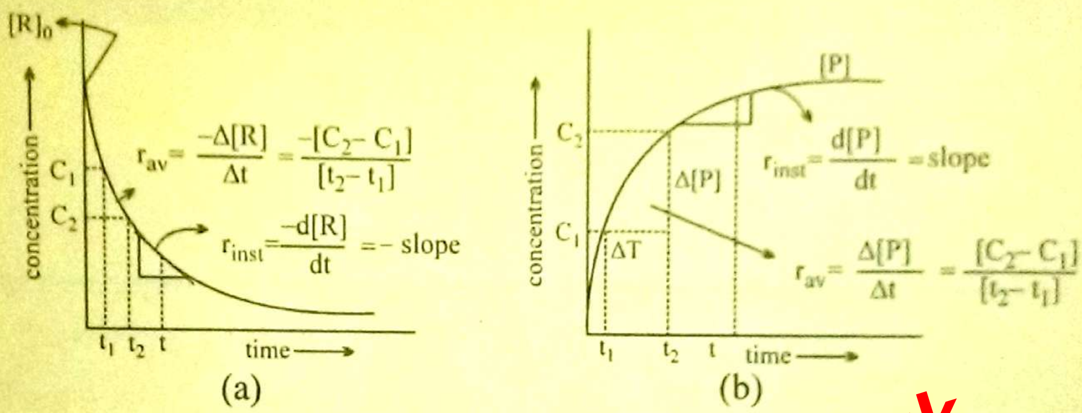
THE KEY

CHEMICAL KINETICS :

It is a branch of physical chemistry which deals with the "Rate of Chemical Reactions" including the effect of temperature, pressure, concentration, etc., on the rates, and the mechanism by which the reaction takes place.

RATE OF CHEMICAL REACTION is defined as the change in concentration of a reactant (or a product) in a particular time interval. Type of rate of reaction (i) Average (ii) Instantaneous

Average rate. The rate of reaction measured over a long time interval is called average rate of reaction. It is equal to $\Delta x/\Delta t$ as shown in fig.(a) and (b).



Instantaneous and average rate of reaction

Instantaneous rate. It is the rate of reaction when the average rate is taken over a very small interval of time. It is equal to dx / dt as shown in fig. (a) and (b).

Rate law Expression :

For a general reaction $aA + bB \longrightarrow cC + dD$

The rate of disappearance of A = $-\frac{d[A]}{dt}$

Rate of disappearance of B = $-\frac{d[B]}{dt}$

Rate of appearance of C = $\frac{d[C]}{dt}$

Rate of appearance of D = $\frac{d[D]}{dt}$.

The positive sign shows that concentrations of C and D increases with time and the negative sign indicating that concentrations of A and B decrease with time. Thus the rate of general reaction.

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

Unit of Reaction Rate are unit of concentration divided by the unit of time ($mol\ L^{-1}s^{-1}$ or $mol\ L^{-1}min^{-1}$ or so on).

IMPORTANT TERMS AND DEFINITIONS

1. **Rate of reaction.** It is defined as the change in concentration of reactant (or product) in a particular time interval. Its unit is mol $L^{-1}s^{-1}$. If time is in minutes, then units are mol L^{-1} min^{-1} and so on.

2. **Rate law or rate equation.** It is the expression which relates the rate of reaction with concentration of the reactants. The constant of proportionality 'k' is known as rate constant.

3. **Rate constant.** When concentration of both reactants are unity, then the rate of reaction is known as rate constant. It is also called specific reaction rate.

4. **Molecularity.** Total number of molecules of the reactants involved in the reaction is termed as its molecularity. It is always in whole number, It is never more than three. It cannot be zero.

5. **Order of a reaction.** The sum of the powers of the concentration of reactants in the rate law is termed as order of the reaction. It can be in fraction. It can be zero also.

6. **Zero order reaction.** In zero order reaction the rate of reaction does not change with the concentration of the reactants, i.e., $\text{rate} = k[A]^{\circ}$

7. **First order reaction.** In first order reaction the rate of reaction is directly proportional to the concentration of reacting substance. Rate constant of first order reaction is

$$k = \frac{2.303}{t}\log\frac{a}{a-x} \text{ or } k = \frac{2.303}{t}\log\frac{[A_0]}{[A]}$$

where 'a' is initial concentration, (a–x) is the concentration of reactants after time 't'. The unit of 'k' is s^{-1} or min^{-1}. A plot between *ln* [A] vs. t is a straight line with slope equal to –k. [A] is concentration of reactants after time t.

8. **Half–life of a reaction.** The time taken for a reaction when half of the starting material has reacted is called half–life of a reaction. For first order reaction

$$t_{1/2} = \frac{0.693}{k}$$, where k is rate constant.

9. **Second order reaction**. The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 2, e.g.,

$$\frac{dx}{dt} = k[A]^1[B]^1$$

10. **Third order reaction.** The reaction in which sum of powers of concentration terms in rate law or rate equation is equal to 3, e.g.,

$$\frac{dx}{dt} = k[A]^x[B]^y \text{ where } x + y = 3$$

11. **Specific rate constant (k).** It is defined as equal to rate of reaction when molar concentration of reactant is unity.

12. **Initial rate.** The rate at the beginning of the reaction when the concentrations have not changed appreciably is called in initial rate of reaction.

13. **Elementary processes.** Some reactions occur by a series of elementary steps and such simple steps are called elementary processes.