

CHEMICAL KINETICS

5.1 INTRODUCTION

In this chapter, we introduce fundamental aspects of chemical kinetics. Contents of the chapter cover the concept of the rate of reaction, factors affecting the rate of reaction, rate law expression and order of reaction, kinetics of simple zero, first, second and third order reactions, kinetics of opposing, parallel and consecutive reactions, various techniques used in determination of the order of reaction, mechanism of chemical reactions and various theories of reaction rates.

Chemical kinetics is the branch of chemistry which deals with the study of the rate of reaction, the factors affecting the rate of reaction such as concentration, pressure, temperature, surface area, catalyst etc and the mechanism of reaction.

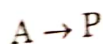
All the chemical reactions do not proceed at the same rate. For example, neutralization reaction is very fast, involving the mixing of a strong acid with a strong base and resulting in the formation of salt and water rapidly. Rusting of iron, on the other hand, is a very slow reaction and may take place over the years. A variety of reactions occur in nature which are neither too fast nor too slow, rather the rates of such reactions are intermediate between the two. Inversion of cane sugar in the presence of hydrochloric acid is one of such reactions.

It is very important to have the knowledge of rate of a chemical reaction in order to understand the mechanism of a reaction as well as to select the optimum conditions for industrial purposes, so that it may proceed at a rate to give maximum yield.

Chemical kinetics can be divided into two classes: homogeneous and heterogeneous kinetics. The branch of chemical kinetics which deals with the kinetics of reactions in single phase is called homogeneous kinetics. The branch of chemical kinetics which deals with the kinetics of reactions in two or more phases is called heterogeneous kinetics. This chapter is associated with homogeneous kinetics while chapter 6 of this book covers heterogeneous kinetics.

5.2 RATE OF REACTION

Rate of a reaction is defined as the change in molar concentration of any of reactant or product with respect to time. Consider the following reaction



in which a reactant A changes into the product P in time t. Rate of the above reaction in terms of the change in concentration of A with respect to time t is given by

$$\text{Rate of reaction} = \text{Rate of disappearance of A} = -\frac{d[A]}{dt}$$

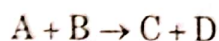
Where, the negative sign indicates the decrease in concentration of A with the passage of time.

Rate of the reaction in terms of the change in concentration of P with respect to time is given below

$$\text{Rate of reaction} = \text{Rate of appearance of P} = \frac{d[P]}{dt}$$

There is no negative sign as the concentration of the product increases with the passage of time.

Now we consider a some what more complex reaction



For such reaction, rate can be written in the following ways

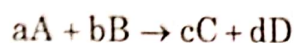
$$\text{Rate} = -\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Where,

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = \text{Rate of consumption of reactant}$$

$$\frac{d[C]}{dt} = \frac{d[D]}{dt} = \text{Rate of formation of product}$$

If in a reaction, the number of moles of the reactants or those of the products is not unity, e.g.



The rate of the reaction is written as

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

Where,

$$\text{Rate of consumption of A} = -\frac{d[A]}{dt}$$

$$\text{Rate of consumption of B} = -\frac{d[B]}{dt}$$

$$\text{Rate of formation of C} = \frac{d[C]}{dt}$$

$$\text{Rate of formation of D} = \frac{d[D]}{dt}$$

5.3 FACTORS AFFECTING THE RATE OF REACTION

Reaction rate has been found to increase with the increase in the concentration of reactants in case of liquids while it increases with pressure if the reactants are in gaseous state. Same is the case with surface area, i.e. greater the surface area, higher will be the rate of reaction, as more sites are available for the reaction to take place. Experiments have revealed the fact that the rate of a reaction increases with the increase in temperature. We shall discuss the factors affecting the rate of reaction in detail in later sections. Here, we introduce concentration dependence of the rate of reaction.

5.4 RATE LAW AND ORDER OF REACTION

Rate law for a reaction gives the concentration dependence of the rate of reaction. Rate law expression for an elementary reaction (single step) can be predicted from balanced chemical equation but it cannot be predicted for secondary reactions (involving more than one step). Since, chemical equation of reaction does not tell us whether the reaction is either elementary or secondary. Therefore the rate law for a reaction cannot be written without experimental verification. Consider the following reaction



in which a reactant A is going to the product P. The rate law expression for such a reaction can be written as

$$\text{Rate} \propto [A]^n$$

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

Above mathematical expression is a relation between the rate of reaction and the available concentration of A at any time t, where, proportionality constant k is the rate constant of the reaction which depends upon temperature and some other factors. Actually k is the rate of reaction when the available concentration of reactant is unity. The units of k depend upon the value of n. The exponent of concentration term in the rate law expression is called the order of reaction. Order of a reaction specifies the concentration dependence on the rate of that reaction. For example, when n is zero then the rate of reaction is independent of the concentration of reactant and when n is one then the rate of reaction is directly proportional to the available concentration of reactant and the reaction is called 1st order reaction. The concentration dependence of the rate of a reaction increases with the increase in the value of n. The experimental rate law for a general reaction $A + B + C \rightarrow P$ can be written as

$$\text{Rate} = k[A]^\alpha [B]^\beta [C]^\gamma$$

Where, $\alpha + \beta + \gamma$ is called overall order of reaction. α , β and γ represent the order of reaction with respect to A, B and C respectively. It means that the concentration dependence of the rate of a reaction may be different for one reactant from that of another.

