

**Subunit 10: Chemical Kinetics, Catalysis & Photochemistry****Key Terminologies:**

**Basic Terms:** Rate of a Reaction [2.10.2], Order of a reaction [2.10.3], Molecularity [2.10.4], Zero order reaction [2.10.6], First order reaction [2.10.11], Second order reaction [2.10.16], Half life period of a reaction [2.10.10], Unit of rate constant [2.10.29], Reversible Reaction [2.10.31], Consecutive Reaction [2.10.32], Parallel Reaction [2.10.33], Chain Reaction [2.10.44], Catalysis [2.10.47], Homogeneous Catalysis [2.10.48], Homogeneous Acid catalysis [2.10.56], Homogeneous Base catalysis [2.10.57], Heterogeneous Catalysis [2.10.58], Photochemical reaction [2.10.70], Lambert-Beer's law [2.10.72], Absorbance [2.10.73], Grothus-Draper Law [2.10.76], Einstein's law of photochemical equivalence [2.10.76], Quantum yield [2.10.76], Secondary Process [2.10.78], Thermopile [2.10.81], Actinometer [2.10.81].

**Standard Terms:** n-th order reaction [2.10.22], Arrhenius Equation [2.10.35], Steady State Approximation [2.10.37], Collision Theory [2.10.38], Transition state Theory [2.10.40], Lindemann Theory [2.10.43], Enzyme catalysis [2.10.63], Michaelis-Menten equation [2.10.64], Turn Over Number [2.10.65], Lineweaver-Burk Plot [2.10.66], Frank-Condon Principle [2.10.77], Dimerization of Anthracene [2.10.84], Fluorescence [2.10.85], Phosphorescence [2.10.86].

**Advanced Terms:** Half order of reaction [2.10.20], Wegscheider's Test [2.10.34], Activation Energy & Frequency Factor [2.10.36], Probability Factor [2.10.39], Internal Energy of Activation [2.10.41], Entropy of Activation [2.10.42], Primary Salt Effect [2.10.45], Secondary salt effect [2.10.69], Photosensitized reaction [2.10.82], Photochemical Equilibrium [2.10.83], Chemiluminescence [2.10.87].

**Key Conceptual Points:****Subunit 10A: Chemical Kinetics**

2.10.1. **Chemical Kinetics** is a physical experimental method that deals with the speed of a given reaction and a plausible mechanism of that reaction can be evaluated from that data.

2.10.2. The decrease in concentration of reactants for the increase in concentration of products with time consumption, is called **rate of a reaction**, denoted mathematically by

$$r = -dC/dt = K_n C^n$$

where, r = rate of the Reaction,  $K_n$  = Rate Constant, C = concentration of the reactant, n = order of the Reaction

$$-dC/dt = K[A]^a[B]^b[C]^c$$

When more than one reactant are involved in a reaction.

**2.10.3. Order of a reaction:** The number of concentration of reactants involved in a rate equation of a given reaction, that means those who control the rate of the reaction, is called as order of a reaction.

$-dC/dt = K[A]^a[B]^b[C]^c$  from this rate equation, the order of the reaction is  $n = a + b + c$ . So, the summation of the exponential terms of concentrations involved in the reaction rate equation will be the overall order of the reaction and the exponent of a particular concentration will be order of the reaction with respect to the corresponding reactant.

**2.10.4. Molecularity** of a reaction the molecularity of a reaction is defined as the number of molecules or atoms which take part in the process of a chemical change. The reactions are said to be unimolecular, bimolecular or termolecular according to one, two or three molecules are involved in the reaction leading to a chemical change. Generally, a reaction takes place in a number of steps and when we speak of molecularity, we should say molecularity of each step.

**2.10.5. The differences between order and molecularity of a reaction** are as

(I) Order is an experimentally determined quantity which is obtained from the rate equation for overall reaction whereas molecularity is a theoretical concept which depends on the rate determining step in the reaction mechanism.

(II) Order would be any value including zero but molecularity could not be 0 or exceeding 3.

(III) Order may be whole number or fractional value whereas molecularity always be a whole number.

(IV) Order cannot be obtained from a balanced chemical reaction whereas molecularity can be evaluated from a single balanced chemical equation.

