important facts and theories relating to the rates with which chemical reactions occur and covers main points in a manner so that the reader achieves a sound understanding of the principles of chemical kinetics. A detailed stereochemical discussion of the reaction steps in each mechanism and their relationship with kinetic observations has been considered.

I would like to take the opportunity to thank Professor R.C. Srivastava and Professor N. Sathyamurthy with whom I had the privilege of working and who inspired my interest in the subject and contributed in one way or another to help complete this book. I express my heavy debt of gratitude towards Professor M.C. Agrawal who was gracious enough for sparing time out of his busy schedule to go through the manuscript. His valuable comments and suggestions, of course, enhanced the value and importance of this book. I also express my gratitude to my colleagues, friends and research students, especially Dr. Neelu Kambo who took all the pains in helping me in preparing, typing and checking the manuscript.

Finally, I thank my wife Mrs. Manju Upadhyay, daughter Neha and son Ankur for their continuous inspiration during the preparation of the text.

SANTOSH K. UPADHYAY

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Chemical Kinetics and Reaction Dynamics

1
Elementary

Chemical kinetics deals with the rates of chemical reactions, factors which influence the rates and the explanation of the rates in terms of the reaction mechanisms of chemical processes.

In chemical equilibria, the energy relations between the reactants and the products are governed by thermodynamics without concerning the intermediate states or time. In chemical kinetics, the time variable is introduced and rate of change of concentration of reactants or products with respect to time is followed. The chemical kinetics is thus, concerned with the quantitative determination of rate of chemical reactions and of the factors upon which the rates depend. With the knowledge of effect of various factors, such as concentration, pressure, temperature, medium, effect of catalyst etc., on reaction rate, one can consider an interpretation of the empirical laws in terms of reaction mechanism. Let us first define the terms such as rate, rate constant, order, molecularity etc. before going into detail.

1.1 Rate of Reaction

The rate or velocity of a reaction may be expressed in terms of any one of the reactants or any one of the products of the reaction.

The rate of reaction is defined as change in number of molecules of reactant or product per unit time, i.e.

$$\text{Rate of reaction} = -\frac{dn_R}{dt} = \frac{dn_p}{dt} \tag{1.1}$$

where dn_R and dn_p are the changes in number of molecules of reactant and product, respectively, for a small time interval dt. The reactant is being consumed, i.e. number of molecules of reactant decreases with time. Hence, minus sign is attached so that rate will be positive numerically. For comparing the rates of various reactions, the volume of reaction system must be specified and rate of reaction is expressed per unit volume. If V_t is the volume of reaction mixture, then

$$\text{Rate of reaction} = -\frac{1}{V_t}\frac{dn_R}{dt} = \frac{1}{V_t}\frac{dn_p}{dt} \tag{1.2}$$

At constant V,

$$\text{Rate of reaction} = -\frac{d(n_R/V)}{dt} = \frac{d(n_p/V)}{dt} \tag{1.3}$$

Again n_R/V is the molar concentration of reactant and n_p/V the molar concentration of product. Therefore, in terms of molar concentrations

$$\text{Rate of reaction} = -\frac{d[\text{Reactant}]}{dt} = \frac{d[\text{Product}]}{dt} \tag{1.4}$$

where [Reactant] and [Product] are the molar concentrations of reactant and product, respectively. This conventional way of representing the rate of reaction is valid only at constant volume. However, if there is a change in the volume of the reactants, $-\frac{d(n_R/V_t)}{dt}$ would yield

$$-\frac{d(n_R/V_t)}{dt} = \frac{1}{V_t}\frac{dn_R}{dt} + \left(\frac{(n_R)}{(V_t)}\right)^2 \frac{dV_t}{dt} \tag{1.5}$$

and, therefore, $-\frac{d[\text{Reactant}]}{dt}$ will not be equal to $-\frac{1}{V_t}\frac{dn_R}{d_t}$ and corrections need to be applied.

