

Attention: All the students of Semester II having Chemistry as General Paper (GE 2 and C 2)

SOLIDS

1. Difference between Crystalline and Amorphous solids:

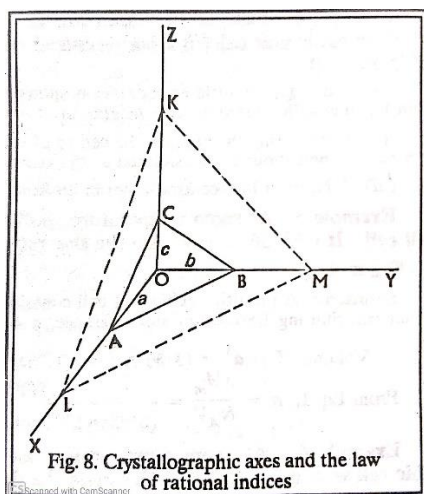
	Crystalline	Amorphous
1	Ordered arrangement	No ordered arrangement
2	Anisotropic	Isotropic
3	Sharp melting point	No sharp melting point
4	Electrical and thermal conductivity	Not conduct electricity and heat

2. Laws of Crystallography:

Law of constancy of interfacial angles : The angles between the corresponding faces of various crystals of the same substance are constant.

- In spite of the differences in shape, the angles between corresponding faces of a particular crystal are always the same.

Law of rational indices : Intercepts of the planes of the various faces of a crystal are small integral multiples of the intercepts made by the unit plane.



Let OX, OY and OZ represent the three crystallographic axes and let ABC be a unit plane. The unit intercepts will then be a, b and c. Accordingly the intercept of any face such as KLM, on the same three axes will be simple whole number multiple of a, b and c respectively.

Miller Indices:

A set of integers (h,k,l) which are used to describe a given plane in a crystal.

To obtain Miller indices for any crystal plane, the ratios of the intercepts made by the unit plane to those made by the given plane are converted to whole numbers.

- The intercepts made by the unit plane ABC are a, b and c and the intercepts made by the plane KLM are 2a, 2b and 3c.

$$\text{Then the ratio of the intercepts are } \frac{a}{2a} : \frac{b}{2b} : \frac{c}{3c} = \frac{1}{2} : \frac{1}{2} : \frac{1}{3}$$

$$\text{Then, } h : k : l = 3 : 3 : 2$$

The plane KLM is then said to be (332) plane.

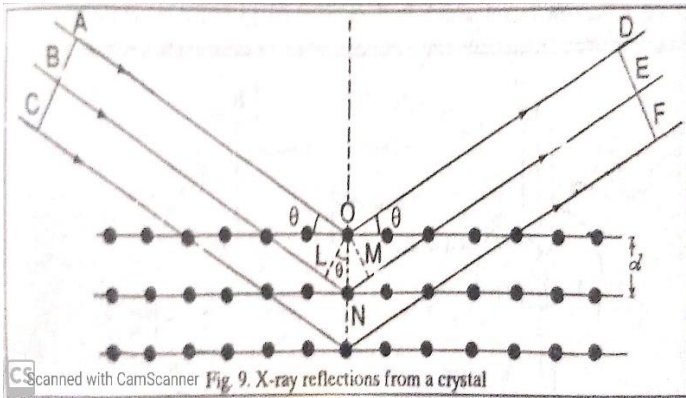
Interplanar distance in a crystal system:

In an orthorhombic crystal (it has unit cell vectors $a \neq b \neq c$ and interaxial angles $\alpha = \beta = \gamma = 90^\circ$) the interplanar distance d_{hkl} is given by $\frac{1}{(d_{hkl})^2} = \left(\frac{h}{a}\right)^2 + \left(\frac{k}{b}\right)^2 + \left(\frac{l}{c}\right)^2$, where h, k, l are the Miller indices of the planes.

- For a cubic system, $a = b = c$ and so $d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$

Bragg's law:

The X-rays waves reflected by different layer planes will be in phase with one another (constructive interference) only if the difference in the path lengths of the waves reflected from the successive planes is equal to an integral number of the wave lengths.



