

## CHAPTER II

### PRINCIPLE OF CHEMICAL KINETICS

Chemical kinetics is concerned with the dynamics of chemical reactions and the details of the process whereby a system gets from one state to another and with the time required for the transition. In particular, it deals with the rates of chemical reactions and reaction mechanisms. Ideally, a complete reaction mechanism would involve a knowledge of all the molecular details of the reaction, including the energies and stereochemistry, e.g., interatomic-distances and bond angles throughout the course of the reaction of the individual molecular steps involved in the mechanism.

The earliest kinetic investigations were made upon systems where the changes of concentrations of a reactant or product could easily be followed by chemical analysis over period of time. The concentration can be expressed in any convenient unit quantity per unit volume, e.g., moles per liter, moles per cubic centimeter, or grams per cubic centimeter. The rate will be defined as a positive quantity, regardless of the component whose concentration changes are measured. In a general stoichiometric reaction:



The rate can be expressed as  $-\frac{d[A]}{dt}$ ,  $-\frac{d[B]}{dt}$ ,  $\frac{d[C]}{dt}$  or  $\frac{d[D]}{dt}$  ;

where A , B , C and D denote concentration. Variables other

than concentration may be used in defining rate, e.g., pressure as in a gas reaction or optical rotation as in a racemization inversion or mutarotation reaction. In general the reaction rate can be a function of all the species present in a reaction mixture. Thus

$$R = f(C_1, C_2, \dots, C_j)$$

This equation is called the rate law for a given reaction. The manner in which the rate of a reaction varies with the concentrations of the reacting substances can sometimes be indicated by stating the order of reaction, so that

$$\text{Rate} = K C_A^\alpha C_B^\beta \dots\dots\dots$$

the overall order of the reaction is simply

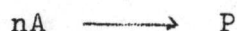
$$n = \alpha + \beta + \dots\dots\dots$$

Such a reaction would be said to be of the  $\alpha$ th order with respect to A, the  $\beta$ th order with respect to B.

The rate of elementary reaction depends on two things only: the frequency of encounters of kind described by the left hand side of its reaction equation, and the fraction of encounters that are reactive. In experiment performed at constant temperature, the encounter frequency is directly proportional to the concentration of each species represented. Unimolecular reactions with one species on the left hand side of the reaction equation, have rates proportional to one concentration. Bimolecular reactions have rates proportional

to the product of two concentrations, or, if the encounter is between two identical molecules, to the square of one concentration. Termolecular reactions have rates proportional to the product of three concentrations, or to the cube of one concentration.

In a kinetic study of a reaction there is no way of measuring the rate directly in a simple manner; normally the rate is measured at constant temperature by various methods which allow the concentration of either reactants or products to be followed with time. It is fairly easy to show experimentally that the rates of chemical reactions vary with time, but careful experiments are needed to show that this variation is regular and can be described by a mathematical equation. Thus consider the reaction:



If  $X$  is the amount of  $A$  per unit volume that has disappeared in time  $t$ , the amount of  $A$  remaining is  $a_0 - X$ ; the rate of disappearance of  $A$  is thus

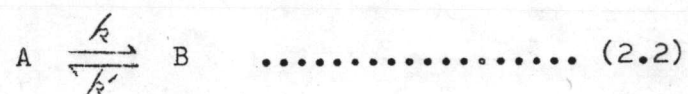
$$-\frac{d[a_0 - X]}{dt} = -\frac{d[A]}{dt} = \frac{dX}{dt} = k [a_0 - X]^n$$

If  $n$  is other than unity, the solution is

$$k = \frac{1}{t(n-1)} \left[ \frac{1}{(a_0 - X)^{n-1}} - \frac{1}{a_0^{n-1}} \right] \dots\dots (2.1)$$

Some methods may be used for yielding the integrated equation to the experimental data such as graphical method, half life method etc.