At constant volume, the rate of a general reaction, A + B → C + D in terms of molar concentration of reactant or product may be given as

$$\text{Rate of reaction} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt} \tag{1.6}$$

$$\text{Rate of reaction} = \left\{\begin{matrix}\text{Decrease in molar}\\ \text{concentration of a}\\ \text{reactant per unit time}\end{matrix}\right\} = \left\{\begin{matrix}\text{Increase in molar}\\ \text{concentration of a}\\ \text{product per unit time}\end{matrix}\right\}$$

However, if reaction is not of a simple stoichiometry but involves different number of moles of reactants or products, the rate should be divided by corresponding stoichiometric coefficient in the balanced chemical equation for normalizing it and making it comparable. For example, for a general reaction aA + bB → cC + dD

$$\text{Rate of reaction} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt} \tag{1.7}$$

1.1.1 Experimental Determination of Rate

For the determination of rate of reaction at constant volume the concentration of a chosen reactant or product is determined at various time intervals. The change in concentration ΔC, for a given time interval $\Delta t(t_2 - t_1)$ is obtained. An average rate of reaction is then obtained by calculating $\Delta C/\Delta t$. The smaller the value of Δt, the closer the value of the rate will be to the real rate at time $(t_1 + t_2)/2$ because

$$\lim_{\Delta t \to 0} \frac{\Delta C}{\Delta t} \to \frac{dC}{dt} \tag{1.8}$$

The rate of reaction can also be obtained by plotting concentration of reactant or product against time and measuring the slope of the curve (dc/dt) at the required time. The rate of reaction obtained from such method is known as *instantaneous rate*. The concentration of the reactant or product varies exponentially or linearly with time as shown in Fig. 1.1.

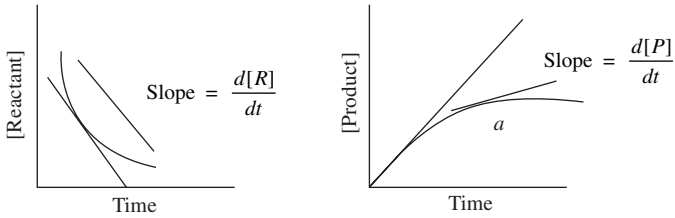

Fig. 1.1 Concentration variation of the reactant/product with time.

For determination of the instantaneous rate at any point *a*, the slope of the curve is determined. It may also be noted from Fig. 1.1 that if the concentration varies linearly with time, the slope of the curve or rate of the reaction will remain same throughout the course of reaction. However, if concentration of the reactant or product varies exponentially with time the slope of the curve or the rate of reaction will be different at different time intervals. Thus, it is not necessary that rate of reaction may always remain same throughout the course of reaction. The reaction may proceed with a different rate in the initial stage and may have different rate in the middle or near the end of the reaction.

In place of concentration of reactant or product any physical property, which is directly related with concentration, such as viscosity, surface tension, refractive index, absorbance etc. can be measured for the determination of the rate of reaction.

1.2 Rate Constant

For a general reaction

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

the rate is proportional to $[A]^a \times [B]^b$, i.e.

$$\text{Rate} = k\,[A]^a\,[B]^b \tag{1.9}$$

where proportionality constant k, relating rate with concentration terms, is known as *rate constant* or *velocity constant* at a given temperature.

When the reactants are present at their unit concentrations,

$$\text{Rate} = k$$

Thus, the rate constant is the rate of reaction when concentrations of the reactants are unity. The rate constant under these conditions is also known as the *specific rate* or the *rate coefficient*. The rate constant for any reaction can be determined

(i) either by measuring the rate of the reaction at unit concentrations of the reactants.
(ii) or by knowing the rate at any concentration of reactant using the relation

$$\text{Rate constant} = \text{Rate}/[\text{A}]^a\,[\text{B}]^b \tag{1.10}$$

The rate constant is measured in units of moles dm^{-3} sec^{-1}/(moles $dm^{-3})^n$, where $n = a + b$. Time may also be in minutes or hours. It should be noted that in case where the reaction is slow enough, the thermal equilibrium will be maintained due to constant collisions between the molecules and k remains constant at a given temperature. However, if the reaction is very fast the tail part of the Maxwell-Boltzmann distribution will be depleted so rapidly that thermal equilibrium will not be re-established. In such cases rate constant will not truly be constant and it should be called a rate coefficient.

1.3 Order and Molecularity

For reaction

$$\alpha\text{A} + \beta\text{B} + \ldots \rightarrow \text{Product}$$

rate of reaction is proportional to α^{th} power of concentration of A, to the β^{th} power of concentration of B etc., i.e.

$$\text{Rate} = k\,[\text{A}]^\alpha\,[\text{B}]^\beta \ldots \tag{1.11}$$

Then the reaction would be said to be α^{th} order with respect to A, β^{th} order with respect to B, . . . and the overall order of reaction would be $\alpha + \beta + \ldots$. Thus, order of reaction with respect to a reactant is the power to which the concentration of the reactant is raised into the rate law, and the overall order of reaction is the sum of the powers of the concentrations involved in the rate law.

