1 Introduction to kinetics

1.1. Introduction

Chemical reactions can be studied in two general ways. The direction that a reaction is likely to take and the concentrations at equilibrium can be predicted from the free energies of the reactants and products of the reaction. This thermodynamic approach to the study of a chemical reaction gives no information about the rate at which the reaction proceeds to equilibrium. The kinetic approach, however, is concerned with the rates at which reactions occur and with the factors that affect the rate of a reaction, such as pH, temperature, presence of catalysts, and is therefore essentially an experimental investigation. The interpretation of the kinetic results obtained for a chemical reaction and their dependence on other factors can lead to a fuller understanding of the mechanism of the reaction. The difference between the thermodynamic and kinetic approaches to the study of a chemical reaction can be seen more fully by considering the reaction between hydrogen and oxygen. Thermodynamic calculations indicate that this reaction should proceed spontaneously since it is accompanied by a large decrease in free energy. No reaction is detectable at room temperature and atmospheric pressure, however, even over a period of years. The introduction of a catalyst or spark causes the reaction to proceed at a considerable rate. An explanation of this will be given later.

1.2. Reaction rates

Before discussing the effects of enzymes on the rates of reactions, it is necessary to introduce a number of terms and relationships that frequently occur in chemical kinetics. Chemical reactions may be classified in two ways. They may be described on the basis of the number of molecules that react to form products (molecularity). Thus reactions such as

$$\mathrm{A} \xrightarrow{k} \mathrm{B} \tag{1.1}$$

are *unimolecular* whereas reactions such as

$$A + B \xrightarrow{k} C$$

are *bimolecular*. These reactions may also be classified on a kinetic basis, i.e. by *reaction order*. Thus if the rate, v, of a reaction is proportional to the concentration of only one component,

$$v = kc, \tag{1.2}$$

then the reaction is said to be *first order*. The proportionality constant, k, is the *rate constant* for the reaction. In equation (1.1) the rate of the reaction, v, is proportional to the concentration of reactant A. The rate of the reaction can be described either by the rate of loss of A or by the rate of formation of B. Thus the velocity

$$v = -\frac{d[A]}{dt} = \frac{d[B]}{dt}.$$

Therefore

$$-\frac{d[A]}{dt} = \frac{d[B]}{dt} = k[A]. \tag{1.3}$$

An equation like (1.3) is called a *rate equation*. Rate equations are *differential equations* that may be integrated to give equations into which the experimental results may be substituted directly. An example of a first order reaction is the decomposition of ethane,

$$C_2H_6 \xrightarrow{k} C_2H_4 + H_2.$$

The rate of production of ethylene is proportional to the concentration of ethane present,

$$\frac{d[C_2H_4]}{dt} = \frac{d[H_2]}{dt} = k[C_2H_6].$$

A *second order* reaction can be of two types; the rate of reaction can depend on the square of a single concentration

$$v = kc^2$$

or it can depend on the product of the concentrations of two reacting species,

$$v = kc_a c_b. \tag{1.4}$$

In general the overall order, n, of a reaction is the sum of the powers

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of the concentrations of the reactants. Thus if

$$v = kc_a^{n_a}c_b^{n_b}$$

then the order, n, of the reaction is given by

$$n = n_a + n_b.$$

An example of the first type of second order reaction is the decomposition of hydrogen iodide into hydrogen and iodine.

$$2\mathrm{HI} \xrightarrow{k_f} \mathrm{H_2} + \mathrm{I_2},$$

thus

$$v = \frac{\mathrm{d[H_2]}}{\mathrm{d}t} = \frac{\mathrm{d[I_2]}}{\mathrm{d}t} = k_f[\mathrm{HI}]^2.$$

The reverse reaction is also second order and is an example of the second type:

$$\mathrm{H_2} + \mathrm{I_2} \xrightarrow{k_r} 2\mathrm{HI}.$$

The rate of the reaction v is given by

$$v = k_r[\mathrm{H_2}]\,[\mathrm{I_2}].$$

It must be stressed that the order of a reaction is an experimental quantity and cannot necessarily be deduced from the chemical equation. The reaction between hydrogen and bromine can be described by an equation similar to that for the reaction between hydrogen and iodine:

$$\mathrm{H_2} + \mathrm{Br_2} \xrightarrow{k} 2\mathrm{HBr}. \tag{1.5}$$

At first sight the reaction might be thought to be second order, but an investigation of the experimental conditions that affect the rate of production of hydrogen bromide shows that it obeys a complex rate equation

$$\frac{\mathrm{d[HBr]}}{\mathrm{d}t} = \frac{k[\mathrm{H_2}]\,[\mathrm{Br_2}]^{1/2}}{1 + k'([\mathrm{HBr}]/[\mathrm{Br_2}])}.$$

The fact that the reaction between hydrogen and bromine is not a simple second order reaction indicates that the reaction does not take place according to the simple reaction scheme described in equation (1.5).

