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Chapter 1

Chemical Kinetics

1.1 Introduction to Chemical Kinetics:

Chemical kinetics helps us to understand how chemical reaction occurs. For any chemical reaction, chemist try to find out:

- Feasibility of chemical reaction which can be predictable by thermodynamics. ($\Delta G < 0$)
- Extent to which chemical reaction proceeds can be determined from chemical equilibrium.
- Speed of reaction i.e. time taken by a reaction to reach equilibrium.

Along with all these properties, it is equally important to study rate or speed or velocity of reaction and factors controlling the rate of reaction for example, which parameter determines as to how rapidly food gets spoiled. All these questions can be answered by new branch of physical chemistry which deals with study of reaction rate and their mechanism called "Chemical Kinetics" where kinetics is derived from Greek word kinesis meaning movement.

Reactions are classified into various types. Based on the speed of the reaction, the reactions are broadly classified as fast reactions and slow reactions.

Sr. No.	Fast Reactions	Slow Reactions
1.	Are usually Ionic Reactions	Are usually Non-Ionic Reactions or Molecular Reaction
2.	can be studied by special experimental technique	rate can be measured experimentally by simple method
3.	Oxidation $Fe^{+2} \rightarrow Fe^{+3}$ only transfer of e^{-}	Can be homogeneous or heterogeneous reaction $2N_2O_5\ (g)\ \ 4NO_2\ (g)$ $CaCO_3\ (s)\ CaO(s)\ + CO_2\ (g)$

This chapter deals with kinetics of homogenous reaction.

1.2 Rate of Reaction:

Rate of reaction is defined in terms of concentration of reactant at that time.

$$\text{Rate} = \frac{\text{Change in concentration}}{\text{change in Time}}$$

Rate = change in concentration of reactant per unit time or

(i) Rate of decrease in concentration of any one of the reactants

(ii) Rate of increase in concentration of any one of the products.

Example: $R \rightarrow P$

One mole of R produces one mole of P.

If $[R_1]$ and $[P_1]$ are concentrations at time t_1, $[R_2]$ and $[P_2]$ at time t_2

$$\text{Rate of disappearance of R } (V_{av}) = \frac{[R_2] - [R_1]}{[t_2] - [t_1]} = \frac{-\Delta[R]}{\Delta t}$$

$$\text{Rate of appearance of P } (V_{av}) = \frac{[P_2] - [P_1]}{[t_2] - [t_1]} = \frac{\Delta[P]}{\Delta t}$$

.

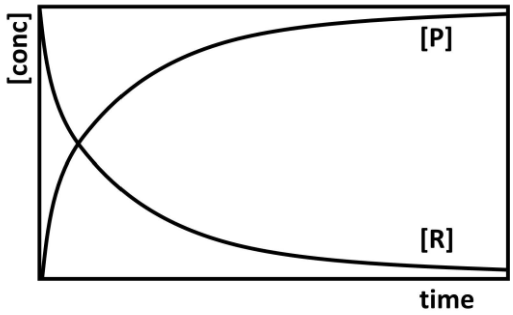
Rate is always positive quantity but the negative sign symbolizes decrease in the concentration.

Rate of reaction at every moment is different, the rate at any instant is

$$\text{Instanteneous Rate (r)} = \frac{-\text{d[R]}}{\text{dt}} = \text{Slope}$$

$$\text{Instanteneous rate} = \frac{\text{d[P]}}{\text{dt}} = \text{Slope}$$

Graphical Representation:



Units of Rate of Reaction:

$$\text{Rate} = \frac{\Delta\text{Conc}}{\Delta\text{Time}}$$

$$\text{Rate} = \frac{\text{mol L}^{-1}}{\text{s}}$$

$$\text{Rate} = \text{mol L}^{-1}\,\text{s}^{-1}$$

In gaseous reaction concentration is expressed in terms of pressure so the unit is atm.s^{-1}.