$$k = \frac{1}{(n-m)} \left[\ln \frac{a(x-z)}{a'(x-z)} \right]$$

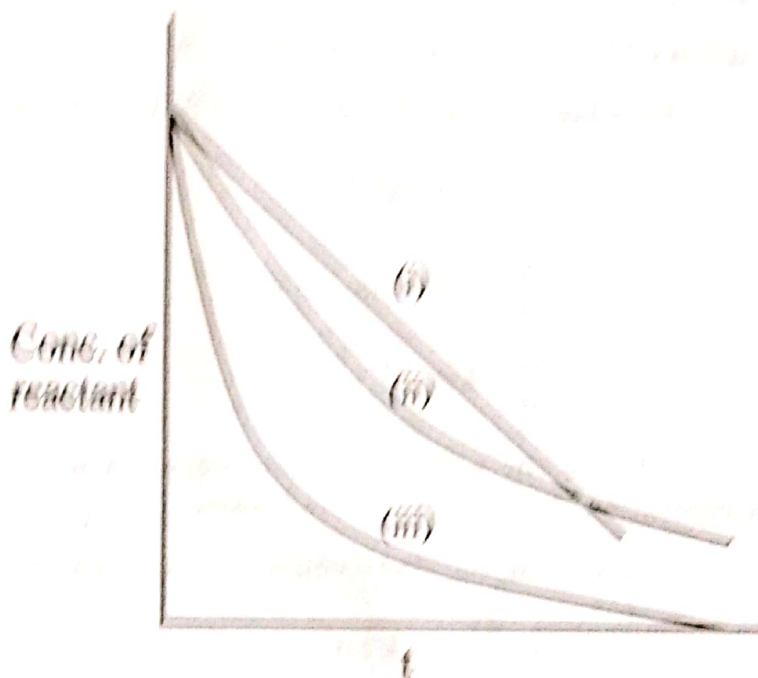
$$k = \frac{1}{m(a-x)^m}$$

$$k = m(a-x)^{m-1} x^{-1}$$

(A) Knowing the units of rate constant, the order of reaction can be predicted which, in this case, is 2.

Example 6.18

Variation in the reactant concentration with time is given in the following figure. Label the curves as zero, first and second order reaction for $A \rightarrow B$.



Solution

- (i) is zero order reaction
- (ii) is 1st order reaction
- (iii) is 2nd order reaction

The figure has been labelled so because with the increase in the order of reaction, the dependence of the concentration of reactant on time increases.

5.8 THIRD ORDER REACTIONS

In a third order reaction, the sum of exponents of the concentrations of reactants in the rate law is equal to three. The reaction between NO and H₂ to give N₂ and H₂O, which follows third order kinetics, is shown below



The rate law for the above reaction is given by

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

It is clear from the above equation that the reaction is third order. However, order of reaction can't be determined from balanced chemical equation. It is purely experimental quantity. Therefore order of reaction with respect to H₂ is one but order of reaction with respect to NO is two and overall order of reaction is three. The units of k are dm⁶ mol⁻² s⁻¹. Four different cases of 3rd order reactions have been discussed here.

5.2.1 When the Initial Concentration of all the Reactants is Same

Consider the following reaction in which A, B and C reactants are converting into products in an elementary reaction. All reactants have same initial concentration a . After time t , the concentration of each reactant becomes equal to $a-x$ as given below.

	A	+	B	+	C	→	Products
When $t = 0$	a		a		a		0
When $t = t$	$a - x$		$a - x$		$a - x$		x

Rate law for such a reaction can be written as

$$\frac{dx}{dt} = k[A][B][C]$$

$$\frac{dx}{dt} = k(a-x)(a-x)(a-x)$$

$$\frac{dx}{dt} = k(a-x)^3$$

This is the differential rate equation for a third order reaction in which concentration of all the reactants is same.