(V) Order cannot provide any information regarding the Mechanism of the reaction concerned but molecularity does.

(VI) Order is equal to the sum of the exponents of the molar concentration of the reactant in the rate equation molecularity is equal to the number of molecules of the reactants which are taking part in a single step chemical reaction.

**2.10.6. Zero order reaction:** When a reaction whose rate is independent of concentration of the reactant is a zero order reaction. Thus, for a zero order reaction,

Rate of a zero order reaction will be

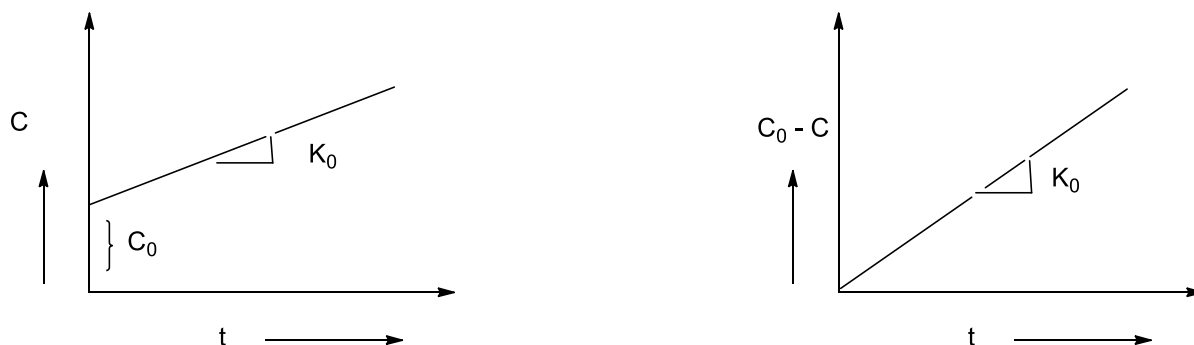
$$R = C_0 - C = K_0t \quad \text{or} \quad X = K_0t$$

Where  $C_0$  = initial concentration of reactant,  $C$  = intermediate concentration of reactant at time  $t$ ,  $X$  = final concentration of reactant at time  $t$ ,  $K_0$  = rate constant

## 2.10.7. Examples for zero order reaction

- (i) enzyme catalyzed reactions
- (ii) decomposition of hydrogen iodide on gold surface

2.10.8. From zero order reaction rate equation it is clear that the reactant decreases with time whereas product increases with time; therefore, if a plot is drawn between  $(C_0 - C)$  and  $t$  we should get a straight line passing through the origin with slope  $K_0$ .



## 2.10.9. Time of completion of a zero order reaction

$$t_c = C_0/K_0$$

2.10.10. The time required when half of the reactant is converted into product is called **Half life period of a reaction** and it is represented by  $t_{1/2}$ . The  $t_{1/2}$  of zero order reaction is

$$t_{1/2} = C_0/2K_0$$

2.10.11. **First order reaction:** A reaction is said to be first order when the reaction rate is proportional to the concentration of a reactant. A reaction of first order is represented as

$$C = C_0 e^{-K_1 t}$$

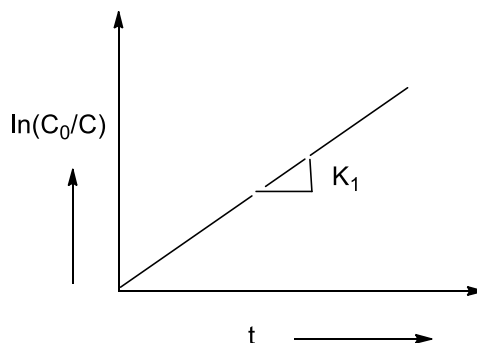
$$\ln(C_0/C_0 - C) = K_1 t$$

2.10.12. Completion time for first order reaction is infinity, that means the reaction cannot be completed at all.

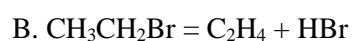
2.10.13 The Half Life period for first order reaction is

$$t_{1/2} = 0.693/K$$

2.10.14 From the first order rate equation, if we draw the plot of  $\ln(C_0/C)$  vs.  $t$  would give a straight line passing through the origin having slope  $K_1$