Rate of reaction depends upon the experimental conditions such as concentration of reactants (pressure in case of gases), temperature and catalyst.

1.3 Reaction Mechanism:

A reaction mechanism is the detailed picture of how a reaction occurs at molecular level.

It consists of a set of proposed elementary steps involving molecular species – reactants as well as reaction intermediates.

A reaction mechanism explains how a given reaction might occur at molecular level and from which a rate law can be derived, which must agree with the one determined experimentally.

If the mechanism consists of more than one elementary step, the sum of these steps must be equal to the overall balanced equation for the reaction.

For example, the reaction: $2\text{A} + \text{B} \rightarrow \text{C} + \text{D}$ may involve the following elementary steps:

Step-1: $\text{A} + \text{B} \rightarrow \text{X};$

Step-2: $\text{A} + \text{X} \rightarrow \text{Y};$

Step-3: $\text{Y} \rightarrow \text{C} + \text{D};$

Overall Reaction: $2\text{A} + \text{B} \rightarrow \text{C} + \text{D};$

.

1.4 Elementary Steps and Molecularity:

Elementary steps or elementary reactions are simple steps that together make up the reaction mechanism for a given reaction. Each elementary reaction describes individual molecular event, such as two particles combining or a particle (simple or complex) decomposing. An elementary reaction is characterized by its molecularity, which is the number of particles/molecules involved in the formation of transition-state complex. Thus, an elementary reaction may be characterized as unimolecular, bimolecular, or trimolecular. Unimolecular and bimolecular reactions are considered to be the most common elementary processes.

1.5 Rate Law of Elementary Steps:

Elementary Reactions	Molecularity	Rate Law
$A \rightarrow$ product	Unimolecular	$\text{Rate} = k[A]$
$2A \rightarrow$ product	Bimolecular	$\text{Rate} = k[A]^2$
$A + B \rightarrow$ product	Bimolecular	$\text{Rate} = k[A][B]$
$2A + B \rightarrow$ product	Trimolecular	$\text{Rate} = k[A]^2[B]$

For example, in the reaction:

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

The proposed mechanism is:

Step-1: $N_2O_5 \rightarrow NO_2 + NO_3$ (Unimolecular)

Step-2: $NO_2 + NO_3 \rightarrow 2NO_2 + O$ (Bimolecular)

Step-3: $N_2O_5 + O \rightarrow 2NO_2 + O_2$ (Bimolecular)

Trimolecular event is considered very rare; the chances that three particles colliding at the same time, with proper orientation and sufficient energy, are considered extremely small.

A possible trimolecular event is thought to occur during the formation of ozone from oxygen in the outer atmosphere:

$2O_2 + N_2 \rightarrow O_3 + O + N_2^*$

A complex reaction is made up of many elementary reactions. The rate of the complex reaction is determined by the slowest step of the reaction.

Unit of rate constant for various order of reaction

Consider a general reaction,

aA + bB→cC + dD

$\text{Rate} = k\,[A]^x\,[B]^y$

$\text{Rate} = k\,[\text{conc.}]^{x+y}$

x + y = overall order of reaction = q

$\text{Rate} = k\,[\text{conc.}]^q$

$$k = \frac{\text{Rate}}{[\text{Conc}]^q} = \frac{\text{Conc}}{\text{Time}\,[\text{Conc}]^q}$$

$k = [\text{conc}]^{1-q}\,\text{time}^{-1}$

Unit of [conc] is moldm^{-3} or mol L^{-1}

Order	Unit
Zero	$\text{conc time}^{-1} = \text{mol L}^{-1}\ \text{s}^{-1}$
First	s^{-1}
Second	$\text{mol}^{-1}\ \text{L}^1\ \text{s}^{-1}$
n^{th}	$(\text{mol L}^{-1})^{1-n}\text{s}^{-1}$

.