Third order reactions, which depend on the product of three concentration terms, are relatively rare. Some chemical reactions have rates which are independent of the concentration of any reactant and the kinetics of these reactions are *zero order*. As will be seen later, many

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catalysed reactions are zero order with respect to the reactants; the rate of the reaction depends only on the concentration of the catalyst. Consider the reaction,

$$A + B \xrightarrow{k} C;$$

the rate equation that describes this reaction is

$$v = \frac{d[C]}{dt} = k[A][B].$$

The reaction is normally second order. If the concentration of one of the reactants is much higher than the other, e.g. $[B] \gg [A]$, then the concentration of B will not change appreciably during the course of the reaction. The rate will therefore appear to depend solely on the concentration of A. The reaction is said to obey *pseudo first order* kinetics. The apparent rate constant, k', is given by the equation

$$\frac{d[C]}{dt} = k'[A],$$

where $k' = k[B]$.
The reaction is therefore *zero order* with respect to reactant B.

The rate constant, k, is numerically equal to the rate of the reaction when the concentration of all the reactants is unity. Its *dimensions* can be deduced from the rate equation and will vary with the order of the reaction. For a first order reaction, equation (1.2), the units of k are those of velocity, v, (mol l^{-1} s^{-1}) divided by those of concentration, c, (mol l^{-1}) and are therefore s^{-1}. For a second order reaction, equation (1.4), the units of k will be those of velocity, v, (mol l^{-1} s^{-1}) divided by the product of c_a and c_b (mol l^{-1})^2 and are therefore l mol^{-1} s^{-1}. In general for a reaction of order n, the dimensions of k are mol$^{(1-n)}$ l$^{(n-1)}$ s^{-1}.

1.3. Analysis of kinetic results

In a kinetic study of a chemical reaction, the change in concentration with time of one or more reactants or products is followed. The change in concentration of a reactant or product may be determined directly or indirectly by following the change in some other parameter related to concentration, e.g. change in optical density, fluorescence, pH, or by measuring the acid or alkali uptake required to maintain a constant pH. In order that the rate constant and order of reaction may be determined from these results, it is necessary to convert the rate equation into more

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suitable forms. Since the rate equations are differential equations there are two methods of determining the rate constant and order of reaction.

1.3.1. Differential method. The differential method uses the differential equation directly. The term dx/dt (where x represents the concentration of product formed or reactant consumed in time t) refers to the rate of the reaction. From a plot of x against time the slope of the graph (dx/dt) at various values of x can be determined and these values are substituted directly into the rate equation (see fig. 1.1). Although apparently simple, it lacks accuracy owing to the difficulty in determining the slope of a curve, especially if the curve is not smooth. Alternatively, instead of determining the velocity at various points along a curve, the initial velocity of the reaction is measured at the very beginning of the curve, and this process is repeated at different initial concentrations of substrate(s) (see fig. 1.2). Determination of the initial rate of the

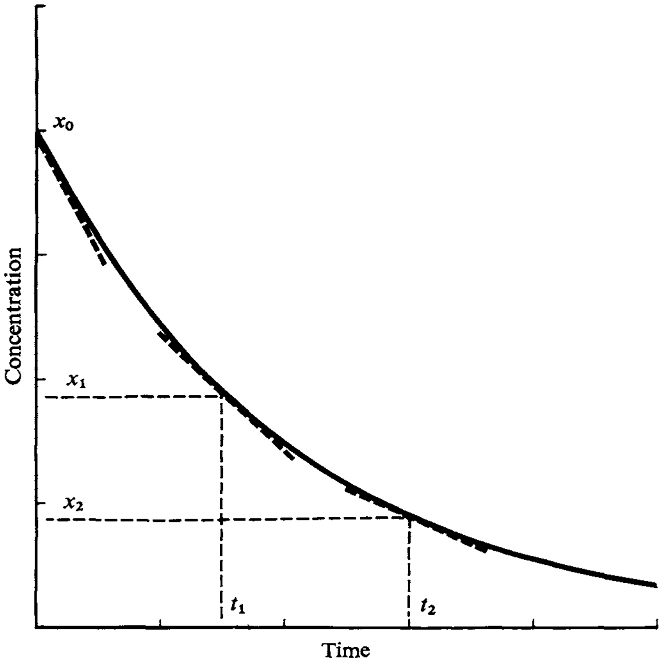

Fig. 1.1. Schematic plot of concentration against time. Tangents (dx/dt) are drawn at the initial concentration x_0 at $t = 0$ and at concentrations x_1 and x_2 at times t_1 and t_2 respectively.

