CHAPTER II

PRINCIPLE OF CHEMICAL KINETICS

The subject of chemical kinetics is intimately concerned with the three variables time, concentration, and temperature. Experimentally, we study the rate of change of one substance into another, and it is found that this rate depends on the concentrations of the reactants. Different reactions show different concentration dependence, and this allows us to learn about the mechanism of a reaction.

The reaction rate is usually defined[12] as the rate of change of concentration of a substance involved in the reaction with a minus or plus sign attached, depending on whether the substance is a reactant or product. In a general reaction with stoichiometric equation

$$aA \quad + \quad bB \quad + \quad cC \quad + ... \quad = \quad pP \quad + \quad qQ \quad + \quad rR \quad + ...$$

the rate of reaction will be defined as :

$$-\frac{1}{a}\frac{dA}{dt} = -\frac{1}{b}\frac{dB}{dt} = -\frac{1}{c}\frac{dC}{dt} = +\frac{1}{p}\frac{dP}{dt} = +\frac{1}{q}\frac{dQ}{dt} = ...$$

and is often found to depend on the molar concentrations of the reactants :

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

where t is time and brackets mean concentration. The sign is attached so that the rate will be positive numerically. The exponent α is termed the order of the reaction with respect to A, whilst the overall order n is $\alpha + \beta + \gamma + \cdots\cdots$ The constant k is known as the rate constant ; its units depend on the value of n ; thus, for a second order reaction the units of k are liters $mole^{-1}$ sec^{-1}, whereas for a reaction of the first order the units are sec^{-1} and zero order the units are moles $liter^{-1}$ sec^{-1}.

Suppose, for example, that a reaction is of the nth order and involves substances that initially have a concentration a_0, such a reaction may be represented schematically as[13]

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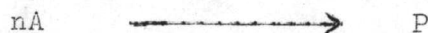
If x is the amount of A per unit volume that has disappeared in time t , the amount of A remaining is a_0-x ; the rate of disappearance of A is thus

$$-\frac{d(a_0-x)}{dt} = \frac{dx}{dt} = k(a_0-x)^n \quad\ldots\ldots\ldots\ldots(2.1)$$

This must be integrated subject to the boundary condition that x = 0 when t = 0. If n is other than unity, the solution is

$$k = \frac{1}{t(n-1)} \left(\frac{1}{(a_0-x)^{n-1}} - \frac{1}{a_0^{n-1}} \right) \quad\ldots(2.2)$$

If n is unity, the solution is

$$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x} \quad \dots\dots\dots\dots\dots\dots\dots\dots (2.3)$$

The integrated rate equations for various values of n are given in Table 2.1

Table 2.1

Summary of Rate Equations.

Order	Rate equation		Units of the rate constant
	Differential form	Integrated form	
0	$\frac{dx}{dt} = k$	$k = x/t$	Mole liter^{-1} sec^{-1}
1/2	$\frac{dx}{dt} = k(a_0 - x)^{1/2}$	$k = \frac{2}{t}\left[a_0^{1/2} - (a_0 - x)^{1/2}\right]$	Mole$^{\frac{1}{2}}$ liter$^{-\frac{1}{2}}$ sec^{-1}
1	$\frac{dx}{dt} = k(a_0 - x)$	$k = \frac{1}{t} \ln \frac{a_0}{a_0 - x}$	Sec^{-1}
3/2	$\frac{dx}{dt} = k(a_0 - x)^{3/2}$	$k = \frac{2}{t}\left[\frac{1}{(a_0 - x)^{1/2}} - \frac{1}{a_0^{1/2}}\right]$	Liter$^{\frac{1}{2}}$ mole$^{-\frac{1}{2}}$ sec^{-1}
2	$\frac{dx}{dt} = k(a_0 - x)^2$	$k = \frac{1}{t} \frac{x}{a_0(a_0 - x)}$	Liter mole^{-1} sec^{-1}
3	$\frac{dx}{dt} = k(a_0 - x)^3$	$k = \frac{1}{2t} \frac{2a_0 x - x^2}{a_0^2(a_0 - x)^2}$	Liter^2 mole^{-2} sec^{-1}

Variables other than concentration may be used in defining rate, for examples, pressure as in a gas reaction or viscosity as in a polymerization reaction or optical rotation as in a racemization, inversion, or mutarotation reaction.

If λ_0 is the value of some physical property at time $t = 0$, if λ is its value at any time t, and if λ_∞ is its final value at infinite time, then the fraction unreacted and remaining unchanged at time t is

$$\frac{\lambda_\infty - \lambda}{\lambda_\infty - \lambda_0}$$

while the fraction reacted or the fractional progress of the reaction is

$$\frac{\lambda - \lambda_0}{\lambda_\infty - \lambda_0}$$

The property λ is assumed to be linear function of the extent of the reaction. This is true of the pressure of an isothermal constant-volume reaction for which $\Delta n(g)$ is not zero. It may be true also of optical activity, dielectric constant, viscosity, and so on.