Integrating the above equation after separating variables, we get

$$\int \frac{dx}{(a-x)^3} = k \int dt$$

$$-\int (a-x)^{-3} (-1) dx = k \int dt$$

$$\frac{(a-x)^{-3+1}}{-3+1} = kt + c$$

$$\frac{1}{2(a-x)^2} = kt + c$$

(5.20)

When $t = 0$, $x = 0$, putting these values in equation (5.20), the value of c comes out to be

$$c = \frac{1}{2a^2}$$

Hence, equation (5.20) takes the form

$$\frac{1}{2(a-x)^2} = kt + \frac{1}{2a^2}$$

$$\frac{1}{(a-x)^2} = 2kt + \frac{1}{a^2}$$

(5.21)

This is the equation of straight line in intercept form. Plotting $1/(a-x)^2$ versus t , gives a straight line, the slope of which is equal to the $2k$.

$$\frac{1}{2(a-x)^2} - \frac{1}{2a^2} = kt$$

$$\frac{a^2 - a^2 - x^2 + 2ax}{2a^2(a-x)^2} = kt$$

$$\frac{-x^2 + 2ax}{2a^2(a-x)^2} = kt$$

$$\frac{x(2a-x)}{(a-x)^2} = 2a^2kt \quad (5.22)$$

Following results can be deduced from equation (5.22).

- (1) This is the equation of straight line passing through origin.
 (2) The plot of $x(2a-x)/(a-x)^2$ versus t gives a straight line the slope of which is given by

$$\text{Slope} = 2a^2k$$

Hence, the value of k can be determined from the slope as

$$k = \frac{\text{Slope}}{2a^2}$$

- (3) Units of k can be determined by rearranging equation (5.22)

$$k = \frac{1}{2a^2t} \frac{x(2a-x)}{(a-x)^2}$$

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

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

- (4) When $x = a/2 = 0.5a$, then $t = t_{1/2}$, putting these values in equation 5.22 and rearranging, half life period can be determined as

$$t = \frac{1}{2a^2k} \frac{x(2a-x)}{(a-x)^2}$$

$$t_{1/2} = \frac{1}{2a^2k} \frac{0.5a(2a-0.5a)}{(a-0.5a)^2}$$

$$t_{1/2} = \frac{3}{2ka^2} = \frac{1.5}{ka^2}$$

It is evident from the above equation that the half life period for a third order reaction is inversely proportional to the square of the initial concentration of the reactant.

Example 5.13

A third order reaction of the type $A \rightarrow P$ was started with initial concentration 0.5 M of A. The rate constant for the reaction is $2 \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$. Calculate half life period of the reaction.

Solution

From the given data, we have

Initial concentration of the reactant = $a = 0.5 \text{ mol dm}^{-3}$

Rate constant = $k = 2.1 \times 10^{-4} \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$

Half life = $t_{1/2} = ?$

We know that for a third order reaction half life period is

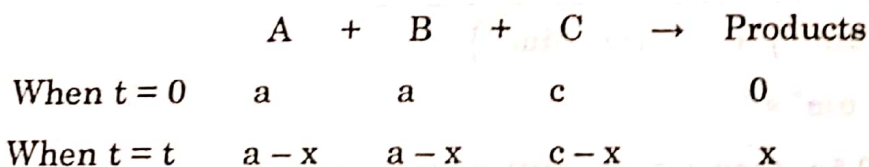
$$t_{1/2} = \frac{1.5}{ka^2}$$

By putting values in above equation, we get

$$t_{1/2} = \frac{3}{2(2.1 \times 10^{-4})(0.5)^2} = 2.85 \times 10^4 \text{ s}$$

5.8.2 When the Initial Concentration of Two Reactants is Same and that of the Third One is Different

Consider the following reaction in which the reactants A and B have same initial concentrations equal to a but reactant C has different concentration equal to c as given below.



Rate law for such a reaction is given by

$$\frac{dx}{dt} = k[A][B][C]$$

$$\frac{dx}{dt} = k(a-x)(a-x)(c-x)$$

$$\frac{dx}{dt} = k(a-x)^2(c-x)$$

This is the differential rate equation for a third order reaction in which the concentrations of two reactants are same and that of the third one is different.

Integrating the above equation, it will take the form

$$\int \frac{dx}{(a-x)^2(v-x)} = k \int dt \quad (5.23)$$

Using partial fraction, we can write as

$$\frac{1}{(a-x)^2(v-x)} = \frac{A}{(a-x)} + \frac{B}{(a-x)^2} + \frac{C}{(v-x)} \quad (5.24)$$

$$1 = A(a-x)(v-x) + B(v-x) + C(a-x)^2 \quad (5.25)$$

When $v-x=0$, then $x=v$ putting this value in equation (5.25), the value of C is obtained as