Bragg's equation: $2 \sin \theta = n\lambda$, $n = 1, 2, 3, \dots$

Where, X-rays falls on the crystal at glancing angle θ , d be the interplanar distance, λ is wave length of X-rays and n is the order of reflection.

CHEMICAL KINETICS

1. RATE OF A REACTION

Definition: Change of concentration with time

Mathematical Expression: $\text{Rate} = \frac{1}{\nu} \left(\frac{dC}{dt} \right)$,

ν = stoichiometric coefficient (positive for products and negative for reactants)

C = concentration

t = time

Example:

For the reaction $2A + B \rightarrow 3C$

$$\text{Rate} = -\frac{1}{2} \left(\frac{dC_A}{dt} \right) = - \left(\frac{dC_B}{dt} \right) = \frac{1}{3} \left(\frac{dC_C}{dt} \right)$$

Unit : moles /litre/sec

Factors on which rate depends:

- (i) Concentration of reactants
- (ii) time of reaction
- (iii) Temperature of reaction
- (iv) {Presence of catalyst

2. RATE EXPRESSION

$$\frac{1}{\nu} \left(\frac{dC}{dt} \right) = k C^n, \quad n = \text{order of reaction, } k = \text{rate constant}$$

Example: For the reaction $2A + B \rightarrow 3C$

$$\text{Rate} = -\frac{1}{2} \left(\frac{dC_A}{dt} \right) = - \left(\frac{dC_B}{dt} \right) = \frac{1}{3} \left(\frac{dC_C}{dt} \right) = k C_A^n C_B^m \quad n, m = \text{order with respect to A and B respectively}$$

3. RATE CONSTANT

Definition: Rate at unit concentration of reactants

Unit: Depends on order of reaction

Factors on which rate depends: Temperature of reaction

4. ORDER & MOLECULARITY OF REACTION

ORDER	MOLECULARITY
1. Power to which concentration terms are raised in the rate expression	1. Number of molecules participating in the rate determining step of the reaction
2. Can be fraction, integer, negative	2. Is always positive integer
3. Determined by experiment	3. Predicted from theory

5. CHARACTERISTICS OF DIFFERENT ORDER REACTIONS:

Order	Zero	First	Second
Differential Equation	Rate = k	Rate = kC	Rate = kC ²
Integral Equation	C ₀ -C = kt	$\ln \left(\frac{C_0}{C} \right) = kt$ C = concentration of reactant at time t	$\frac{1}{C} - \frac{1}{C_0} = kt$ C ₀ = initial concentration of reactant

Unit of rate constant	Mole lit ⁻¹ sec ⁻¹	sec ⁻¹	Mole ⁻¹ litre sec ⁻¹
Half life	$t_{1/2} = \frac{C_0}{2k}$, directly proportional to initial concentration	$t_{1/2} = 0.693/k$, independent of initial concentration	$t_{1/2} = \frac{1}{C_0 k}$, inversely proportional to initial concentration
Time of completion	Finite	Infinity	Infinity
Example	Decomposition of HI on gold surface	Decomposition of H ₂ O ₂	Basic hydrolysis of ester

6. PSEUDO UNIMOLECULAR REACTION:

Definition: If a reaction involves two or more reactants, but the rate depends only upon the concentration of one of them and is independent of the others., the reaction is called pseudo unimolecular reaction. The reaction looks like a second or third order reaction but behaves like a first order one.

Reason: One of the reactants is of very high concentration as compared to the other, and its concentration remains virtually unchanged with time. Therefore its concentration can be considered to be constant and reaction depends only on the concentration of the other constituent.