2.10.15. Examples for first order reaction



C. Radioactive decays

2.10.16. **Second order reaction:** A reaction is said to be second order when the reaction rate would depend upon the product of the two reactants concentration or square of one reactant concentration. The rate equation for second order reaction is

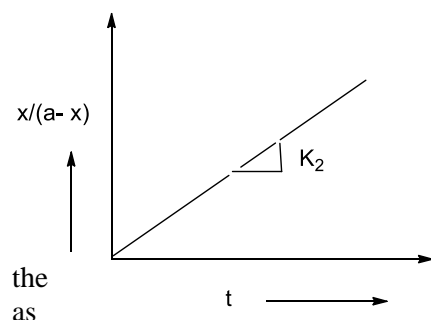
$$dx/dt = K_2(a-x)^2 \text{ [when the concentrations of reactants are equal]}$$

$$x/a(a-x) = K_2t$$

$$dx/dt = K_2(a-x)(b-x) \text{ [when the concentrations of reactants are unequal]}$$

$$\ln[b(a-x)/a(b-x)] / (a-b) = K_2t$$

2.10.17. The plot of  $\ln[b(a-x)/a(b-x)] / (a-b)$  vs.  $t$  would give a straight line passing through the origin having slope  $K_2$ .



2.10.18. The Half Life period for a second order reaction when initial concentrations of the reactants are equal can be measured

$$t_{1/2} = 1/aK_2$$

2.10.19. Examples for second order reaction

A.  $H_2 + I_2 = 2HI$

B. Alkaline hydrolysis of esters

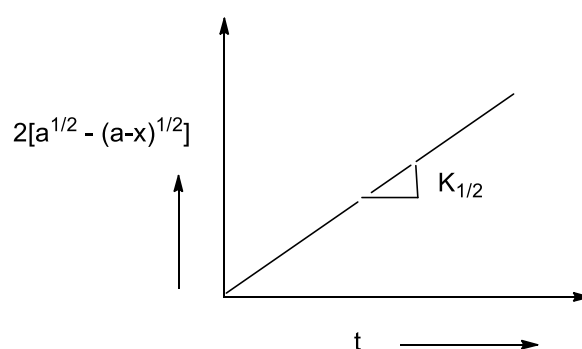
C. Esterification of acids

D.  $S_N2$  and  $E2$  Reactions

2.10.20. Rate equation for **Half order reaction**

$$2[a^{1/2} - (a-x)^{1/2}] = K_{1/2}t$$

Graphical representation of a half order reaction will be as follows,



2.10.21. Half-life period for a half order reaction

$$t_{1/2} = 0.586a^{1/2}/K_{1/2}$$

2.10.22. Rate equation for **n-th order reaction**

$$K_n = 1/t(n-1)[1/(a-x)^{n-1} - 1/a^{n-1}]$$

2.10.23. **Half-life period for n-th order reaction**

$$t_{1/2} = 1/K_n^{(n-1)}[2^{n-1} - 1/a^{n-1}]$$

2.10.24. Ratio of  $t_{1/2}$  and  $t_{3/4}$  for n-th order, First order and Second order reactions would be

$$t_{1/2}/t_{3/4} = 1/2^{n-1} + 1 \text{ [for n-th order reaction]}$$

$$t_{1/2}/t_{3/4} = 1/2 \text{ [for first order reaction]}$$

$$t_{1/2}/t_{3/4} = 1/3 \text{ [for second order reaction]}$$

2.10.25. **Pseudo-unimolecular Reaction:** There are several reactions in which more than one species are involved in the rate determining step, but the order of the reaction is one; such types of reactions are called pseudo-unimolecular reactions. Examples are