$$1 = A(0) + B(0) + C(a-v)^2$$

$$C = \frac{1}{(a-v)^2} \quad (5.26)$$

Solving equation (5.25), we get

$$1 = A(av - ax - vx + x^2) + B(v-x) + C(a^2 + x^2 - 2ax)$$

$$1 = Aav - Aax - Avx + Ax^2 + Bv - Bx + Ca^2 + Cx^2 - 2Cax \quad (5.27)$$

Comparing the coefficients of x^2 in equation 5.27, we have

$$0 = A + C$$

$$A = -C$$

Putting the value of C from equation (5.26), we get

$$A = -\frac{1}{(a-v)^2} \quad (5.28)$$

Comparing the coefficients of x in equation (5.27), we have

$$0 = -Aa - Av - B - 2Ca$$

$$0 = -A(a+v) - B - 2Ca$$

$$0 = \frac{(a+v)}{(a-v)^2} - B - \frac{2a}{(a-v)^2}$$

$$B = \frac{a+v-2a}{(a-v)^2}$$

$$B = \frac{v-a}{(a-v)^2} \quad (5.29)$$

Putting the values of A , B and C from equation (5.28), (5.29) and (5.26) respectively in equation (5.24), following equation is obtained as

$$\frac{1}{(a-x)^2(c-x)} = -\frac{1}{(a-c)^2(a-x)} + \frac{(c-a)}{(a-c)^2(a-x)^2} + \frac{1}{(a-c)^2(c-x)}$$

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

Integrating the above equation, we get

$$\int \frac{dx}{(a-x)^2(c-x)} = \frac{1}{(a-c)^2} \left[\int -\frac{dx}{(a-x)} + \int \frac{(c-a)dx}{(a-x)^2} + \int \frac{dx}{(c-x)} \right]$$

$$\int \frac{dx}{(a-x)^2(c-x)} = \frac{1}{(a-c)^2} \left[\int \frac{(-1)dx}{(a-x)} - (c-a) \int \frac{(-1)dx}{(a-x)^2} - \int \frac{(-1)dx}{(c-x)} \right]$$

Hence, equation (5.23) can be written as

$$\int \frac{1}{(a-c)^2} \left[\int \frac{(-1)dx}{(a-x)} - (c-a) \int \frac{(-1)dx}{(a-x)^2} - \int \frac{(-1)dx}{(c-x)} \right] = k \int dt$$

$$\frac{1}{(a-c)^2} \left[\ln(a-x) - (c-a) \left[\frac{(a-x)^{-2+1}}{-2+1} \right] - \ln(c-x) \right] = kt + c$$

$$\frac{1}{(a-c)^2} \left[\ln \frac{(a-x)}{(c-x)} + \frac{(c-a)}{(a-x)} \right] = kt + c \quad (5.30)$$

When $t = 0$, $x = 0$, putting these values in the above equation, the value of c can be determined as

$$\frac{1}{(a-c)^2} \left[\ln \frac{a}{c} + \frac{(c-a)}{a} \right] = c$$

Putting the value of c in equation (5.30), it will take the form

$$\frac{1}{(a-c)^2} \left[\ln \frac{(a-x)}{(c-x)} + \frac{(c-a)}{(a-x)} \right] = kt + \frac{1}{(a-c)^2} \left[\ln \frac{a}{c} + \frac{(c-a)}{a} \right]$$

$$\frac{1}{(a-c)^2} \left[\ln \frac{(a-x)}{(c-x)} + \frac{(c-a)}{(a-x)} \right] - \frac{1}{(a-c)^2} \left[\ln \frac{a}{c} + \frac{(c-a)}{a} \right] = kt$$

$$\frac{1}{(a-c)^2} \left[\ln \frac{(a-x)}{(c-x)} + \frac{(c-a)}{(a-x)} - \ln \frac{a}{c} - \frac{(c-a)}{a} \right] = kt$$

$$\frac{1}{(a-c)^2} \left[\ln \frac{c(a-x)}{a(c-x)} + (c-a) \left(\frac{a-a+x}{(a-x)a} \right) \right] = kt$$

$$\frac{1}{(a-c)^2} \left[\ln \frac{c(a-x)}{a(c-x)} + (c-a) \left(\frac{x}{(a-x)a} \right) \right] = kt$$

$$\ln \frac{c(a-x)}{a(c-x)} + \frac{x(c-a)}{a(a-x)} = (a-c)^2 kt \quad (5.31)$$

This is the equation of straight line passing through the origin, from the slope of which k can be determined if initial concentrations are known.

$$\text{Slope} = (a-c)^2 \times k$$

$$k = \frac{\text{Slope}}{(a-c)^2}$$

Units of k in above equation are $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$. Hence, the above equation is for 3rd order reaction. The half life period can't be determined for such type of reaction.

Example 5.14

Determine the units of k using equation (5.31).

