Introduction:

The birth of chemical kinetics is often is taken to have occurred in 1850, when the German chemist Ludwig Ferdinnand Wilhelmy (1812-1864) studied the rate of inversion of sucrose. This pioneering work is of special significance as being the first in which a quantitative approach was made too reaction rates. Wilhelmy interpreted the course of the reaction by the use of a differential equation and also proposed an empirical equation to express the temperature dependence of the rate. Wilhelmy's work remained almost unnotices for over 30 years, after which Friedrich Wilhelm Ostwald (1853-1932) called attention to it.

Scope of Chemical Kinetics: Chemical kinetics deals with the rates of chemical reactions with how the rates depends on the factors such as concentration and temperature. Such studies are important in providing essential evidence as to the mechanisms of chemical processes. Valuable evidence about mechanisms also is provided by nonkinetic investigation –such as the detection of reaction intermediates and isotope exchange studies- but knowledge of a mechanism can be satisfactory only after a careful kinetic investigation has been carried out. Even then the mechanism cannot be deduced with certainly, since subsequent   investigations may reveal unexpected complications. A kinetic study can disprove a mechanism but it cannot establish a mechanism with certainty.

Kinetic studies cover a very wide range, from several points of view. The half life of a reactant, the time taken for half of the reactant to be consumed, can range from a small fraction of a microsecond to a period longer than the age of universe. For example, a stiochiometric mixture of hydrogen and oxygen gases at room temperature reacts so slowly that no change could be detected after hundreds of years; it is impossible to measure such a rate, but from reliable kinetic data it can be estimated that the half-life is greater than 10^{25} years. However, if a flame or a spark is applied to the mixture an explosion occurs with a half –life less than 10^{-6} second -an increase in rate by a factor of over $10^{38.}$

Chemical reactions occur in the gas phase, in solution in a variety of solvents, at gas –solid and other interfaces, in the liquid state , and in the solid state. Experimental methods, some of them very sophisticated have been developed for studying the rates of these various types of reaction and even for following very rapid reactions such as explosions. Theoretical treatments also have been worked out for the various types of reaction.

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Some idea of the significance and wide scope of chemical kinetics is given in the **table** 1.

Some Branch of Science to Which Kinetic is Relevant

Branch	Applications of kinetics
Biology	Physiological process (e.g., digestion and mechanism), bacterial growth
Chemical engineering	Reactor design
Geology	Flow process
Inorganic chemistry	Reaction mechanisms
Mechanical engineering	Physical metallurgy, crystal dislocation mobility
Organic chemistry	Reaction mechanisms
Pharmacology	Drug action
Physics	Viscosity, diffusion, nuclear processes
Psychology	Subjective time, memory

Reaction Rate and Rate equations:

When a reaction like $v_1A + v_2B = v_3C + v_4D$ ……………………….. (1)

takes place, the molecules of A and B changes to products. Since v_2 moles of B change to product while v_1 moles of A react, the rate of change of A with time cannot be equal to the rate of change of B with time.

i.e dn_A/dt cannot be equal to dn_B/dt

Let α be the degree of advancement of a reaction (like degree of dissociation, etc). Then the number of moles of any species i at a particular time is

$$n_{i} = n_i^{0} + v_i\,\alpha \quad ………………………………………..(2)$$

Therefore,

$$dn_i/dt = v_i\,d\alpha/dt \quad ………………………………………..(3)$$

$d\alpha/dt$ is the rate of change of degree of advancement with time. It is identical for all reactants and may be defined as rate. Hence for reaction (1), the rates in terms of A, B, etc may be

$R = d\alpha/dt = -(1/\mathbf{v_1})\,(dn_A/dt) = -(1/\mathbf{v_2})\,(dn_B/dt) = (1/\mathbf{v_3})\,(dn_C/dt) = (1/\mathbf{v_4})\,(dn_D/dt)$……..(4)

We may determine the rate by measuring the change of any convenient property with time. The properties may be pressure, density, refractive index, viscosity, color, optical and electrical properties. These are all related to concentration which can be determined by analysis.