A general equation can be derived[12] for relating a measured physical quantity with concentration if a linear relationship exists. Suppose we have the reaction which goes to completion

$$nA \quad + \quad mB \quad + \quad pC \quad = \quad rZ \quad \ldots\ldots\ldots\ldots\ldots\ldots(2.4)$$
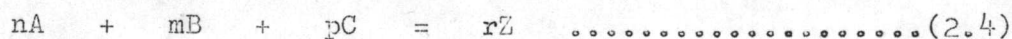
where Z includes all products. Let λ be the value of the physical property at any time t.

$$\lambda = \lambda_M + \lambda_A + \lambda_B + \lambda_C + \lambda_Z \quad \ldots\ldots\ldots(2.5)$$

where the first term is the contribution of the medium and the

others vary with concentration as, for example,

$$\lambda_A = k_A [A]$$

k_A being a proportionality constant. Let the initial concentrations of reactants be a, b, and c, respectively, and the reaction variable x be the equivalents reacting in time t, then

$$\lambda = \lambda_M + k_A(a-nx) + k_B(b-mx) + k_C(c-px)$$
$$+ k_Z rx \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2.6)$$

and

$$\lambda_0 = \lambda_M + k_A a + k_B b + k_C c \quad \ldots\ldots\ldots\ldots(2.7)$$

$$\lambda_\infty = \lambda_M + k_B(b-\frac{ma}{n}) + k_C(c-\frac{pa}{n}) + k_Z \frac{ra}{n} \ldots(2.8)$$

where λ_0 and λ_∞ are the initial and final values of λ, and in equation (2.8) it is assumed that A is the reactant present in limiting amount.

Substracting (2.7) from (2.8) gives us

$$\lambda_\infty - \lambda_0 = k_Z \frac{ra}{n} - k_A a - k_B \frac{ma}{n} - k_C \frac{pa}{n} \quad \ldots\ldots\ldots(2.9)$$

and (2.7) from (2.6)

$$\lambda - \lambda_0 = k_Z rx - k_A nx - k_B mx - k_C px \quad \ldots\ldots\ldots(2.10)$$

so that we may write

$$\lambda - \lambda_0 = x \Delta k, \qquad \lambda_\infty - \lambda_0 = (\frac{a}{n}) \Delta k$$

and

$$\lambda_\infty - \lambda = (\frac{a}{n} - x) \Delta k$$

where

$$\Delta k = k_Z r - k_A n - k_B m - k_C p$$

From these we may get the kinetically useful relationships

$$\frac{nx}{a} = \frac{\lambda - \lambda_0}{\lambda_\infty - \lambda_0} \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2.11)$$

$$\frac{a}{a-nx} = \frac{\lambda_\infty - \lambda_0}{\lambda_\infty - \lambda} \qquad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(2.12)$$

It is also possible to express $(b-mx)$ and $(c-px)$ in terms of the measured variable. The result is of the form

$$\frac{b}{b-mx} = \frac{(b/a)(\lambda_\infty - \lambda_0)}{(b/a)(\lambda_\infty - \lambda_0) - (m/n)(\lambda - \lambda_0)} \qquad \dots\dots\dots(2.13)$$

Considerable simplification can be obtained by using equivalent concentrations of reactants so that $b/a = m/n$, etc. Reactions which do not go to completion can be handled also if the equilibrium constant is known independently.

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. Method of integration is one way to get an integrated rate equation, thus, let us consider a reaction of the type [14]

$$A + B \longrightarrow \text{Product} \qquad \dots\dots\dots\dots(2.14)$$

If a_0 and b_0 are the initial concentrations of A and B, and if x is the amount of A that has disappeared per unit volume in time t (and is therefore also the amount of B that

has disappeared in time t), the amount of A and B remaining at time t are (a_0-x) and (b_0-x), respectively. The rate of disappearance of A, equal to the rate of disappearance of B, is therefore given by

$$\frac{dx}{dt} = k(a_0-x)(b_0-x) \quad \dots\dots\dots\dots\dots\dots\dots(2.15)$$

If a_0 and b_0 are different, the solution of this is

$$k = \frac{1}{t(a_0-b_0)} \ln \frac{b_0(a_0-x)}{a_0(b_0-x)} \quad \dots\dots\dots\dots\dots(2.16)$$

If a_0 and b_0 are identical, the reaction (2.14) can be written as

$$A + A \longrightarrow \quad Product$$

thus the rate of disappearance of A is given by

$$\frac{dx}{dt} = k(a_0-x)^2 \quad \dots\dots\dots\dots\dots\dots\dots\dots(2.17)$$

the solution of this equation is

$$k = \frac{1}{t} \frac{x}{a_0(a_0-x)} \quad \dots\dots\dots\dots\dots\dots\dots\dots(2.18)$$

Some of the procedures that may be used for applying the integrated equation to the experimental data may be tabular method, graphical methods, etc.

In the kinetic study we always find that increase in temperature generally leads to a tremendous increase in reaction rate and hence in rate constants. Arrhenius[15] first pointed out the variation of rate constants with temperature which can be

represented by the equation

$$\frac{d \ln k}{dt} = \frac{E_a}{RT^2} \quad \dotsb (2.19)$$

in this Arrhenius equation k is the reaction rate constant, T the absolute temperature, R the gas constant, and E_a the energy of activation which plays a very important role in chemical kinetics.

When equation (2.19) is integrated on the supposition that E_a is constant, we obtain

$$\ln k = - \frac{E_a}{RT} + C'$$

or

$$\log_{10} k = (- \frac{E_a}{2.303R}) \frac{1}{T} + C \quad \dotsb (2.20)$$

where C' and C are constants of integration. However, if we integrate between the limit $k = k_1$ at $T = T_1$ and $k = k_2$ at $T = T_2$, then

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} (\frac{T_2 - T_1}{T_1 T_2}) \quad \dotsb (2.21)$$

According to the equation (2.20) plot of $\log_{10} k$ against $1/T$ should be a straight line with

$$\text{slope} = - \frac{E_a}{2.303R}$$

and with y-intercept equal to C.