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Chemical Kinetics

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Chemical Kinetics is the study of chemical reactions with respect to reaction rates, effect of various variables rearrangement of atoms and formation of intermediates.

The rate of a reaction

The rate of a reaction is concerned with decrease in concentration of reactants or increase in concentration of products per unit time. It can be expressed as an instantaneous rate at a particular instant of time and average rate over a large period of time.

Factors affecting rate of reaction

A number of factors such as nature of reactants and products, exposure to radiations, temperature, concentration of reactants, catalyst and surface area of solid reactants effect the rate of a reaction.

Rate Law

Rate law is the mathematical representation for rate of reaction, it can be determined experimentally and cannot be predicted.

Order of a reaction

Order of a reaction with respect to a reactant is the power of its concentration term which appears in the rate law, it is an experimentally determined quantity.

Molecularity

Molecularity of a reaction is the number of reacting species taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction. Molecularity of a reactant greater than 3 are rare, order and molecularity of elementary reactions are same.

Rate Constant

Rate constant is the proprotionality constant in rate law.

Integrated Rate

Integrated rate equations can be determined by integrating the differential rate equations.

Half Life

Half life is the time, in which half of the initial amount of reactants is converted into products. (Time taken for 50% completion of reactions)

## In Collision Theory Activation Energy

In collision theory activation energy and proper orientation of the molecules together determine the criteria for an effective collision and hence rate of a reaction.

Nuclear Chemistry

Nuclear chemistry is the study of chemical reactions involving changes in nuclei of atoms. It provides information about kinetic of radioactive decay and time period (unaffected by temperature, pressure catalyst).
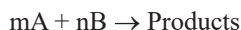
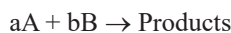## Formulae Chart

(i) For a general chemical transformation

$$nA + mB \rightarrow pC + qD$$
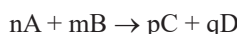
$$\text{Rate} = \frac{-1}{n}\frac{d[A]}{dt} = \frac{-1}{m}\frac{d[B]}{dt} = +\frac{1}{p}\frac{d[C]}{dt} = +\frac{1}{q}\frac{d[D]}{dt}$$

(ii) For general chemical changes

$$mA + nB \rightarrow \text{Products}$$

$$\text{Theoretical rate} = \frac{dx}{dt} = k[A]^m \times [B]^n$$

(iii) For a general reaction:

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

$$\text{Rate} = \frac{dx}{dt} = k[A]^m \times [B]^n$$

Order of reaction w.r.t. A = m

Order of reaction w.r.t. B = n

(iv) Unit of rate constant $= (\text{mole litre}^{-1})^{1-n} (\text{time}^{-1})$

where, n = order of reaction

(v) For a zero order reaction: $A \rightarrow B$

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]^0 = k(\text{constant})$$

(vi) For a first order reaction $A \rightarrow B$

$$\text{Rate} = \frac{-d[A]}{dt} = k[A]$$

$$k = \frac{2.303}{t}\log_{10}\frac{[A]_0}{[A]_t} = \frac{2.303}{t}\log_{10}\left(\frac{a}{a-x}\right)$$

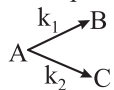(vii) For a first order reaction, $A \rightarrow B$

$$\log_{10}[A]_t = \frac{-k}{2.303}t + \log_{10}[A]_0$$

(viii) For a zero order reaction $t_{1/2} = \dfrac{[A]_0}{2k}$

For a first order reaction $t_{1/2} = \dfrac{0.693}{k}$

For an nth order reaction, $t_{1/2} = \dfrac{1}{[A]_0^{n-1}}$ (for $n \geq 2$)

(ix) For a parallel reaction

$$A \underset{k_2}{\overset{k_1}{\diagdown}} \begin{matrix} B \\ C \end{matrix}$$

$$\frac{-d[A]}{dt} = (k_1 + k_2)[A]$$

(x) For a first order reaction: A→B+C a reactant reacts with as A, B and C

$$k = \frac{2.303}{t}\log_{10}\left(\frac{V_\infty - V_0}{V_\infty - V_t}\right)$$

(V = vol. of reagent)

(xi) For hydrolysis of sucrose, $S \xrightarrow{H^+} G + F$

$$k = \frac{2.303}{t}\log_{10}\left(\frac{r_0 - r_\infty}{r_t - r_\infty}\right).$$

(r = rotation due to all S, G and F)

(xii) Temperature coefficient $= \dfrac{k_{T+10}}{k_T} = 2 \text{ to } 3$

Arrhenius equation, $k = Ae^{-E_a/RT}$

$$\log_{10}\frac{k_2}{k_1} = \frac{E_a}{[2.303R]}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

(A = Arrhenius's constant E_a = Activation energy)

$$\log_{10}k = \log_{10}A - \frac{E_a}{2.303RT}$$

(xiii) Binding energy, B.E. $= \Delta m \times 931.5$ MeV

Δm = mass defect = calculated At. mass – observed At mass

B.E. per nucleon $= \dfrac{\text{B.E.(total)}}{\text{mass number}}$

1 Mev $= 9.6 \times 10^{10}$ joule mol^{-1}

(xiv) Packing fraction, P.F.

$$= \frac{\text{isotopic atomic mass} - \text{mass number}}{\text{mass number}} \times 10^4$$

(xv) In a radioactive decay, $N_t = N_0 e^{-\lambda t}$

Amount of radioactive substance after 'n' half life periods

$$N = \left(\frac{1}{2}\right)^n N_0$$