Now conc. $C_i = n_i/V$ ……………………………………..(4)

Where n_i is the number of moles present in the volume V. if V is constant, then

$$dC_{i=} dn_i/V ………………………………………………(5)$$

so, $dn_i = V dC_i$,   then $dn_i/dt = V\, dC_i/dt$

so that $d\alpha/dt = (1/|v_i|)\,(dn_i/dt) = (1/|v_i|)\,V(dC_i/dt)$

   $(1/V)\,d\alpha/dt = (1/|v_i|)\,(dC_i/dt)$ …………………………………… (6)

If V is constant , we like to define $(1/V)\,d\alpha/dt$ as rate since such a rate is in terms of an easily measurable quantity concentration, so that for reaction (1)

$R = (1/V_i)\,d\alpha/dt = -\,(1/v_1)\,(dC_A/dt) = -\,(1/v_2)\,(dC_B/dt) = (1/v_3)\,(dC_C/dt) = (1/v_4)\,(dC_D/dt)$ ……..(7)
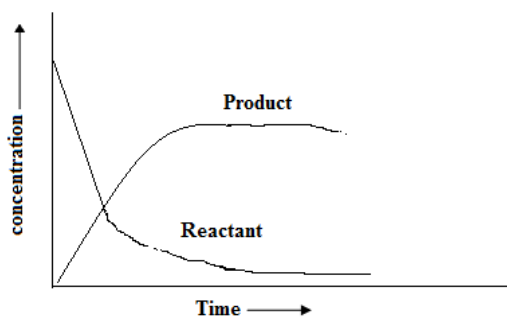

Fig 1: Plot of the concentration vs time for the reactants and products of a reaction

The variation in the concentration of the reactants and products with time is shown in Fig1. In the initial stages of the reaction , the rate of disappearance of the reactants is large and decreases as the reaction proceeds and finally approaches a limiting value. In other words, the reaction never proceeds to completion. Similarly, the rate of appearance of the product is large in th initial stages of the reaction and ultimately attains a limiting value. The rate of the reaction at any instant during the course of the reaction is equal to the slope of the concentration time curve at any instant.

Rate Equation :It has been found that the rate of a reaction depends on the concentration of reactants and sometimes on the products and even foreign substances.

   The equation expressing the dependence of rate on the concentration of substances is termed as the rate equation.

Every chemical reaction is found to have a characteristic rate equation under a particular set of conditions . The rate equation may change if condition are changed. **The rate equation is an experimental quantity.**

The rate equation of a particular reaction, unlike equilibrium constant, is independent of how we write an equation. Perhaps the first gereralisation in this direction is the law of mass action of Guldberg and Wage which led to the equilibrium constant K_a of a reaction. According to this law, for the reaction

$$v_1A_1 + v_2 A_2 \rightleftharpoons v_3 A_3 + v_4 A_4 \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \text{(8)}$$

The rate of forward reaction R_f is

$$R_f = k_f C^{v_1}_{A_1} . C^{v_2}_{A_2} \quad \dots\dots\dots\dots\dots\dots\dots\dots \text{(9)}$$

And the rate of backward reaction R_b is

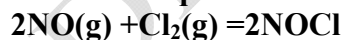$$R_b = k_b C^{v_3}_{A_3} . C^{v_4}_{A_4} \dots\dots\dots\dots \text{(10)}$$

k_f and k_b are the specific rates of the forward and backward reactions respectively. The above rate expressions are hypothetical and are always true only for elementary reactions. Many reactions take place in more than one step- they are termed as multi-step reactions.

For general reaction of the type equation (8) , the experimental rate equation in simple cases may be of the type

$$R = kC^{\acute{v}_1}_{A_1} C^{\acute{v}_2}_{A_2} C^{\acute{v}_3}_{X}$$

$$\dots\dots\dots\dots\dots\dots \text{(11)}$$

Where $\acute{v}_1$ and $\acute{v}_2$ may be different from or identical with stoichiometric coefficients v_1 and v_2 respectively. X may be a product or any foreign substance and $\acute{v}_3$ is its power.

Some rate equation:

$2NO(g) + Cl_2(g) = 2NOCl$

$$R = kC^2_{NO} . C_{Cl_2}$$

$CH_3COCH_3 + I_2 \xrightarrow[\text{Catalyst}]{H^+} CH_3COCH_2I + HI$

$$R = kC_{CH_3COCH_3} C^{H^+}$$

Any foreign substance that does not take part in the reaction, and is not a product but affects the rate by being present in the rate equation is catalyst.

The power $\acute{\upsilon}_1$ and $\acute{\upsilon}_2$, etc will be equal to the coefficients always if the reaction is elementary [takes place in one step]. If there is no catalyst and the rate is independent of product concentration, then $\acute{\upsilon}_3 = 0$.