The term '*molecularity*' is the sum of stoichiometric coefficients of reactants involved in the stoichiometric equation of the reaction. For example, a reaction whose stoichiometric equation is

$$2\text{A} + 3\text{B} = 3\text{C} + 2\text{D}$$

the stoichiometric coefficient of A and B are 2 and 3, respectively, and, therefore, the molecularity would be 2 + 3 = 5.

There is not necessarily a simple relationship between molecularity and order of reaction. For differentiating between molecularity and order of a reaction, let us consider some examples.

For the reaction, $\text{A} + 2\text{B} \rightarrow \text{P}$, the molecularity is 1 + 2 = 3. If the reaction

occurs in a single step the order of reaction with respect to A would be one and order with respect to B would be two, giving overall order of reaction 3. Thus the molecularity and order would be same. However, if the reaction occurs in two different steps giving overall same reaction, e.g.

(a) $A + B = I \rightarrow \text{Slow}$

(b) $\dfrac{I + B = P \rightarrow \text{fast}}{A + 2B \rightarrow P}$

Now the rate of reaction will be governed by only slow step (a) and order of reaction would be one with respect to each reactant, A and B, giving overall order two. And, therefore, the order and molecularity will be different.

The inversion of cane sugar is

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

and the rate of inversion is given by

$$\text{Rate} = k\,[\text{Sucrose}]\,[H_2O] \tag{1.12}$$

This reaction seems to be second order, i.e. first order with respect to each sucrose and H_2O. The $[H_2O]$ is also constant as it is used as solvent and present in large amount. Therefore, the reaction is only first order with respect to sucrose.

The hydrolysis of ester in presence of acid is first order reaction (keeping catalyst constant)

$$CH_3COOC_2H_5 + H_2O \xrightarrow{[H^+]} CH_3COOH + C_2H_5OH$$

Since $[H_2O]$ remain constant as in case of inversion of cane sugar, it does not effect the rate of reaction and reaction is simply first order with respect to ester. However, the hydrolysis of ester in presence of alkali

$$CH_2COOC_2H_5 + NaOH \rightarrow CH_3COONa + C_2H_5OH$$

is second order being first order with respect to both ester and NaOH. While the molecularity of the reaction in each case, i.e. in hydrolysis of ester in presence of acid as well as in presence of alkali, is two.

The reactions, in which molecularity and order are different due to the presence of one of the reactant in excess, are known as *pseudo-order reactions*. The word (pseudo) is always followed by order. For example, inversion of cane sugar is pseudo-first order reaction.

The molecularity will always be a whole integer while order may be an integer, fraction or even a negative number. Molecularity is a theoretical concept, whereas order is empirical. Molecularity is, therefore, less significant as far as kinetic studies are concerned.

The order of reaction provides the basis for classifying reactions. Generally, the order of reaction can be anywhere between zero and three. Reactions having order three and above are very rare and can be easily counted.

The rate of a chemical reaction is proportional to the number of collisions taking place between the reacting molecules and the chances of simultaneous collision of reacting molecules will go on decreasing with an increase in number of molecules. The possibility of four or more molecules coming closer and colliding with one another at the same time is much less than in case of tri- or bi molecular reactions. Therefore, the reactions having order four or more are practically impossible. Further, many reactions which appear to be quite complex proceed in stepwise changes involving maximum two or three species. The stoichiometric representation has no relation either with the mechanism of reaction or with the observed order of reaction.

In older literature the terms unimolecular, bimolecular and termolecular have been used to indicate the number of molecules involved in a simple collision process and should not be confused with first, second and third order reactions.

1.4 Rate Equations

For a reaction

$$n\text{A} \xrightarrow{k} \text{Product}$$

The rate is related with concentration of A with the following differential form of equation

$$\text{Rate} = -\frac{d[\text{A}]}{dt} = k[\text{A}]^n \tag{1.13}$$

or

$$\log\left(-\frac{d[\text{A}]}{dt}\right) = \log k + n \log [\text{A}] \tag{1.14}$$

where k is the rate constant.

As discussed previously the rate is determined by drawing a graph between concentration and time and taking the slope corresponding to a concentration. If we have the values of the rates for various concentrations, we can find the order of reaction by plotting log (rate) against log [concentration]. The slope of the straight line obtained from the plot gives the order of reaction n while the intercept gives log k. Thus, order and rate constant can be determined.

