

CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT BASED NOTES OF CHAPTER -04)

GANESH KUMAR

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4. CHEMICAL KINETICS

The branch of Chemistry that deals with the rate of chemical reaction, factors affecting the rate and the mechanism of a reaction is called **Chemical Kinetics**.

Rate of a chemical reaction

The rate of a chemical reaction is the change in concentration of any one of the reactant or product in unit time. Or, it is the rate of decrease in concentration of any one of the reactant or the rate of increase in concentration of any one of the product.

For a chemical reaction, if Δx is the change in concentration of a reactant or a product in a time Δt , the rate of reaction (r) = $\Delta x/\Delta t$.

For a hypothetical reaction $R \rightarrow P$, the rate of reaction can be expressed by decrease in concentration of reactants or by increase in concentration of products.

i.e., Rate of reaction = Rate of disappearance of R

$$r = \frac{\text{Decrease in concentration of R}}{\text{Time taken}}$$

$$\text{Or, } r = \frac{-\Delta[R]}{\Delta t}$$

[Since, $\Delta[R]$ is a negative quantity (as concentration of reactants is decreasing), it is multiplied with -1 to make the rate of the reaction a positive quantity].

$$\text{Or, Rate of reaction} = \text{Rate of appearance (formation) of P} \\ = \frac{\text{Increase in concentration of P}}{\text{Time taken}}$$

$$\text{i.e., } r = \frac{\Delta[P]}{\Delta t}$$

The above rate expressions are also called Average rate.

Units of Rate of reaction

If concentration is expressed in moles/L and time is in second, the unit of rate of reaction is mol/L/s. In general the dimension of rate of reaction is Concentration/Time. For gaseous reactions, the concentration is replaced by partial pressure and so the unit of rate of reaction is atm/s.

Instantaneous Rate of a reaction

The rate of a reaction at a particular instant of time is called Instantaneous Rate of a reaction. Or, it is the rate of a reaction when the time interval approaches zero.

$$\text{i.e., Instantaneous Rate of a reaction} = \lim_{\Delta t \rightarrow 0} \frac{\Delta x}{\Delta t} = \frac{dx}{dt}$$

For the reaction, $R \rightarrow P$, the Instantaneous Rate is given by, $r_{\text{inst}} = -\frac{d[R]}{dt} = \frac{d[P]}{dt}$

For the reaction, $2\text{N}_2\text{O}_5 \rightarrow 4\text{NO}_2 + \text{O}_2$, $r_{\text{inst}} = -\frac{1}{2} \frac{d[\text{N}_2\text{O}_5]}{dt} = \frac{1}{4} \frac{d[\text{NO}_2]}{dt} = \frac{d[\text{O}_2]}{dt}$

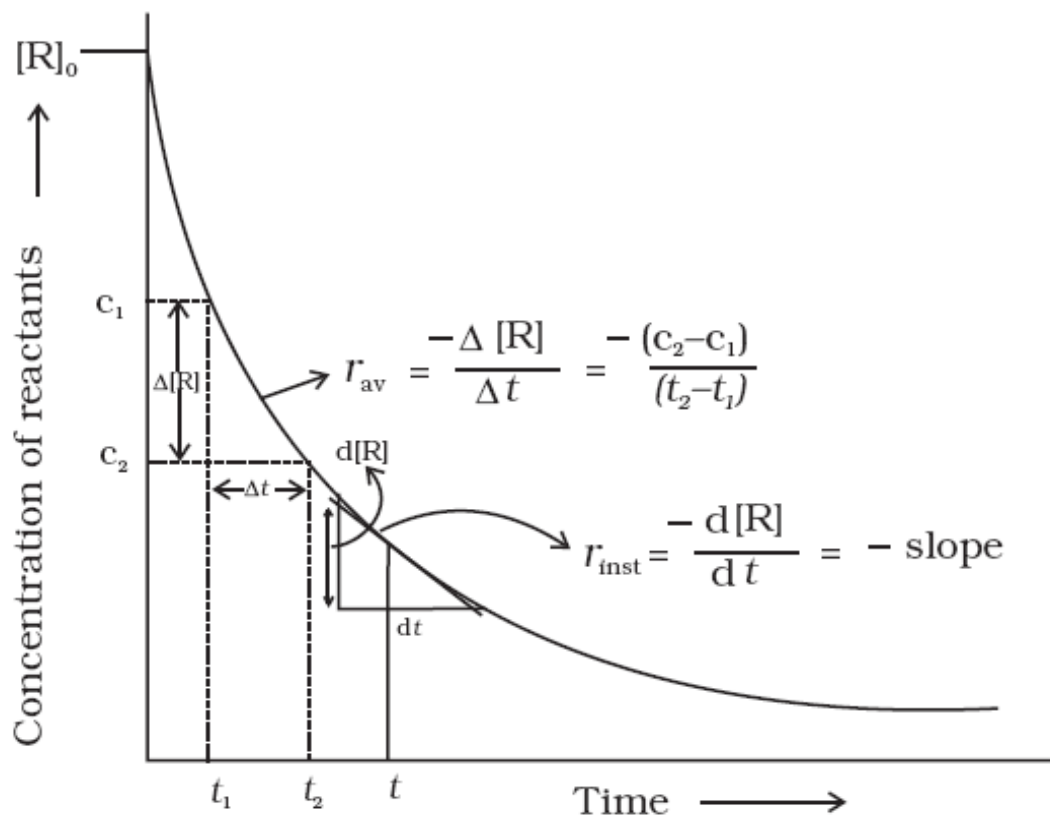
For the reaction, $\text{H}_2 + \text{I}_2 \rightarrow 2\text{HI}$, $r_{\text{inst}} = -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = \frac{1}{2} \frac{d[\text{HI}]}{dt}$