Example: Ester hydrolysis Ester + H₂O → alcohol + acid

Rate = k [Ester][H₂O]. since [H₂O] >> [ester], [H₂O] = [H₂O]₀ = constant

Therefore, rate = k' [ester] where k' = k[H₂O] = pseudo first order rate constant

7. ARREHENIUS EQUATION (TEMPERATURE DEPENDENCE OF k)

$$k = Ae^{-\frac{E_a}{RT}} \text{-----(1)}$$

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

k = rate constant

A = Frequency or Pre exponential factor (unit same as k)

E_a = Activation energy (Jmole⁻¹)

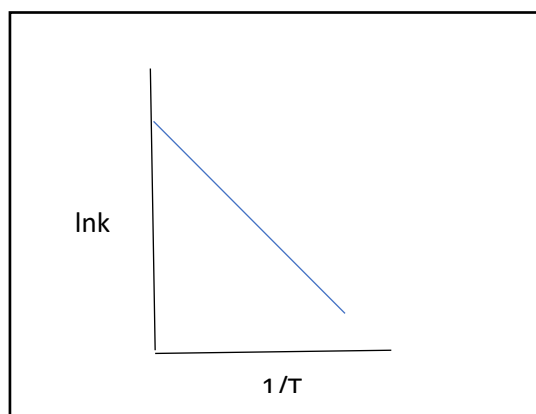
R = Universal gas constant (JK⁻¹mole⁻¹)

T = Temperature (K)

Significance: As temperature increases rate of reaction increases.

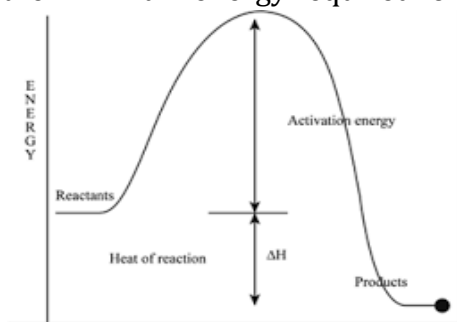
Graphical representation: Taking logarithm of both sides of equation (1)... $\ln k = \ln A - \frac{E_a}{RT}$

Plotting $\ln k$ vs $1/T$



Slope = $-E_a/R$ $E_a = \text{slope} \times R$ Intercept = $\ln A$

Activation energy (E_a): It is the minimum energy required for a chemical reaction to occur.



8. WORKED OUT PROBLEMS:

1. A first order reaction is 75% complete in 32 mins. Calculate its half life. (WBSU 2018)

Ans. Reaction 75% complete, ie 25% reactant left. For a first order reaction

$$\ln\left(\frac{C_0}{C}\right) = kt \quad \text{---} \ln\left(\frac{C_0}{0.25C_0}\right) = k \times 32 \quad \text{---} \quad k = 0.04 \text{ min}^{-1}$$

$$t_{1/2} = 0.693/k = 0.693/0.04 = 17.3 \text{ mins}$$

2. Rate constant for a first order decomposition process is $1.37 \times 10^{-5} \text{ sec}^{-1}$ and $5.15 \times 10^{-5} \text{ sec}^{-1}$ at 25 and 37°C respectively. Calculate its activation energy. (WBSU 2017)

Ans.

$$\ln\left(\frac{k_1}{k_2}\right) = \frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{1.37 \times 10^{-5}}{5.15 \times 10^{-5}}\right) = \frac{E_a}{8.314} \left(\frac{1}{(37 + 273)} - \frac{1}{(25 + 273)}\right)$$

$$E_a = (1.32 \times 8.314) / 1.3 \times 10^{-4} = 84.5 \text{ kJ/mole}$$

3. A first order reaction takes 20 mins to complete 50% of the reaction. Calculate the time taken to complete 75%. (WBSU 2011)

Ans. Reaction 50% complete, ie 50% reactant left. For a first order reaction

$$\ln\left(\frac{C_0}{C}\right) = kt \quad \text{---} \ln\left(\frac{C_0}{0.5C_0}\right) = k \times 20 \quad \text{---} \quad k = 0.035 \text{ min}^{-1}$$

For 75% completion of reaction, 25% reactant left.

$$\ln\left(\frac{C_0}{C}\right) = kt \quad \text{---} \ln\left(\frac{C_0}{0.25C_0}\right) = 0.035 \times t \quad \text{---} \quad t = 39.6 \text{ mins}$$