A. Acid catalyzed hydrolysis of esters

B. Inversion of Cane sugar

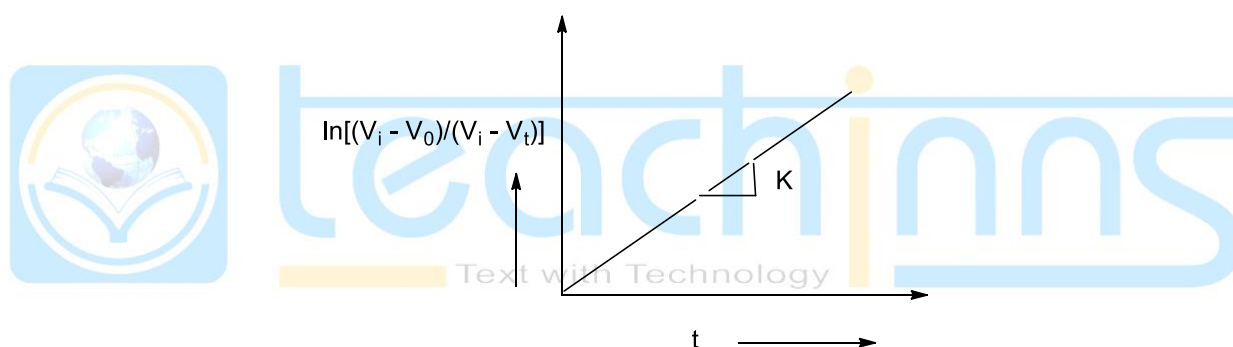
**2.10.26. Rate equation for Acid catalyzed hydrolysis of Ester:** Hydrolysis of esters in presence of acids follows first order reaction kinetics; this is because the water is present in large excess and its active mass remains practically constant. Therefore, its active mass gets included in the constant. Since the rate of the reaction is determined by one concentration term with respect to ester only, the reaction is of first order. Such reactions are bimolecular and seems to be second order but in actual first order. Hence, the amount of acid formed 'x' after different intervals of time 't' can be calculated. As the progress of the reaction is followed by determining the amount of acid formed at different intervals through titration against standard alkali solution. Actually, the amount of alkali used is equivalent to the total amount of inorganic acid catalyst present initially and the carboxylic acid formed from ester during course of the reaction. The amount of acid formed at the end of the reaction is equivalent to the initial concentration 'a' of the ester. Suppose the volume of standard alkali solution (say 0.1N NaOH solution) required for the titration, at the start, after time t, and at the end of the reaction are  $V_0$ ,  $V_t$  and  $V_\infty$  respectively, then the initial concentration of ester, 'a' is proportional to  $(V_\infty - V_0)$ . Therefore, the concentration of ester present after time t, i.e.,  $(a-x)$  is proportional to  $\{(V_\infty - V_0) - (V_t - V_0)\} = (V_\infty - V_t)$ .

Reaction is  $\text{CH}_3\text{COOC}_2\text{H}_5 + \text{H}_3\text{O}^+ \rightarrow \text{CH}_3\text{COOH} + \text{C}_2\text{H}_5\text{OH}$

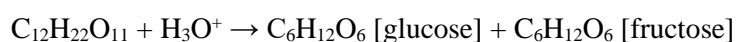
The rate equation will be

$$\ln[(V_\infty - V_0)/(V_\infty - V_t)] = Kt$$

Graphical plot will be



**2.10.27. Rate equation for inversion of Cane sugar:** The inversion of cane sugar in presence of a mineral acid as catalyst is presented as



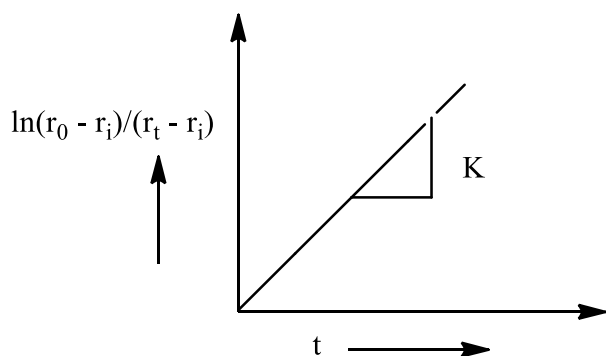
An important characteristic of the reaction is that sucrose is dextro-rotatory whereas products of hydrolysis, i.e., glucose and fructose are dextro- and laevo-rotatory respectively. Further, the magnitude of laevo-rotation of fructose is greater than the magnitude of dextro-rotation of glucose at the same concentration. Therefore, the mixture of products as a whole becomes laevo-rotatory. Thus on hydrolysis, dextro-rotation decreases and becomes zero, then eventually laevo-rotation starts. The progress of reaction can be followed by measuring the angle of rotation of the plane of plane-polarized light in a polarimeter.