And $r_{\text{av.}} = -\frac{\Delta[\text{H}_2]}{\Delta t} = -\frac{\Delta[\text{I}_2]}{\Delta t} = \frac{1}{2} \frac{\Delta[\text{HI}]}{\Delta t}$

Determination of Instantaneous Rate of a reaction

Instantaneous Rate of a reaction can be determined graphically. First conduct the chemical reaction and find out the concentration of reactants or product at a regular interval of time. Then plot a graph between concentration along y-axis and time along x-axis.

In order to determine the Instantaneous Rate at a particular time, mark the point on the graph at that time and draw a tangent at the point. The slope of this tangent gives the instantaneous rate at that time.



For a general reaction $aA + bB \rightarrow cC + dD$,

The rate is given by $r_{\text{inst}} = \frac{-1}{a} \frac{d[A]}{dt} = \frac{-1}{b} \frac{d[B]}{dt} = \frac{1}{c} \frac{d[C]}{dt} = \frac{1}{d} \frac{d[D]}{dt}$

Factors affecting rate of a reaction

The important factors which affect the rate of a chemical reaction are:

1. Nature of the reactants
2. Concentration of the reactants
3. Temperature
4. Pressure (for gaseous reaction only)
5. Effect of catalyst
6. Influence of radiation

Dependence of Rate of reaction on concentration

It is found experimentally that Rate of reaction is directly proportional to the concentration of reactants.

Thus for a general reaction, $aA + bB \rightarrow cC + dD$, Rate $\propto [A]^x [B]^y$

Or, $r = k [A]^x[B]^y$ (where x and y may or may not be equal to a and b)

This expression is known as **rate law or rate equation**.

Thus rate law is a “mathematical equation relating the rate of a chemical reaction and concentration of reactants, in which each concentration term is raised to a power which may or may not be equal to the stoichiometric coefficients in the balanced chemical equation.”

In the above equation ‘k’ is a constant called *rate constant or velocity constant or specific reaction rate of the reaction*. It is defined as the rate of the reaction when the concentration of each of the reactants is unity.

Order of reaction

Order is the sum of the powers of the concentration terms of the reactants in the rate law. It is an experimental quantity. It can have the values 0,1,2,3,..... or a fraction. It is applicable to both elementary and complex reactions.

For a general reaction, $aA + bB \rightarrow cC + dD$; $r = k[A]^x[B]^y$,

Order of the reaction = $x + y$

If the order of a reaction is zero, it is called zero order reaction, if it is one, it is called first order reaction, if it is two, it is called second order reaction and so on.

Molecularity of a reaction

It is **the total number of reacting species collides simultaneously in a chemical reaction**. It is a theoretical quantity. It cannot be zero or fractional. It can have values 1,2,3 etc. it is applicable only to elementary reactions.

If the molecularity of a reaction is 1, it is called Unimolecular reaction.

e.g. Decomposition of ammonium nitrite $NH_4NO_2 \rightarrow N_2 + 2H_2O$

If the molecularity of a reaction is 2, it is called bimolecular reaction.

e.g. Decomposition of Hydrogen Iodide $2HI \rightarrow H_2 + I_2$
