3. CHEMICAL KINETICS

STUDY NOTES

3. 0 **Chemical kinetics** is concerned with the study of the **speed** of chemical reactions. Chemical kinetics deals with the Rates of reactions , Factors that affect them and the Mechanism by which the reactions take place.

3.1 **Rate of reaction:** During a chemical reaction, as time passes, the concentration of reactants decreases and the concentration of products increases.
Hence, the rate of reaction is defined as the change in molar concentration of any one of reactants or products per unit time. $\boxed{R \rightarrow P}$

For reactants: Rate = $-\frac{d[R]}{dt}$, **For products:** Rate = $+\frac{d[P]}{dt}$

-ve sign indicates that concentration of reactants decrease.
+ve sign indicates increase in conc. of the products.
Units : mol $L^{-1}S^{-1}$

3. 2 **Factors influencing Rate of reaction:**

3. 2.1 **i) Concentration:** Higher concentration $\rightarrow$ more collisions$\rightarrow$ faster the rate of reaction.
ii) Temperature: Increase in temp. $\rightarrow$ Increase in K.E $\rightarrow$ Increase in rate exponentially.
Note: In many reactions, the specific rate (k) doubles for every 10º C raise of temperature
iii) Catalyst: Catalyst increases the rate of reaction by changing the path having low activation energy. As the activation energy decreases the rate of reaction increases..
iv) Nature of reactants: Ionic reaction - fast; Covalent reactions -slow

3. 2.2 **Rate expression & Rate constant:**
Consider a general equation aA+bB$\rightarrow$cC+dD
The rate expression is $\text{Rate} \propto [A]^x[B]^y \Rightarrow \text{Rate} = k[A]^x[B]^y$

$$\Rightarrow \frac{-d[R]}{dt} = k[A]^x[B]^y$$

Here the proportionality constant k is called rate constant.

3. 2.3 **Order of a reaction:**
In the rate equation, $\text{Rate} = k[A]^m[B]^n$
Here, overall order of reaction = m+n
Order of a reaction is the he sum of the powers of the concentration terms in the rate equation
Note: order of reaction can be 0,1,2,3 or even a fraction also.
In **zero order reactions**, the rate of a reaction is independent of concentrations of reactants.
The reaction taking place in one step are called **Elementary reactions.**

3. 2.4 Molecularity of a reaction: It is the number of reactive species (atoms, ion or molecules) participating in the rate determining step.
Uni molecular reactions involve only one reactant species.
Bi molecular reactions involve collision between two reactant species.
Tri molecular reactions involve collision among three reactant species.

3. 2.5 Integrated Rate equation: The integrated rate equation to get a relation, to calculate concentration at any time and rate constant.

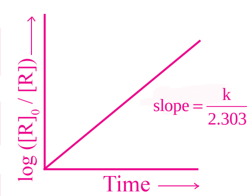
3. 3.1 Zero order reaction:

Rate constant $k = \frac{[R]_0 - [R]}{t}$. **Units:** mol $L^{-1}s^{-1}$

It's graph $[R] = -kt + [R]_0$ is a straight line in the form y=mx+c with slope m=–k

3. 3.2 First order reaction:

Rate constant $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$ **Units:** s^{-1}



It's graph is a straight line with slope $= \frac{k}{2.303}$

3. 3.2 Half life of a reaction is the time required to reduce half of the initial concentration of reactant.

For a zero order reaction, $t_{1/2} = \frac{[R]_0}{2k}$ $[R]_0$= Initial concentration of reactants.

For a first order reaction, $t_{1/2} = \frac{0.693}{k}$ **Ex:** Radioactive decays

3. 4 Temperature dependence of a rate of a reaction (Arrhenius Equation):

3. 4.1 The temperature dependence of the rate of a chemical reaction can be accurately given by the Arrhenius equation, rate constant $k = A\,e^{-Ea/RT}$.

Where A is frequency factor, E_a activation energy.

Note: High temperature →more molecules cross activation energy.

3. 4.2 Arrhenius equation in log form: $\ln k = \ln A - \frac{E_a}{RT}$ (or) $\log k = \log A - \frac{E_a}{2.303RT}$

3. 4.3 $\ln\frac{k_2}{k_1} = \frac{E_a}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$ (or) $\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$

3. 5 Collision theory of chemical reactions:
Reactions occur when molecules collide effectively.
Conditions for effective collisions:
i) Proper orientation ii) Energy > Activation energy
Rate Expression: Rate ∝ No. of effective collisions