Solution

Left hand side of the equation (5.31) is a dimensionless quantity. Hence,

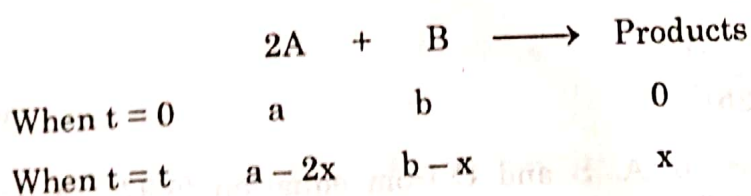
$$1 = \left\{ (\text{mol dm}^{-3})^2 \text{s} \right\} k$$

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

Hence the units of k are $\text{dm}^6 \text{mol}^{-2} \text{s}^{-1}$.

5.8.3 When only Two Reactants are Involved

Sometime the rate of a reaction has more dependence on the concentration of one reactant than that of the other. For example, 3rd order reactions, rate of reaction may be directly proportional to the square of concentration of one reactant and concentration of the other reactants. Consider a third order reaction of the type in which two moles of reactant A are reacting with one mole of reactant B to give products. The initial concentration of reactant A is a and that of B is b as given below.



$$\frac{dx}{dt} = k[A]^2[B]$$

$$\frac{dx}{dt} = k(a-2x)^2(b-x)$$

By separating variables in the above equation and integrating, we get

$$\int \frac{dx}{(a-2x)^2(b-x)} = k \int dt \quad (5.32)$$

$$\frac{1}{(a-2x)^2(b-x)} = \frac{A}{(a-2x)} + \frac{B}{(a-2x)^2} + \frac{C}{(b-x)} \quad (5.33)$$

$$1 = A(a-2x)(b-x) + B(b-x) + C(a-2x)^2 \quad (5.34)$$

When $b - x = 0$, $x = b$, putting these values in the above equation, we get

$$1 = A(0) + B(0) + C(a - 2b)^2$$

$$C = \frac{1}{(a - 2b)^2} \quad (5.35)$$

Solving equation (5.34), we get

$$1 = A(ab - ax - 2bx + 2x^2) + B(b - x) + C(a^2 - \overset{4x^2}{x^2} - 4ax)$$

$$1 = Aab - Aax - 2Abx + 2Ax^2 + Bb - Bx + Ca^2 - \overset{4Cx^2}{Cx^2} - 4Cax \quad (5.36)$$

Comparing the coefficients of x^2 in equation (5.36)

$$0 = 2A + 4C$$

$$2A = -4C$$

$$A = -\frac{2}{(a - 2b)^2} \quad (5.37)$$

Comparing the coefficients of x in equation (5.36)

$$0 = -Aa - 2Ab - B - 4Ca$$

$$B = -A(a + 2b) - 4Ca$$

$$B = \frac{2(a + 2b)}{(a - 2b)^2} - \frac{4a}{(a - 2b)^2}$$

$$B = \frac{2a + 4b - 4a}{(a - 2b)^2}$$

$$B = \frac{4b - 2a}{(a - 2b)^2}$$

$$B = \frac{2(2b - a)}{(a - 2b)^2} \quad (5.38)$$

Putting the values of A , B and C from equation (5.37), (5.38) and (5.35) respectively in equation (5.33), we get

$$\frac{1}{(a - 2x)^2 (b - x)} = \frac{-2}{(a - 2b)^2 (a - 2x)} + \frac{2(2b - a)}{(a - 2b)^2 (a - 2x)^2} + \frac{1}{(a - 2b)^2 (b - x)}$$

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

$$\int \frac{dx}{(a-2x)^2(b-x)} = \frac{1}{(a-2b)^2} \left[\int \frac{-2dx}{(a-2x)} - (2b-a) \int \frac{-2dx}{(a-2x)^2} - \int \frac{-2dx}{(b-x)} \right]$$

$$\int \frac{dx}{(a-2x)^2(b-x)} = \frac{1}{(a-2b)^2} \left[\ln(a-2x) - (2b-a) \left(\frac{(a-2x)^{-2+1}}{-2+1} \right) - \ln(b-x) \right]$$

$$\int \frac{dx}{(a-2x)^2(b-x)} = \frac{1}{(a-2b)^2} \left[\ln \frac{(a-2x)}{(b-x)} + \frac{(2b-a)}{(a-2x)} \right]$$

Comparing equation (5.32) with above equation

$$\frac{1}{(a-2b)^2} \left[\ln \frac{(a-2x)}{(b-x)} + \frac{(2b-a)}{(a-2x)} \right] = k \int dt$$

$$\frac{1}{(a-2b)^2} \left[\ln \frac{(a-2x)}{(b-x)} + \frac{(2b-a)}{(a-2x)} \right] = kt + c \quad (5.33)$$