Let,  $r_0$  = polarimeter reading at time zero,  $r_t$  = polarimeter reading at any time  $t$ ,  $r_\infty$  = polarimeter reading at infinite time (generally consider over 24 hours); therefore, the rate equation will be

$$\ln[(r_0 - r_i)/(r_t - r_i)] = Kt$$

Graphical plot will be



#### 2.10.28. Determination of the order of a reaction

$$n = \log(r_1/r_2)/\log(C_1/C_2) \text{ [Differential method]}$$

$$n = 1 + (\log t_{1/2(1)}/t_{1/2(2)})/(\log C_2/\log C_1) \text{ [Half-life method]}$$

#### 2.10.29. Unit of rate constant

$$\text{Unit of } K_n = \text{unit of } r / \text{unit of } C_n = \text{mol L}^{-1} \text{s}^{-1} / (\text{mol L}^{-1})^n$$

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

**2.10.30. Simultaneous Reactions:** In a chemical reaction when the reactants or the products undergo more change than one considered; these kinds of reactions are known as simultaneous reactions. Simultaneous reactions generally are of three types:

- A. Opposing or reversible reaction
- B. Consecutive or sequential reaction
- C. Parallel or side reaction



2.10.31. **Opposing or reversible reaction:** Opposing or reversible reaction are those in which both forward and backward reaction take place simultaneously.

Rate equation

$$K_1 + K_{-1} = \ln[(K_1 a) / \{K_1 a - (K_1 + K_{-1})x\}] / t$$

Where, 'a' be initial concentration of reactant and 'x' be the concentration of product at time t. Moreover,  $K_1$  be the rate of forward reaction and  $K_{-1}$  be the rate of backward reaction.

Alternative rate equation for Opposing or reversible reaction:

$$K_1 = x_e \ln(x_e / x_e - x) / at$$

$$\text{And } K + K_{-1} = \ln(x_e / x_e - x) / t$$

Where ' $x_e$ ' be the concentration of product at equilibrium and  $K$  is equilibrium constant;  $K = K_1 / K_{-1}$ .

2.10.32. **Consecutive or sequential reaction:** When reaction proceeds from reactant to product through one or more intermediate species, is called consecutive reaction.

If  $C_0$  is initial concentration of the reactant and  $C_1, C_2, C_3$  be the concentration of reactant, intermediate, and product respectively at any time  $t$ .

$$C_0 = C_1 + C_2 + C_3$$

$$C_1 = C_0 e^{-K_1 t} \quad [\text{where } K_1 \text{ is rate constant for the conversion from reactant to intermediate}]$$

$$C_2 = K_1 C_0 [e^{-K_1 t} - e^{-K_2 t}] / (K_2 - K_1)$$

$$C_3 = C_0 \{ [1 - (K_2 / K_2 - K_1) e^{-K_1 t}] + [1 - (K_1 / K_2 - K_1) e^{-K_2 t}] \}$$

At time  $t_{\max}$  the concentration of B is reached at its maximum value  $C_{2(\max)}$ ; hence  $dC_2/dt = 0$

$$t_{\max} = \ln(K_1 / K_2) / (K_1 - K_2)$$

$$C_{2(\max)} = C_0 (K_2 / K_1) K_2 / K_1 - K_2$$

2.10.33. **Parallel or competing reaction:** If the reacting substances follow more than one path to give different products, then the different paths are termed as parallel or side reaction or competing reaction.

Rate equation for a Parallel reaction

$$R = C_1/C_2 = K_1/K_2$$

where,  $C_1$  and  $C_2$  are concentrations of product 1 and product 2;  $K_1$  and  $K_2$  are rate constants for path 1 and path 2.

2.10.34. **Wegschieder's Test:** The ratio of amount of the product 1 and product 2 at any time interval would be same, provided the orders of the two parallel reactions be the same. This is known as Wegschieder's test for side reaction distinguishing them from opposing or consecutive reactions. This experiment will not be applicable if the orders of the two side reactions are not the same. As for example, Nitration of phenol there is two products would be obtained; first one *o*-Nitrophenol and second product *p*-Nitrophenol possessing the rate of both the paths are same here ( $K_1 = K_2$ ).

