B. Sc. Part II (Subsidiary)

Paper : Physical Chemistry
Topic : Chemical Kinetics

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Chemical Kinetics is the branch of physical chemistry which deals with the study of rate of reactions and the factors governing rate of reaction.

L. F. Wilhelmy, a German Chemist, is known as father of chemical kinetics.

Most chemical reactions are spontaneous reactions, i.e. these reactions occur from left to right till all the reactants are converted to products. Chemical reactions occurs at a variety of rates from very slow to very fast. The rusting of iron is a very slow reaction that occurs over the years. On the other hand, the reaction between aqueous NaCl and aqueous $AgNO_3$ is a fast reaction which instantaneously gives precipitate of AgCl.

Between these two extremes, there are many reactions, involving both organic and inorganic substances, whose speeds at room temperature can be easily measured.

Important applications of kinetic studies of chemical reactions are :

(a) in determination of rates of reactions and factors governing rates.

(b) in predicting the conditions for maintaining the reaction rate.

(c) in determination of yield of reaction in a certain time period.

(d) in calculating the time required for completion of a reaction, and

(e) in suggesting the mechanism or sequence of steps by which a reaction occurs.

Rate of Reaction :-

Let us consider a simple reaction

$$A \longrightarrow B$$

The rate of the reaction at any given time will depend upon the concentration of the reactant A at that time. As the reaction progresses, the concentration of the reactant A decreases and that of product B increases with time.

The rate of reactions is defined as the change in concentration of any of reactant or product per unit time.

For the above reaction,

rate of reaction = rate of disappearance of A
= rate of appearance of B

which can further be expressed as

$$r = -\frac{d[A]}{dt}$$

$$= +\frac{d[B]}{dt}$$

where '[ ]' represents the concentration in moles per litre where as 'd' represents infinitesimally small changes either in concentration or in time. Negative sign shows the concentration of reactant A decreases whereas the positive sign indicates the increase in concentration of product B.

The unit of rate of a chemical reaction is the unit of concentration divided by the unit of time. Since, the concentration is normally measured in moles per litre ($mol\,L^{-1}$) the unit of reaction rate is specified as $mol\,L^{-1}\,s^{-1}$ as time is measured generally in second.

Let us consider a specific reaction, the decomposition of gaseous nitrogen pentoxide

$$2\,N_2O_5\,(g) \rightarrow 4\,NO_2\,(g) + O_2\,(g)$$

The rate for this reaction can be determined by measuring the increase in the molar concentration of O_2 in a given time interval. The rate of reaction can be written as

$$\text{Rate of formation of } O_2 = \frac{d[O_2]}{dt}$$

But if we consider to measure the decrease in the molar concentration of

N_2O_5. The rate of reaction for this choice will be

Rate of decomposition of $N_2O_5 = -\frac{d[N_2O_5]}{dt}$

From the chemical equation we see that two moles of N_2O_5 is needed to produce one mole of O_2. In other words, the rate of decomposition of N_2O_5 is twice as fast as the rate of formation of O_2. If we wish to equate the two rate expressions, then we must devide the rate of decomposition of N_2O_5 by 2. Thus

$$r = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{d[O_2]}{dt}$$

The rate of this reaction can also be written in terms of the rate of formation of NO_2 as

$$r = \frac{d[O_2]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt}$$

Thus for a general reaction of the type

$$aA + bB \longrightarrow cC + dD$$

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

Since all these quantities are equal, it is natural to take the formal definition of the "rate of reaction" as the time derivative of a concentration divided by the appropriate stoichiometric coefficients.

<u>The Rate Law and the Rate Constant</u> :-

At a fixed temperature, the rate of a given reaction depends on concentration of reactants. The rate of the reaction:
A ⟶ Products, is experimentally found to be given by

$$r = k[A]$$

(i.e. the rate of a reaction is directly proportional to the reactant concentrations, each concentration being raised to some power.)
where k is the rate constant of the reaction at the given temperature. For a reaction of the type

$$aA + bB \longrightarrow \text{Products}$$

the rate of reaction

$$r = k[A]^a[B]^b$$

If the concentrations of A and B are unity, then $r = k$ or $k = r$

Thus, the rate constant of a reaction, in general, is defined as the rate of the reaction when the concentration of each reactant is unity.

Under such condition (ie all concentrations were set equal to unity) the rate constant is more formally known as Specific Reaction Rate.

To be continued....