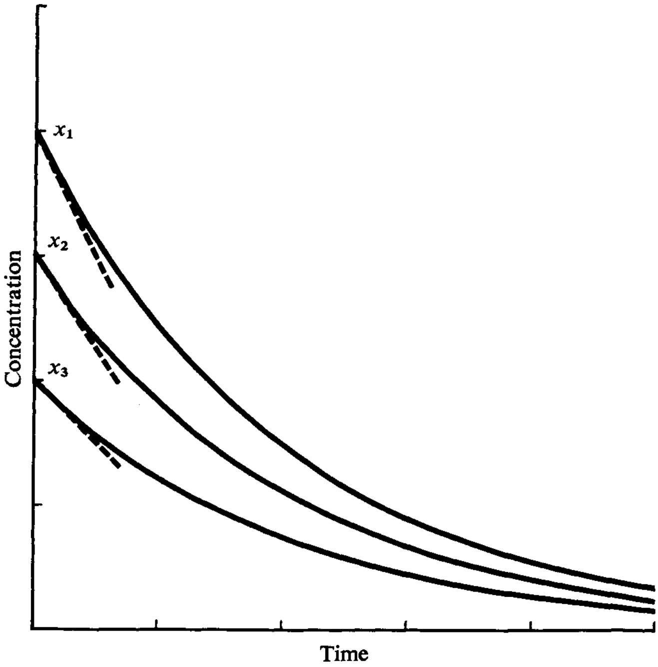

Fig. 1.2. Schematic plot illustrating the determination of initial velocities at $t = 0$ for three different concentrations of x.

reaction has an advantage, since no products have been formed that could modify the reaction mechanism during the course of the reaction.

The rate of the reaction can be related to the concentration by the equation,

$$v = kc^n.$$

Taking logarithms, a linear equation is obtained,

$$\ln v = \ln k + n \ln c,$$

so that a plot of $\ln v$ against $\ln c$ should be a straight line of slope n, the order of the reaction, and intercept $\ln k$ where k is the rate constant for the reaction.

1.3.2. Integration method. This method involves integrating the various rate equations and obtaining a solution for the variation of the concentration of a reactant x with time.

Zero order kinetics. Reactions of zero order are not common except in heterogeneous systems and in catalysed reactions in solution. The rate of the reaction is independent of the concentration of the reactants,

$$v = \frac{\mathrm{d}x}{\mathrm{d}t} = k,$$

where x is the concentration of the product formed. Integration of this equation with respect to time gives

$$x = kt + c.$$

Since $x = 0$ when $t = 0$, then $c = 0$. Therefore

$$x = kt,$$

which is the equation of a straight line of slope k passing through the origin. The dimensions of k are mol l^{-1} s^{-1}. The *half life* of a reaction is the time taken for half of the reactant to be consumed or half of the product to be produced. For zero order kinetics, $t = t_{1/2}$ when $x = x_0/2$ (where x_0 is the initial concentration of the reactant or final concentration of the product). Therefore

$$t_{1/2} = \frac{x_0}{2k}.$$

The half life is proportional to the initial concentration of reactant or final concentration of product.

First order reactions. A first order reaction can be described by the equation

$$\mathrm{A} \xrightarrow{k} \mathrm{B}.$$

Let the initial concentration of A at $t = 0$ be a, while the concentration of B at this time is zero. After a time t, a quantity x has been transformed from A into B; therefore the new concentrations of A and B are respectively $(a - x)$ and x. The rate of formation of B is $\mathrm{d}x/\mathrm{d}t$ so that

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a - x),$$

which can be integrated to give

$$-\ln (a - x) = kt + c.$$

Since $x = 0$ when $t = 0$, $c = -\ln a$ and hence the complete solution for the equation is

$$\ln [a/(a - x)] = kt. \tag{1.6}$$

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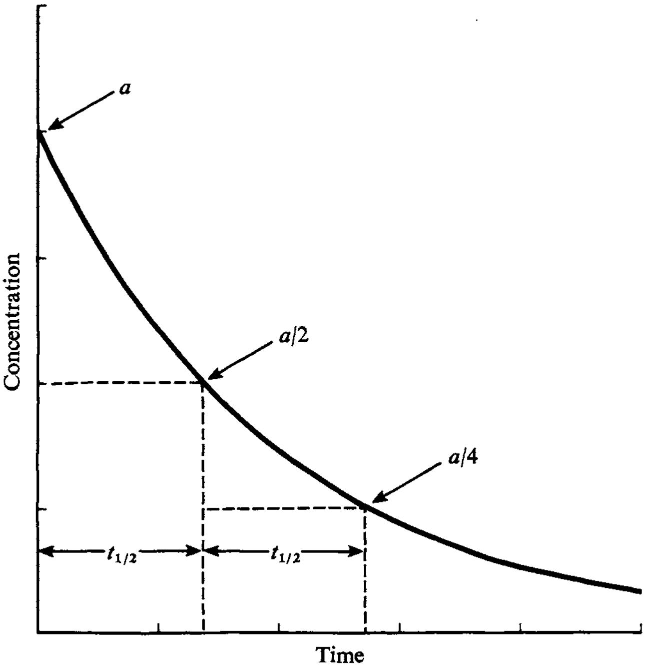