When $t = 0$, $x = 0$, it implies

$$\frac{1}{(a-2b)^2} \left[\ln \frac{a}{b} + \frac{(2b-a)}{a} \right] = c$$

Putting the value of c in equation (5.33), we get

$$\frac{1}{(a-2b)^2} \left[\ln \frac{(a-2x)}{(b-x)} + \frac{(2b-a)}{(a-2x)} \right] = kt + \frac{1}{(a-2b)^2} \left[\ln \frac{a}{b} + \frac{(2b-a)}{a} \right]$$

$$\frac{1}{(a-2b)^2} \left[\ln \frac{(a-2x)}{(b-x)} + \frac{(2b-a)}{(a-2x)} \right] - \frac{1}{(a-2b)^2} \left[\ln \frac{a}{b} + \frac{(2b-a)}{a} \right] = kt$$

$$\frac{1}{(a-2b)^2} \left[\ln \frac{(a-2x)}{(b-x)} - \ln \frac{a}{b} + \frac{(2b-a)}{(a-2x)} - \frac{(2b-a)}{a} \right] = kt$$

$$\frac{1}{(a-2b)^2} \left[\ln \frac{(a-2x)}{(b-x)} - \ln \frac{a}{b} + (2b-a) \left(\frac{1}{(a-2x)} - \frac{1}{a} \right) \right] = kt$$

$$\frac{1}{(a-2b)^2} \left[\ln \frac{(a-2x)}{(b-x)} - \ln \frac{a}{b} + (2b-a) \left(\frac{a-a+2x}{(a-2x)a} \right) \right] = kt$$

$$\frac{1}{(a-2b)^2} \left[\ln \frac{b(a-2x)}{a(b-x)} + \frac{2x(2b-a)}{(a-2x)a} \right] = kt$$

$$\left[\ln \frac{b(a-2x)}{a(b-x)} + \frac{2x(2b-a)}{(a-2x)a} \right] = (a-2b)^2 kt \quad (5.40)$$

This is the equation of straight line passing through origin. The value of k can be determined from slope.

$$\text{Slope} = (a-2b)^2 \times k$$

$$k = \frac{\text{Slope}}{(a-2b)^2}$$

Example 5.15

According to equation (5.40), data was plotted for the reaction $2A + B \rightarrow P$ and slope of the plot was found to be 4 s^{-1} . Calculate the value of the rate constant when the initial concentrations of A and B are 0.2 and 0.3 M respectively.

Solution

From the given data, we have

$$\text{Slope} = 4 \text{ s}^{-1}$$

$$\text{Initial concentration of A} = a = 0.2 \text{ M}$$

$$\text{Initial concentration of B} = b = 0.3 \text{ M}$$

As we know that

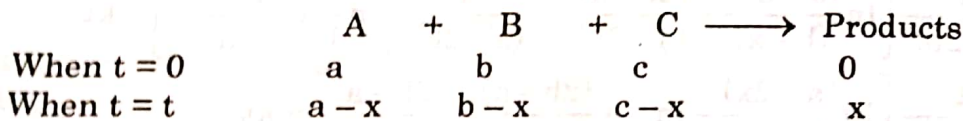
$$k = \frac{\text{Slope}}{(a - 2b)^2}$$

By putting values in above equation, we get

$$k = \frac{4}{[0.2 - 2(0.3)]^2} = 25 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

5.8.4 When the Initial Concentration of all the Reactants is Different

Consider the following reaction in which the initial concentration of reactants A, B and C are a, b and c respectively.



Rate law for the above reaction can be written as

$$\frac{dx}{dt} = k[A][B][C]$$

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

This is the differential rate equation for a third order reaction when the concentrations of all the reactants involved are different.

Separating the variables and integrating the resulting equation, we get

$$\int \frac{dx}{(a-x)(b-x)(c-x)} = k \int dt \quad (5.41)$$

Using partial fraction, we have

$$\frac{1}{(a-x)(b-x)(c-x)} = \frac{A}{a-x} + \frac{B}{b-x} + \frac{C}{c-x} \quad (5.42)$$

Multiplying both sides by $(a-x)(b-x)(c-x)$, we get

Example 5.15

According to equation (5.40), data was plotted for the reaction $2A + B \rightarrow P$ and slope of the plot was found to be 4 s^{-1} . Calculate the value of the rate constant when the initial concentrations of A and B are 0.2 and 0.3 M respectively.