However, the average rates calculated by concentration versus time plots are not accurate. Even the values obtained as instantaneous rates by drawing tangents are subject to much error. Therefore, this method is not suitable for the determination of order of a reaction as well as the value of the rate constant. It is best to find a method where concentration and time can be substituted directly to determine the reaction orders. This could be achieved by integrating the differential rate equation.

1.4.1 Integral Equations for n^{th} Order Reaction of a Single Reactant

Let us consider the following general reaction:

$$n\text{A} \xrightarrow{k} \text{Product}$$

If c_0 is the initial concentration of the reactant and c the concentration of reactant at any time t, the differential rate expression may be given as

$$-dc/dt = kc^n \tag{1.15}$$

Multiplying by dt and then dividing by c^n, we get

$$-dc/c^n = kdt \tag{1.16}$$

which may be integrated. The limits of integration are taken as $c = c_0$ and c at $t = 0$ and $t = t$, respectively, as

$$\int \frac{dc}{c^n} = k \int dt \tag{1.17}$$

For various values of n, the results may be obtained as follows:

$$n = 0; \quad k = \frac{C_0 - c}{t}$$

$$n = 1; \ln c = \ln (c_0) - kt \text{ or } c = c_0\, e^{-kt}$$

$$n = 2; k = 1/t\ [1/c - 1/c_0]$$

$$n = 3; k = 1/2t\ [1/c^2 - 1/c_0^2]$$

$$n = n; k = 1/(n-1)t\ [1/(c^{n-1}) - 1/(c_0^{n-1})]$$

1.4.2 Integral Equations for Reactions Involving More than One Reactants

When the concentrations of several reactants, and perhaps also products, appear in the rate expressions, it is more convenient to use as the dependent variable x, i.e. the decrease in concentration of reactant in time t. Then $c = a - x$, where a is commonly used to indicate the initial concentration in place of c_0 and rate equation (1.15) becomes

$$dx/dt = k\ (a - x)^n \tag{1.18}$$

or

$$\int dx/(a - x)^n = \int kdt$$

which can be integrated taking the conditions: at $t = 0$, x will also be zero, the value of rate constant can be obtained.

For various values of n the results obtained are as follows:

$n = 0$ $\quad dx/dt = k$; $k = x/t$

$n = 1$ $\quad dx/dt = k(a - x)$; $k = 2.303/t \log a/a - x$

$n = 2$ $\quad dx/dt = k(a - x)^2$; $k = 1/t\ [1/a - x - 1/a]$

$n = 3 \quad dx/dt = k(a - x)^3;\ k = 1/2t\ [1/(a - x)^2 - 1/a^2]$

$n = n \quad dx/dt = k(a - x)^3;\ k = 1/(n - 1)t\ [1/(a - x)^{n-1} - 1/a^{n-1}];\ n \geq 2$

1.5 Half-life of a Reaction

The reaction rates can also be expressed in terms of half-life or half-life period. The half-life period is defined as the time required for the concentration of a reactant to decrease to half of its initial value.

Hence, half-life is the time required for one-half of the reaction to be completed. It is represented by $t_{1/2}$ and can be calculated by taking $t = t_{1/2}$ when $x = a/2$ in the integrated rate equation of its order.

Problem 1.1 Write the differential rate equations of the following reactions:

(a) $A + 2B \xrightarrow{k} P$

(b) $3A + 2B \xrightarrow{k'} 3C + D + 2E$

Solution The differential rates of above reactions can be written assuming them to be elementary steps

(a) $$-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{d[P]}{dt} = k\,[A]^2\,[B]$$

(b) $$-\frac{1}{3}\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{1}{3}\frac{d[C]}{dt} = \frac{d[D]}{dt} = \frac{1}{2}\frac{d[E]}{dt} = k'\,[A]^3\,[B]^2$$

Problem 1.2 Write the differential rate equations of the following reactions:

(a) $A + 3B \rightarrow 4C$

(b) $A + 2B \rightarrow C + 3D$

(c) $3A + B + 2C \rightarrow D + 3E$

Solution Assuming these reactions as elementary steps, the differential rate can be written as:

(a) $$-\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt} = \frac{1}{4}\frac{d[C]}{dt} = k\,[A][B]^3$$

(b) $$-\frac{d[A]}{dt} = -\frac{1}{2}\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{1}{3}\frac{d[D]}{dt} = k\,[A][B]^2$$