Fig. 1.3. Schematic plot of a first order exponential decay process. The half life ($t_{1/2}$) can be used to determine the rate constant k.

The equation can be written in the alternative exponential form as

$$(a-x) = ae^{-kt}.$$

This shows that the concentration, $(a-x)$, of the reactant decays exponentially with time from an initial value a at $t = 0$ to zero at $t = \infty$ (see fig. 1.3). From equation (1.6), it can be seen that the rate constant k depends on the ratio of two concentrations and has the dimensions of 1/time or s^{-1}. There are two important points regarding first order reactions. First, the rate constant, k, can be determined from the *ratio* of two concentrations determined at two times; the actual values of the concentrations are not needed. Secondly, the half life of the reaction is a constant and does not depend on the initial concentration. Since $t = t_{1/2}$ when $x = a/2$, substitution in equation (1.6) gives

$$kt_{1/2} = \ln 2$$

or $$t_{1/2} = \frac{0.693}{k}. \qquad (1.7)$$

Provided a reaction follows first order kinetics, the time taken for 50% of the reaction to be completed cannot be altered by changing the concentration of the reactant A. From equation (1.7), it can be seen that the determination of the half life of the reaction gives the rate constant k directly. This is a useful semiquantitive way to determine the rate constant. For accurate determinations of the rate constant, a linear regression analysis (see appendix II) of $\ln(a/(a-x))$ or $\ln(a-x)$ against time t is recommended.

Second order reactions. This is the most common order of reaction that occurs. A second order reaction may be expected to occur if the reaction takes place in a single step and the concentrations of the reactants are of similar magnitudes. As mentioned previously, second order reactions can be of two types:

$$2\mathrm{A} \longrightarrow \mathrm{B} \tag{1.8}$$

or

$$\mathrm{A}+\mathrm{B} \longrightarrow \mathrm{C}. \tag{1.9}$$

For equation (1.8), the rate equation is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-x)^2,$$

where a is the initial concentration of A at $t=0$ and x is the concentration of product at time t. This equation can be rearranged to give

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

which can be integrated directly to give

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

Since at $t=0$, $x=0$, then $c = 1/a$ so that the complete solution becomes

$$\frac{1}{(a-x)} = kt + \frac{1}{a} \tag{1.10}$$

or

$$kt = \frac{x}{a(a-x)}.$$

From equation (1.10) a plot of $1/(a-x)$ against time t is a straight line of slope k and intercept $1/a$. The half life, $t_{1/2}$, can be evaluated by putting

$x = a/2$, hence

$$t_{1/2} = \frac{1}{ka}\cdot$$

The half life of the reaction is now inversely proportional to the initial concentration of reactant A as well as to the rate constant k. This means that an increase in the concentration of A will reduce the time taken to reach 50% reaction.

For the reaction between two different substances, equation (1.9), the rate equation is

$$\frac{\mathrm{d}x}{\mathrm{d}t} = k(a-x)(b-x), \tag{1.11}$$

where a and b are the initial concentrations of reactants A and B and x is the concentration of product at time t. Rearranging equation (1.11) gives

$$\frac{\mathrm{d}x}{(a-x)(b-x)} = k\mathrm{d}t,$$

which can be integrated by the method of partial fractions giving

$$\frac{-1}{(b-a)}\ln(a-x) - \frac{1}{(a-b)}\ln(b-x) = kt + c, \tag{1.12}$$

and since $x = 0$ at $t = 0$, then

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

Hence the complete solution of equation (1.12) is

$$\ln\frac{(a-x)}{(b-x)} = (a-b)kt + \ln\frac{a}{b}\cdot \tag{1.13}$$

From equation (1.13), a plot of $\ln(a-x)/(b-x)$ against time is a straight line of slope $(a-b)k$ and an intercept $\ln a/b$. In this reaction, in which the initial concentrations of the reactants may be different, the evaluation of the half life is not a meaningful concept. Nevertheless it is apparent that an increase in concentration of either reactant will lead to a decrease in reaction time.

Equations with non-integral orders of reaction. There are many reactions in which the rate of reaction does not depend on the concentrations