Dr. L. K. Mishra
Deptt of chemistry

(A)

For Deg I Subsidiary Course (Chemistry)

Chemical Kinetics (Course-material)

Rate of reaction :—

The rate of reaction is defined as the rate of change of concentration of either reactant or Product per unit time.

If C_A is the concentration of reactant A at time t then the rate is defined as $\text{Rate} = -\frac{d(C_A)}{dt}$ —(I)

The minus sign in equation (I) occurs because the concentration of reactant decreases with increasing time.

If a is initial concentration of A and x is the concentration of Product at time t then

$$\text{Rate} = +\frac{dx}{dt} \quad \text{——(II)}$$

$$\text{Rate} = -\frac{d(a-x)}{dt} \quad \text{——(III)}$$

In equation (II) the sign is positive since the concentration of Product increases with time.

Determination of rate of reaction :—

In order to determine the reaction rate, a curve AB of the type shown in fig

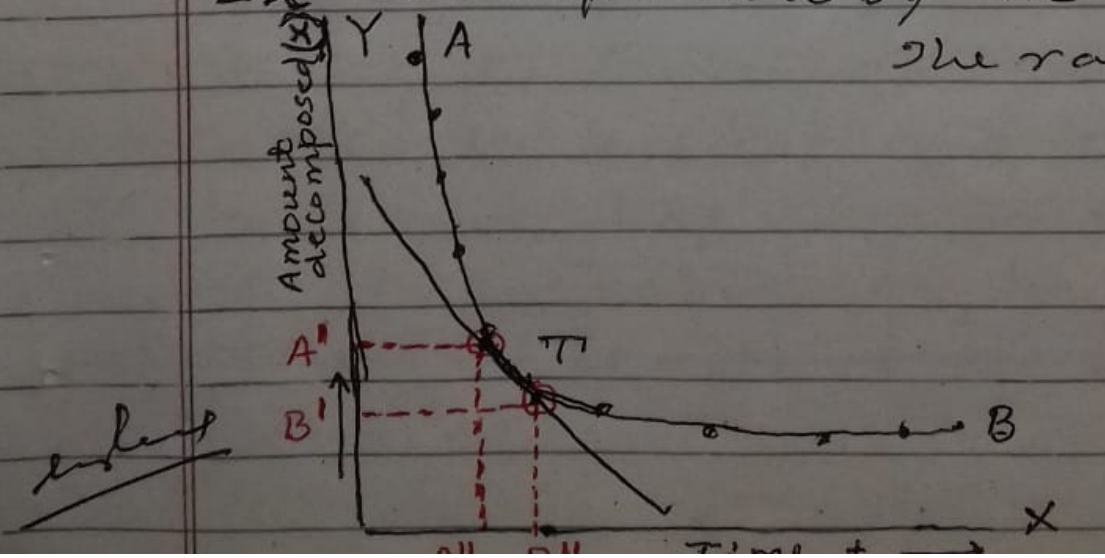
is considered in which the amount decomposed (x) is plotted against time t. A tangent is drawn at the point T on the curve AB. Then two points are selected on the tangent at which the rate is same. After this the line parallel to X-axis and Y axis are drawn corresponding to the two points.

Then the value of Δx is $A'B'$ corresponding to time interval Δt which is $A''B''$ then the rate of reaction will be given by

$$\text{Rate of reaction} = \frac{A'B'}{A''B''} = \frac{\Delta x}{\Delta t}$$

For infinitesimal change Δx and Δt are replaced by dx and dt.

The rate of reaction $= \frac{dx}{dt}$



Factors affecting the rate of reaction

There are number of factors which affects the rate of a reaction. some of the main factors are given below:-

(1) Concentration of the reactants
(2) Nature of reactants and Products
(3) Temperature of reaction
(4) Presence of a Catalyst
(5) Exposure to radiation
(6) Surface area of the reactants

Explanation:-

(1) we know that the rate of reaction is fast inially but as the reaction Progresses its rate starts decreasing since the Concentration of the reactants decrease as they are consumed during the Course of reaction. Hence it is Clear that rate of reaction has some relation with the Concentration of the reactants otherwise the rate should be Constant all the time.

(D)

According to Law of mass action we know that the rate of reaction is directly proportional to the product of the active masses of reactants taking Part in a chemical reaction

e.g. A burning match stick burning slowly in air starts burning intensely when brought in a cylinder of oxygen gas. The concentration of O_2 in cylinder is 100% in comparison to air (21%). Oxygen is one reactant in the burning Phenomenon Lower concentration of reactant corresponds to Lower rate of concentration.

(2) Oxidation of Fe^{++} & oxalate ion by MnO_4^- ion is shown in acidic medium

$$Fe^{2+}(aq) + MnO_4^-(aq) + H^+(aq) \longrightarrow Fe^{3+}(aq) + Mn^{2+}(aq) + H_2O \quad \text{---(I)}$$

$$C_2O_4^{--}(aq) + MnO_4^-(aq) + H^+(aq) \longrightarrow CO_2(g) + Mn^{+2}(aq) + H_2O \quad \text{---(II)}$$

The first reaction is faster in comparision to reaction (II). $MnO_4^-(aq)$ is common to both, the difference is only in the nature of Fe^{2+} and $C_2O_4^-$.

Fe^{2+} ion is simple ion whereas $C_2O_4^{--}$ is poly atomic ion in which higher number of bonds are to be broken and formed. so it is slow.

(3) Temperature affects the rate of reaction which becomes double for every 10°C rise in temperature similarly lower temperature corresponds to low rate of reaction

$$\frac{K_{t+10}}{K_t} \simeq 2 \text{ or } 3 \text{ (sometimes)}$$

(4) A positive catalyst increases the rate whereas the negative catalyst decreases the rate of reaction. Presence of MnO_2 increases the rate of decomposition of $KClO_3$ whereas 1.) ethanol retards the rate of oxidation of $CHCl_3$ (Chloroform)

(5) We know that the energy of one photon associated with radiation of frequency ν is $h\nu$.

$E = h\nu$ where h is Planck's constant and ν is the frequency of radiation.

Rate of certain reaction increases by absorbing the photon of certain radiation.

(6) surface area of the reactants play an important role in heterogeneous reaction. As the Particle size decreases, the surface area increases for the same mass. The smaller Particles react more rapidly than the Larger Particles.

e.g. The Cu-turning react at a higher rate than the plate of Cu during its reaction with conc. H_2SO_4 for the Preparation of SO_2 gas in the Laboratory.

The End