(c) $$-\frac{1}{3}\frac{d[A]}{dt} = -\frac{d[B]}{dt} = -\frac{1}{2}\frac{d[C]}{dt} = \frac{d[D]}{dt} = \frac{1}{3}\frac{d[E]}{dt} = k\,[A]^3\,[B][C]^2$$

Problem 1.3 Express the rate constant k in unit of $dm^3\ mol^{-1}s^{-1}$, if

(i) $k = 2.50 \times 10^{-9}\ cm^3 molecule^{-1}s^{-1}$

(ii) $k = 2 \times 10^{-6}\ s^{-1}\ atm^{-1}$

Solution

(i) $1\ dm^3 = 1000\ cm^3$, i.e. $1\ cm^3 = 10^{-3}\ dm^3$

$1\ mol = 6.02 \times 10^{23}$ molecule

$molecule^{-1} = 6.02 \times 10^{23}\ mol^{-1}$

$k = 2.50 \times 10^{-9}\ cm^3\ molecule^{-1} s^{-1}$

$= 2.50 \times 10^{-9}\ (10^{-3}\ dm^3)(6.02 \times 10^{23}\ mol^{-1}) s^{-1}$

$= 2.50 \times 6.02 \times 10^{-9-3+23}\ dm^3\ mol^{-1}\ s^{-1}$

$= 15.05 \times 10^{11}\ dm^3\ mol^{-1}\ s^{-1}$

(ii) We know $\underset{(1\ atm)}{P} = \frac{n}{v} RT = CRT$

or $C = \frac{P}{RT} = \frac{1\ atm}{0.0821\ atm\ dm^3\ mol^{-1} K^{-1} \times 273\ K}$

$= 0.0446\ mol\ dm^{-3}$

Therefore, $1\ atm = 0.0446\ mol\ dm^{-3}$

or $1\ atm^{-1} = \frac{1}{0.0446}\ mol^{-1}\ dm^3$

$k = 2.0 \times 10^{-6}\ s^{-1}\ atm^{-1}$

$= 2.0 \times 10^{-6}\ s^{-1} . \left(\frac{1}{0.0446}\right) mol^{-1} dm^3$

$= 44.8 \times 10^{-6}\ dm^3\ mol^{-1}\ s^{-1}$

Problem 1.4 For a certain reaction, the value of rate constant is 5.0×10^{-3} $dm^3\ mol^{-1} sec^{-1}$. Find the value of rate constant in (i) dm^3 $molecule^{-1}$ sec^{-1} (ii) $cm^3\ mol^{-1}$ sec^{-1} and (iii) cm^3 $molecule^{-1}$ sec^{-1}.

Solution

(i) in $dm^3\ mol^{-1} sec^{-1}$

Rate constant $= 5.0 \times 10^{-3}\ dm^3\ mol^{-1} sec^{-1}$

$1\ mol = 6.02 \times 10^{23}$ molecules

Rate constant $= 5.0 \times 10^{-3}\ dm^3\ (6.02 \times 10^{23}\ mol)^{-1}\ sec^{-1}$

$= 0.83 \times 10^{-26}\ dm^3\ molecule^{-1}\ sec^{-1}$

(ii) in $cm^3\ mol^{-1} sec^{-1}$

$1\ dm^3 = 1000\ cm^3$

$$\text{Rate constant} = 5.0 \times 10^{-1}\ \text{dm}^3\ \text{mol}^{-1}\text{sec}^{-1}$$
$$= 5.0 \times 10^{-3}(1000)\ \text{cm}^3\ \text{mol}^{-1}\text{sec}^{-1}$$
$$= 5.0\ \text{cm}^3\ \text{mol}^{-1}\ \text{sec}^{-1}$$

(iii) in $\text{cm}^3\ \text{molecules}^{-1}\text{sec}^{-1}$

$$\text{Rate constant} = 5.0\ \text{cm}^3\ (6.02 \times 10^{23})^{-1}\ \text{molecules}^{-1}\text{sec}^{-1}$$
$$= 0.83 \times 10^{-23}\ \text{cm}^3\ \text{molecules}^{-1}\text{sec}^{-1}$$

1.6 Zero Order Reactions

When no concentration term affects the rate of reaction, or the rate of reaction remains same throughout the reaction, the reaction is known as zero-order reaction.