Order of a reaction :

The order of a reaction is defined as the sum of exponents, i.e powers of the concentration terms in the rate equation. This, for equation (11), the order of the reaction is $\acute{\upsilon}_1 + \acute{\upsilon}_2 + \acute{\upsilon}_3$. We may also define the order with respect to the each reactant. Order with respect to any reactant A is the power of its concentration term in the rate equation. Therefore, the order with respect to A_1 is $\acute{\upsilon}_1$, that with respect to A_2 is $\acute{\upsilon}_2$ and so on.

Though theoretically reaction of higher order are possible, but it is doubtful if reactions than third order exist. However, there are reactions in which the order is **fractional and negative order** , i.e1/2,3/2 , -3/2etc. Such fractional orders indicate the complex nature of the reactions.

If the reaction rate is independent of the concentration of the reacting species , the reaction is said to a **zero order** reaction. In such reaction, factors other than the concentration of the reacting species control the rate of the reaction . Some heterogeneous or surface reactions are example of zero order reactions..

Order of a reaction is an experimental quantity and can change depending upon the experimental conditions under which the reaction is investigated.

[Note: Order can be positive as well as negative. It can be integral as well as fractional.]

Reaction is said to a zero order reaction. In such reaction, factors other than the concentration of the reacting species

Units of Rate: The rate is normally expressed in concentration divided by time (moles per liter per sec). k is the specific rate constant and is independent of concentration but depends on temperature and on the nature of reactants [and product]

Importance :The rate equation enable us to predict the reaction rate. The rate equation leads to the classification of reaction according to their order. It is also a guide to the mechanism must lead to the rate equation.

Molecularity of a reaction

Most of the chemical reactions proceed through a series of intermediate steps. These steps are known as the elementary steps. Investigation of these steps constitute the mechanism of the

reaction . *Molecularity of a reaction is defined as the number of reactant molecules which take part in an elementary reaction.*The reaction are said to be unimolecular, bimolecular or trimolecular depending upon whether one, two or three molecules are involved in a chemical reaction. The order and molecularity of a reaction are generally different and the distinction between the two should be clearly understood.

$A \longrightarrow$ Pdt…………………………………. (12)

$A+A \longrightarrow$ Pdt…………………………………. (12a)

$A+B \longrightarrow$ Pdt…………………………………. (12b)

as unimolecular or monomolecular reactions. Reactions represented by eqn. 12(a&b) have ord

$A+2B \longrightarrow$ Pdt…………………………………. (13a)

$2A+B \longrightarrow$ Pdt…………………………………. (13b)

In eqn. (12), the order of the reaction is one and the molecularity is also one. Such reaction are generally known order and molecularity of two. Such reactions are generally referred to as bimolecular reactions. Similarly, reaction given by eqn. 13(a&b) are of order three and of molecularity three. These are called trimolecular reaction.

The reaction between hydrogen and Iodine

$$H_2+I_2 =2HI$$
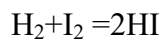
is a 2nd order reaction because the rate of formation of hydrogen iodide is proportional to the conc. Of both the hydrogen and iodine. The reaction involves two molecules and is , therefore, called a bimolecular reaction. For elementary reaction, as stated above, order and molecularity are identical. For other they are different. For example, the inversion of cane sugar in the presence of a mineral acid represented as

$C_{12}H_{22}O_{11} +H_2O \xrightarrow{\;H_3O^+\;} C_6H_{12}O_6 + C_6H_{12}O_6$

Glucose   Fructose

involves two reactant molecules viz, sugar and water and is a bimolecular reaction. In presence of excess water, the order of the reaction is found one- indicating that the order and molecularity of the reaction are different. Such a reaction is generally referred to as a pseudo unimolecular reaction.

The molecularity of a reaction must be an integral value and is applied to individual elementary reactions. If a reaction proceeds through several steps, each step (elementary reaction) has its own molecularity and order which are identical. In such cases, it is meaningless to talk of the molecularity of the overall reaction and there is no correlation between the order and molecularity or between stoichiometric representation and the molecularity.

For example, The decomposition of nitrogen pentoxide represented stoichiometriclly as

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

involves two molecules of N_2O_5 and is a first order reaction. The various steps suggested in the mechanism are as follows :

i) $2N_2O_5 \longrightarrow NO_2 + NO_3$
ii) $NO_2 + NO_3 \longrightarrow NO_2 + O_2 + NO$
iii) $NO_2 + NO_3 \longrightarrow N_2O_5$
iv) $NO + N_2O_5 \longrightarrow 3\,NO_2$

In this scheme three steps are biomolecular and one unimolecular. The slowest steps controls the overall rate of decomposition of N_2O_5.

Order is an empirical quantity and is obtained from the rate law; molecularity of steps refer to the mechanism of the reaction.