Solution

From the given data, we have

$$\text{Slope} = 4 \text{ s}^{-1}$$

Initial concentration of A = $a = 0.2 \text{ M}$

Initial concentration of B = $b = 0.3 \text{ M}$

As we know that

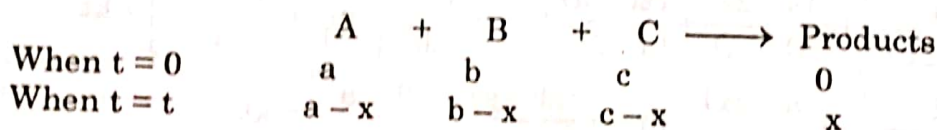
$$k = \frac{\text{Slope}}{(a - 2b)^2}$$

By putting values in above equation, we get

$$k = \frac{4}{[0.2 - 2(0.3)]^2} = 25 \text{ dm}^6 \text{ mol}^{-2} \text{ s}^{-1}$$

5.8.4 When the Initial Concentration of all the Reactants is Different

Consider the following reaction in which the initial concentration of reactants A, B and C are a, b and c respectively.



Rate law for the above reaction can be written as

$$\frac{dx}{dt} = k[A][B][C]$$

$$\frac{dx}{dt} = k(a-x)(b-x)(c-x)$$

This is the differential rate equation for a third order reaction when the concentrations of all the reactants involved are different.

Separating the variables and integrating the resulting equation, we get

$$\int \frac{dx}{(a-x)(b-x)(c-x)} = k \int dt \quad (5.41)$$

Using partial fraction, we have

$$\frac{1}{(a-x)(b-x)(c-x)} = \frac{A}{(a-x)} + \frac{B}{(b-x)} + \frac{C}{(c-x)} \quad (5.42)$$

Multiplying both sides by $(a-x)(b-x)(c-x)$, we get

$$1 = A(b-x)(c-x) + B(a-x)(c-x) + C(a-x)(b-x) \quad (5.43)$$

When $a-x=0$, then $x=a$, putting this value in equation (5.43), we get

$$1 = A(b-a)(c-a) + B(0) + C(0)$$

$$1 = A(b-a)(c-a)$$

$$A = -\frac{1}{(b-a)(c-a)}$$

Multiplying and dividing the right hand side of the above equation by $(b-c)$, the value of A will be

$$A = -\frac{b-c}{(a-b)(b-c)(c-a)} \quad (5.44)$$

When $b-x=0$, then $x=b$, putting this value in equation (5.43), the value of B can be determined as

$$1 = A(0) + B(a-b)(c-b) + C(0)$$

$$1 = -B(a-b)(c-b)$$

$$B = -\frac{1}{(a-b)(c-b)}$$

Multiplying and dividing the right hand side of the above equation by $(c-a)$, the value of B will be

$$B = -\frac{c-a}{(a-b)(b-c)(c-a)} \quad (5.45)$$

When $c-x=0$, $x=c$, putting this value of x in equation (5.43), the value of C is obtained as

$$1 = A(0) + B(0) + C(a-c)(b-c)$$

$$1 = -C(c-a)(b-c)$$

$$C = -\frac{1}{(c-a)(b-c)}$$

Multiplying and dividing the right hand side of the above equation by $(a-b)$, the equation will take the form

$$C = -\frac{a-b}{(a-b)(b-c)(c-a)} \quad (5.46)$$

Using equation (5.44), (5.45) and (5.46), equation (5.42) can be written as

$$\frac{1}{(a-x)(b-x)(c-x)} = -\frac{b-c}{(a-b)(b-c)(c-a)(a-x)} - \frac{c-a}{(a-b)(b-c)(c-a)(b-x)} - \frac{a-b}{(a-b)(b-c)(c-a)(c-x)}$$

$$\frac{1}{(a-x)(b-x)(c-x)} = \frac{1}{(a-b)(b-c)(c-a)} \left[\frac{b-c}{(a-x)} - \frac{c-a}{(b-x)} + \frac{a-b}{(c-x)} \right]$$

Integrating the above equation, we get

$$\int \frac{dx}{(a-x)(b-x)(c-x)} = \frac{1}{(a-b)(b-c)(c-a)} \int \left[\frac{b-c}{(a-x)} - \frac{c-a}{(b-x)} + \frac{a-b}{(c-x)} \right] dx$$

Comparing above equation with equation (5.41)

$$k \int dt = \frac{1}{(a-b)(b-c)(c-a)} \int \left[\frac{b-c}{(a-x)} - \frac{c-a}{(b-x)} + \frac{a-b}{(c-x)} \right] dx$$

$$kt + c = \frac{\left[-(b-c) \int \frac{(-1)dx}{(a-x)} + (c-a) \int \frac{(-1)dx}{(b-x)} + (a-b) \int \frac{(-1)dx}{(c-x)} \right]}{(a-b)(b-c)(c-a)}$$

$$kt + c = \frac{\left[-(b-c) \ln(a-x) + (c-a) \ln(b-x) + (a-b) \ln(c-x) \right]}{(a-b)(b-c)(c-a)}$$