Let us consider a reaction

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

Since the rate of reaction remains same

$$\frac{dx}{dt} = k$$

On integrating the expression as

$$\int dx = k \int dt$$

we get

$$x = kt + z$$

The value of integration constant z may be obtained by taking the conditions $x = 0$, when $t = 0$, the value of z is zero and, therefore, rate equation becomes

$$x = kt \quad \text{or} \quad k = \frac{x}{t} \tag{1.19}$$

which gives the unit of rate constant as mol dm^{-3} sec^{-1} or conc. $(\text{time})^{-1}$ in general.

- The half-life period $t_{1/2}$ of a zero order reaction can be calculated with the help of equation (1.19), taking $t = t_{1/2}$ and $x = a/2$ as

$$t_{1/2} = \frac{a}{2k} \tag{1.20}$$

Thus, the half-life period of zero order reaction is directly proportional to the initial concentration of the reactant. For example, on increasing the initial concentration by two fold, the half-life period of the reaction would also be double.

- According to equation (1.19) the slope of a plot of x or $(a - x)$ (i.e. the concentration of product or concentration of reactant) versus time will give the value of rate constant k (Fig. 1.2).

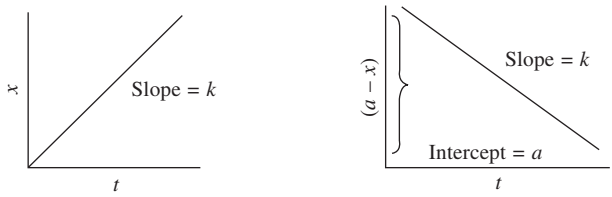

Fig. 1.2 Concentration versus time plot for zero order reaction.

The combination of H_2 and Cl_2 to form HCl in presence of sunlight is a zero order reaction

$$H_2 + Cl_2 \rightarrow 2HCl$$

The rate of formation of HCl is not affected by a change in concentration of either the reactant or product. However, it is influenced by the intensity of sun light.

Problem 1.5 A zero order reaction is 50% complete in 20 min. How much time will it take to complete 90%?

Solution Let $a = 100$ mol dm^{-3}. For a zero-order reaction

$$k = \frac{x}{t} = \frac{50 \text{ (mol dm}^{-3})}{20 \times 60 \text{ (sec)}}$$

When reaction is 90% completed, $x = 90$. Therefore,

Thus, $$\frac{50}{1200} = \frac{90}{t}$$

or $$t = \frac{90 \times 1200}{50} = 2160 \text{ sec} = 36 \text{ min}$$

Problem 1.6 A reaction is 50% complete in 20 min. How much time will be taken to complete 75% reaction?
Solution For a zero order reaction

$$k = x/t$$

$$x = a/2 \text{ for } 50\%$$

$$k = \frac{a}{2t} = \frac{a}{2 \times 20}$$

$$x = \frac{3a}{4} \text{ for } 75\% \text{ reaction}$$

Therefore, $$k = \frac{3a}{4t}$$

or $$\frac{a}{2 \times 20} = \frac{3a}{4t}$$

$$t = \frac{40 \times 3}{4} = 30 \text{ min}$$

75% reaction will complete in 30 min.

1.7 First Order Reactions

Let us consider a first-order reaction

$$\text{A} \longrightarrow \text{Products}$$

Initially,	a	0
At time t,	$a - x$	x

We know that in case of a first-order reaction, the rate of reaction, dx/dt is directly proportional to the concentration of the reactant. Therefore,

$$\frac{dx}{dt} = k(a - x) \quad \text{or} \quad \frac{dx}{(a-x)} = kdt$$

Integrating, we get $\ln (a - x) = kt + z$.

The integration constant z is determined by putting $t = 0$ and $x = 0$. Thus

$$z = \ln a$$

and, therefore, the rate constant for a first order reaction is obtained as

$$k = \frac{1}{t} \ln \frac{a}{a - x}$$

or $$k = \frac{2.303}{t} \log \frac{a}{a - x} \tag{1.21}$$

- The units of rate constant for a first order reaction from equation (1.21) is measured as $(\text{time})^{-1}$ and can be represented as sec^{-1}, min^{-1} or hour^{-1}.
- The half-life period for a first-order reaction may be obtained from equation (b) by substituting $t = t_{1/2}$ when $x = a/2$, i.e.

$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - a/2}$$

or $$t_{1/2} = \frac{2.303 \log 2}{k} \tag{1.22}$$

Thus, the half-life period of a first-order reaction is independent of initial concentration of reactant. Irrespective of how many times the initial concentration of reactant changes, the half-life period will remain same.