It is now necessary to consider the complications arising from the possibility of the occurrence of other process at the same time, e.g., reversible reaction. When a process is reversible, in the chemical sense, the direct and reverse reactions must occur simultaneously, and if the latter is appreciable it must be taken into account. The simplest case to consider is that in which both reactions are of the first order; thus



If  $a_0$  is the concentration of A at the commencement of the experiment, then after time  $t$  the concentration of A and B will be  $a_0 - X$  and  $X$  respectively, so that the net rate of reaction at any instant will be given by

$$\frac{dX}{dt} = k(a_0 - X) - k'X \dots\dots\dots (2.3)$$

where  $k$  is the specific rate of the forward reaction and  $k'$  that of the reverse reaction. When system reaches equilibrium the rates of the two reactions are equal, so that

$$k(a_0 - X_e) = k'X_e \dots\dots\dots (2.4)$$

where  $X_e$  is the amount of B formed or of A destroyed at equilibrium. For any reversible reaction the equilibrium constant  $K_e$  is equal to the ratio of the velocity constants of direct and reverse reactions, provided the systems are virtually ideal so that the kinetics factors (10) are almost unity; that is

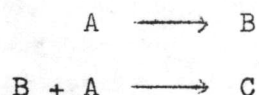
$$K_e = \frac{k}{k'}$$

The basic principle underlying the derivations of the rate law for a mechanism is the principle of mass action. The rate of any elementary reaction is proportional to the frequency of encounters indicated by the chemical equation of the elementary reaction, hence product of concentrations can be used instead. Three notations were used to facilitate this principle of rate law:

First, it is sometimes possible to neglect reverse reactions. This will clearly be satisfactory in the early stages of any reaction, since only low concentrations of the product molecules will be available to serve as reactants for the reverse reactions. It will also be true for later stages if the equilibrium constant of the elementary reaction is large, since in that case the large forward rate constant  $K = K_{eq} \times K_r$  will keep the forward rate much larger than the reverse rate until the product concentrations are much larger than the reactant concentrations.

Second idea is the rate limiting step. A mechanism may contain a sequence of elementary reactions one of which has a much slower rate than the others.

The third idea is called the steady state approximation. In a sequential mechanism such as



It may happen that one or more of the intermediate species has equal

rates of production and destruction following the increase in concentration at the commencing of the reaction. This assumption that intermediate concentrations are at a steady state value can sometimes be subjected to the experimental test.

The equilibrium state mentioned in the previous paragraph (equations (2.3) and (2.4)) is in fact a special kinetic state, namely, that state in which the net change of all components with respect to time is equal to zero. Thus the natural explanation about the reaction rate of such a state is inevitably involving an equilibrium between average molecules and high energy molecules in the initial state and in the so called "transition state" or "activated complex".

The rates of most chemical reactions are very sensitive to temperature changes. The first quantity formulation of the dependence of reaction rates on temperature was given by Arrhenius<sup>(11)</sup> who proposed the following relationship between specific rate constant,  $k$  and the absolute temperature,  $T$

$$k = A e^{-E_a/RT}$$

Where  $A$  is a constant known as the frequency factor and  $E_a$  is known as activation energy,  $R$  is a gas constant. Generally it is necessary for the reaction to be carried out in a system that is carefully maintained at constant temperature.

Reactions in liquids differ markedly from reactions in the gas phase because of the presence of solvent molecules, which are always in intimate contact with the reactants and, in fact, often interact



strongly with them. The most important consequence of this interaction is that ions are often stable species in liquid systems. This is because the energy required to dissociate molecules into ions is compensated in part by the energy released from the process of ion solvation. In liquid solutions elementary steps will rarely be more than bimolecular with respect to solute, since the probability of a three-body solute collision is small and, unlike the gas phase, solvent molecules are readily available for energy transfers. The favoured mechanisms in solution are ionic ones involving formations and interaction of charged particles.

However, experimental techniques have recently so improved particularly with the application of rapid physical methods of analysis, that investigations have now been extended to rapid reactions in solution and in the gas phase that are substantially completed in milliseconds or even microseconds. This has greatly enlightened the knowledge of reactions as diverse as those between ions, enzyme catalyzed reactions proceeding in biological tissue, the reactions of free atoms and radicals formed by irradiating solutions or in the upper atmosphere and high temperature reactions in flames or shock waves.