1.6 Order of Reaction:

Consider a reaction aA + bB→cC + dD

Rate of the reaction can be defined as $\text{Rate} = k\,[A]^x\,[B]^y$

Sum of these exponents (x+y) is called overall order of reaction.

x = Order of reaction with respect to A

y = Order of reaction with respect to B

Sum of power of the concentration of reactants in rate law expression is called order of the "Chemical reaction".

Order can be 0, 1, 2, 3, and fraction

A zero-order reaction means that the rate of reaction is independent of concentration of reactant.

Calculate overall order of reaction which has rate expression

$\text{Rate} = k[A]^{\frac{1}{2}}\,[B]^{\frac{3}{2}}$ order = 2

$\text{Rate} = k\,[A]^{\frac{1}{2}}\,[B]^{-1}$ order = $\frac{1}{2}$

Solved Problems:

1. What are the units for the rate constants of

(i) zero order

(ii) $\frac{1}{2}$ order

(iii) first order

(iv) $\frac{3}{2}$ order

(v) second-order

(vi) $\frac{5}{2}$ order

(vii) third-order reaction

Explanation:

The unit of the rate constant for the n^{th}-order reaction is given by $(dm^3)^{n-1}\,mol^{1-n}\,s^{-1}$.

(i) n = 0, the unit is $dm^{-3}\,mol\,s^{-1}$

(ii) n = $\frac{1}{2}$, the unit is $(dm^3)^{-\left(\frac{1}{2}\right)}mol^{\frac{1}{2}}\,s^{-1}$

(iii) n = 1, the unit is s^{-1}

(iv) n = $\frac{3}{2}$, the unit is $(dm^3)^{\frac{1}{2}}mol^{-\frac{1}{2}}\,s^{-1}$

(v) n = 2, the unit is $dm^3\,mol^{-1}\,s^{-1}$

(vi) n = $\frac{5}{2}$, the unit is $(dm^3)^{\frac{3}{2}}\,mol^{-\frac{3}{2}}\,s^{-1}$

(vii) n = 3, the unit is $dm^6\,mol^{-2}\,s^{-1}$

2. In which of the reactions of the following orders of the molecularity and order can never be same?

(a) Zero order

(b) First order

(c) Second order

(d) Third order

Explanation:

Every reaction has to have atleast one reacting species.

Answer: (a)

.

1.7 Forms of Rate for General Reactions:

1.7.1 Instantaneous Rate of Reaction (Also Called Differential Rate):

Examples:

1. $A + B \rightarrow C$

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

E.g. $Hg\,(l) + Cl_2(g) \rightarrow HgCl_2$

$$\text{Rate} = \frac{-d[Hg]}{dt} = \frac{-d[Cl_2]}{dt} = \frac{d[HgCl_2]}{dt}$$

∴ Stoichiometry coefficient of reactant and product are same.

2. aA + bB→cC + dD

Rate of disappearance of reactant or appearance of product divided by their stoichiometric coefficient.

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

$2HI\,(g) \rightarrow H_2\,(g) + I_2\,(g)$

Here rate of consumption of HI is twice than H_2 and I_2 to make them equal divided by 2.

$$\text{Rate} = \frac{-1}{2}\frac{d[HI]}{dt} = \frac{d[H_2]}{dt} = \frac{d[I_2]}{dt}$$

Solved Problems:

1. In a reaction: $2N_2O_5 \rightarrow 4NO_2 + O_2$

(i) $-\frac{d[N_2O_5]}{dt} = k_1[N_2O_5]$

(ii) $\frac{d[NO_2]}{dt} = k_2[N_2O_5]$

(iii) $\frac{d[O_2]}{dt} = k_3[N_2O_5]$

How k_1, k_2 and k_3 are related?

(a) $2k_1 = k_2 = 4k_3$

(b) $4k_1 = 2k_2 = k_3$

(c) $\frac{1}{2}k_1 = 4k_2 = 2k_3$

(d) $4k_1 = k_2 = 2k_3$

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