- Further, equation (1.21) can be rearranged as

$$\log (a - x) = -\frac{k}{2.303} t + \log a \tag{1.23}$$

which suggests that a plot of log $(a - x)$ versus time will give a straight line with a negative slope (k/2.303) and an intercept log a (Fig. 1.3).

Thus, in case of a first-order reaction a plot between log [conc.] and time will always be linear and with the help of slope, the value of rate constant can be obtained.

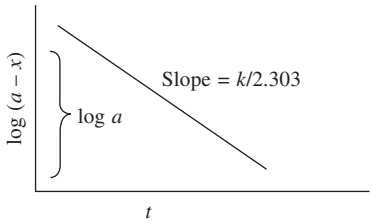

Fig. 1.3 The log [conc.] versus time plot for first-order reaction.

Examples

1. Inversion of cane sugar (sucrose)

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\text{D-glucose}}{C_6H_{12}O_6} + \underset{\text{D-fructose}}{C_6H_{12}O_6}$$

The reaction is pseudo-first order and rate is proportional to [Sucrose]. The progress of the reaction can be studied by measuring the change in specific rotation of a plane of polarised light by sucrose. Let r_0, r_t and r_∞ are the rotation at initially (when $t = 0$), at any time t and final rotation, respectively. The initial concentration a is proportional to $(r_0 - r_\infty)$ and concentration at any time t, $(a - x)$ is proportional to $(r_0 - r_t)$. Thus, the rate constant may be obtained as

$$k = \frac{2.303}{t} \log \frac{(r_0 - r_\infty)}{(r_t - r_\infty)} \tag{1.24}$$

2. The hydrolysis of ester in presence of acid

$$\underset{(a-x)}{CH_3COOC_2H_5} + H_2O \xrightarrow{H^+} CH_3\underset{(x)}{COOH} + C_2H_5OH$$

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

Since one of the product is acetic acid, the progress of reaction may be studied by titrating a known volume of reaction mixture against a standard alkali solution using phenolphthalein as indicator. Let V_0, V_t and V_∞ be the volumes of alkali required for titrating 10 ml of reaction mixture at zero time, at any time t and at the completion of the reaction, respectively.

V_0 = Amount of H^+ (catalyst) present in 10 ml of reaction mix.

V_t = Amount of H^+ (catalyst) in 10 ml of reactions mix + Amount of CH_3COOH formed at any time t.

V_∞ = Amount of H^+ (catalyst) present in 10 ml of reaction mix + Amount of CH_3COOH formed at the end of reaction (or amount of ester present initially because 1 mol of ester gives 1 mol of CH_3COOOH).

Thus, we can take $V_\infty - V_0 = a$

$$V_t - V_0 = x$$

or $$(V_\infty - V_0) - (V_t - V_0) = V_\infty - V_t = a - x$$

Therefore, the rate constant for the reaction may be obtained as

$$k = \frac{2.303}{t} \log \frac{(V_\infty - V_0)}{(V_\infty - V_t)} \tag{1.25}$$

3. Decomposition of N_2O_5

$$N_2O_5 \rightarrow 2\ NO_2 + {}^1/_2\ O_2$$

Nitrogen pentaoxide in carbon tetrachloride solution decomposes to give O_2.

The progress of reaction is monitored by measuring the volume of O_2 at different time intervals and using the relation

$$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t} \tag{1.26}$$

where V_∞ is the final value of O_2 when reaction is complete and corresponds to initial concentration of N_2O_5, V_t is the value of O_2 at any time t and $(V_\infty - V_t)$ corresponds to $(a - x)$.

4. Decomposition of H_2O_2 in aqueous solution

$$H_2O_2 \xrightarrow{Pt} H_2O + O$$

The concentration of H_2O_2 at different time intervals is determined by titrating the equal volume of reaction mixture against standard $KMnO_4$.

Problem 1.7 The specific rotation of sucrose in presence of hydrochloric acid at 35°C was measured and is given as follows:

Time (min)	0	20	40	80	180	500	∞
Rotation (°C)	32.4	28.8	25.5	19.6	10.3	6.1	–14.1

Calculate the rate constant at various time intervals and show that the reaction is first order.

Solution

$$k = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_t - r_\infty}$$

$$k_{20} = \frac{2.303}{20} \log \frac{32.4 - (-14.1)}{28.8 - (-14.1)} = -.00403\ \text{min}^{-1}$$

$$k_{40} = \frac{2.303}{40} \log \frac{32.4 - (-14.1)}{25.5 - (-14.1)} = -.00406\ \text{min}^{-1}$$

$$k_{80} = \frac{2.303}{80} \log \frac{32.4 - (-14.1)}{19.6 - (-14.1)} = -.004025 \text{ min}^{-1}$$

$$k_{200} = \frac{2.303}{200} \log \frac{32.4 - (-14.1)}{6.1 - (-14.1)} = -.004002 \text{ min}^{-1}$$

Average = 0.0040295 min^{-1}

Since the first order rate constant remains same, the reaction is of first order.