When $t = 0$, then $x = 0$, putting these values in the above equation, the value of constant can be determined to be

$$c = \frac{\left[-(b-c) \ln(a-0) + (c-a) \ln(b-0) + (a-b) \ln(c-0) \right]}{(a-b)(b-c)(c-a)}$$

$$c = \frac{\left[-(b-c) \ln a + (c-a) \ln b + (a-b) \ln c \right]}{(a-b)(b-c)(c-a)}$$

Putting the value of constant in the above equation, we get

$$kt + \frac{\left[-(b-c) \ln a + (c-a) \ln b + (a-b) \ln c \right]}{(a-b)(b-c)(c-a)} =$$

$$\frac{\left[-(b-c) \ln(a-x) + (c-a) \ln(b-x) + (a-b) \ln(c-x) \right]}{(a-b)(b-c)(c-a)}$$

$$kt = \left(\frac{1}{(a-b)(b-c)(c-a)} \right) \left[-(b-c) \ln(a-x) + (c-a) \ln(b-x) + (a-b) \right]$$

$$\ln(c-x) - \left[-(b-c) \ln a + (c-a) \ln b + (a-b) \ln c \right]$$

$$kt = \left(\frac{1}{(a-b)(b-c)(c-a)} \right) \left[-(b-c) \ln(a-x) + (c-a) \ln(b-x) + (a-b) \right]$$

$$\ln(c-x) + (b-c) \ln a - (c-a) \ln b - (a-b) \ln c$$

$$kt = \left(\frac{1}{(a-b)(b-c)(c-a)} \right) \left[(b-c) \ln \frac{(a-x)}{a} + (c-a) \ln \frac{(b-x)}{b} + (a-b) \right]$$

$$\ln \frac{(c-x)}{c}$$

$$(a-b)(b-c)(c-a)kt = (b-c)\ln\frac{(a-x)}{a} + (c-a)\ln\frac{(b-x)}{b} + (a-b)\ln\frac{(c-x)}{c} \quad (5.47)$$

This is the integrated rate equation for a third order reaction in which the concentrations of all the reactants are different.

This is the equation of straight line passing through origin, where the left hand side of the equation represents the dependent variable and t is the independent variable. The plot will give a straight line whose slope is given as

$$\text{Slope} = (a-b)(b-c)(c-a)k$$

$$k = \frac{\text{Slope}}{(a-b)(b-c)(c-a)}$$

Hence, the value of k can be determined if the initial concentrations of all the three reactants are known.

Units of k can be determined by rearranging equation (5.47) as follows

$$k = \frac{(b-c)\ln\frac{(a-x)}{a} + (c-a)\ln\frac{(b-x)}{b} + (a-b)\ln\frac{(c-x)}{c}}{(a-b)(b-c)(c-a)t}$$

$$k = \frac{\text{mol dm}^{-3}}{(\text{mol dm}^{-3})^3 \text{ s}}$$

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

5.9 OPPOSING REACTIONS

In opposing reactions, the products, after being formed, react to give back the reactants. In the beginning of the reaction, the reactants combine to give products, as a result of which the concentration of the reactants decreases and that of the products increases with the passage of time. As the reaction proceeds further, the products also react to give back the reactants i.e. a backward reaction also takes place along with the forward reaction. After some time, the rate of forward

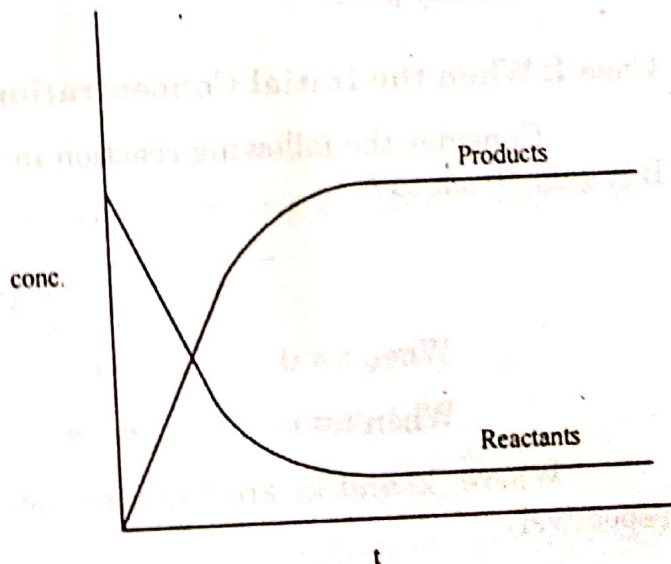


Fig. 5.8 Variation in the concentrations of reactants and products with the passage of