Problem 1.8 A first order reaction is 25% complete in 50 min. What would be concentration at the end of another 50 min if the initial concentration of the reactant is 5.0×10^3 mol dm^{-3}?

Solution Reaction is 25% consumed in 50 min. After 50 min the concentration c will be

$$a - x = 5.0 \times 10^3 - \frac{5.0 \times 10^3 \times 25}{100} = 3.75 \times 10^3$$

Now $$k = \frac{2.303}{t} \log \frac{C_0}{C} = \frac{2.303}{50} \log \frac{(5.0 \times 10^3)}{3.75 \times 10^3} = 5.375 \times 10^3 \text{ min}^{-1}$$

Again, concentration after another 50 min, i.e. (50 + 50 = 100 min)

$$c = c_0 \, e^{-kt} = 5.0 \times 10^3 \, e^{-(5.35 \times 10^{-3}/100)} = 2.81 \times 10^3 \text{ mol dm}^{-3}$$

Problem 1.9 Following observations were made for decomposition of a reactant at 35°C:

[A] mol dm^{-3}	Rate of decomposition $[-d[\text{A}]/dt]$ (mol dm^{-3} sec^{-1})
0.15	0.05
0.30	0.10
0.60	0.20

Find the order of reaction. Calculate rate constant and the rate of decomposition of A, when [A] = 0.45 mol dm^{-3}.

Solution It can be observed from the data that the rate of decomposition in directly proportional to [A], i.e.

$$-\frac{d[\text{A}]}{dt} \propto [\text{A}]$$

or

$$-\frac{d[\text{A}]}{dt} k [\text{A}]$$

where k is the rate constant. Hence, the reaction is first order.

$$k = \frac{-d[\text{A}]/dt}{[\text{A}]} = \frac{0.05}{0.15} = 0.33; \quad \frac{0.10}{0.30} = 0.33 \quad \text{and} \quad \frac{0.20}{0.60} = 0.33 \text{ sec}^{-1}$$

k (average) = 0.33 sec^{-1}

Again, rate of decomposition when [A] = 0.45 mol dm^{-3} is

$$-\frac{d[\text{A}]}{dt} = k\,[\text{A}] = 0.33\ (\text{sec}^{-1}) \times 0.45 \text{ mol dm}^{-3}$$

$$= 0.1485 \text{ mol dm}^{-3} \text{ sec}^{-1} = 0.15 \text{ mol dm}^{-3} \text{ sec}^{-1}$$

Problem 1.10 The kinetics of a reaction was followed by measuring the absorbance due to a reactant at its λ_{max} at 25°C. The log (absorbance) versus time (min) plot was a straight line with a negative slope (0.30×10^{-2}) and a positive intercept. Find the half-life period of reaction.

Solution When log $(a - x)$ versus time plot is straight line, the reaction is first order and slope gives the value of $k/2.303$ while intercept gives the value of log a.

$$\frac{\text{Rate constant } k}{2.303} = \text{Slope} = 0.30 \times 10^{-2}$$

Therefore, $$k = 0.6909 \times 10^{-2} \text{ min}^{-1}$$

$$\text{Half-life period } t_{1/2} = \frac{2.303 \log 2}{k\,(\text{min}^{-1})} = \frac{0.6939}{0.6939 \times 10^{-2}} = 100 \text{ min}$$

Problem 1.11 In a first order reaction the log (concentration of reactant) versus time plot was a straight line with a negative slope $\approx 0.50 \times 10^{4}$ sec^{-1}. Find the rate constant and half-life period of reaction.

Solution The equation of first order rate constant may be written as

$$\log (a - x) = -\frac{k}{2.303}\, t + \log a$$

Thus, plot of log $(a - x)$ versus time will be a straight line with a negative slope equal to $\frac{k}{2.303}$.

Therefore, $$\frac{k}{2.303} = \text{Slope} = 0.50 \times 10^{4} \text{ sec}^{-1}$$

or $$k = 2.303 \times 0.5 \times 10^{4} = 1.1515 \times 10^{4} \text{ sec}^{-1}$$