2.10.35. **Arrhenius equation for activation energy in a reaction:** It is well known fact that the rates of all reactions are generally increased by the increase of temperature. It is found that the rate of a reaction increases by 100% to 200% for 10 degree rise in temperature. The term "temperature coefficient of a reaction is the ratio of two different rate constants having temperature difference by 10°C, that value is in between 2 to 3.

$$K = Ae^{-E_a/RT}$$

Where,  $K$  = Rate constant,  $E_a$  = Activation energy for the Reaction,  $A$  = Frequency Factor (a constant),  $R$  = Universal gas constant,  $T$  = temperature.

For measuring the activation energy of a reaction at two different temperatures  $T_1$  and  $T_2$  possessing obviously at two different rates i.e.,  $K_1$  and  $K_2$  respectively, the equation will be

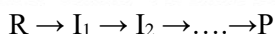
$$\ln(K_2/K_1) = E_a(T_2 - T_1/T_1T_2)/R$$

**2.10.36. Concept of Activation energy and Frequency factor:** The product formation from reactant molecules can be attributed as the reactant molecules come close and collide together at the same time. During the collision, the molecular rearrangement takes place which leads to the formation of the products. The molecular rearrangement usually involves breaking of some bonds and making others. The breaking of bonds or in general molecular rearrangement can take place only when the colliding molecules have energy equal to or greater than the minimum energy required for the said molecular rearrangement. The difference between the minimum energy required to bring about the molecular rearrangement and the average energy of reactant molecules is identified with the constant  $E_a$  and is known as energy of activation for the reaction.

In an assembly of reactant molecules, the energy of each molecule is not necessarily same. Molecules possessing the energy equal to or greater than a particular value, are known as active molecules and the others as passive. Only active molecules are in a position to react. At a given temperature number of active

molecules are constant. But this number increase exponentially according to Boltzmann distribution law for energy with temperature. That is why the rate of reaction increases so highly with temperature. For a passive molecule to react it must receive sufficient energy equal to reach the energy rich intermediate which leads to the product. Therefore, frequency factor depends on the energy distribution in the reactant molecules and the orientation of those for perfect molecular rearrangement which leads to the product.

**2.10.37. Steady state approximation:** In cases where the reactions are investigated under such conditions that the lowest rate determining step does not exist, then one assumes the steady state approximation for the transient species or intermediate in such a mechanism shown below



The rate of formation of an intermediate is equal to the rate of its decomposition, so that  $d[I_1]/dt = d[I_2]/dt = 0$ .

That is when the reaction proceeds steadily there will be no overall accumulation of the intermediate and there would be stationary concentration of the same, i.e.,  $d[I]/dt = 0$ . This fact of constant concentration of the intermediate, an unstable or short-lived species is commonly known as steady state approximation.

**2.10.38. Collision Theory:** The first theory to explain the mechanism of chemical reaction is the collision theory. According to this theory the reactant molecules collide and going to this collision some structural rearrangement occurs which is responsible for chemical reaction. However, if each collision leads to the reaction, then the number of molecules reacting per CC per second should be equal to collision frequency, that is, the number of binary collisions occurring per CC per second. However, the number of molecules reacting per CC per second is much less than the collision frequency. Furthermore, while rate of a reaction increases 100 to 200% for 10°C rise in temperature. But collision frequency increases only by 2 to 3% for the same change in the temperature. It was explained at this time by introducing the concept of activation

energy by Great scientist Arrhenius. According to which for a molecule to react it must have energy approximately equal to or greater than activation energy. These molecules are called active molecules. Collisions between active molecules are fruitful and lead to reaction whereas collisions between passive molecules are fruitless. The equations are used to denote collision theory as follows,

$$\text{Collision frequency } Z = (\pi\sigma^2 C_a N^{*2})/\sqrt{2}$$

Rate equation is

$$-dN^*/dt = \sqrt{2}\pi\sigma^2 C_a N^{*2} e^{-E_a/RT}$$

$$\text{Rate constant } K = \sqrt{2}\pi\sigma^2 C_a N_A 10^{-3} e^{-E_a/RT}$$

$$A = \sqrt{2}\pi\sigma^2 C_a N_A 10^{-3}$$

Where,  $Z$  = Collision Frequency,  $\sigma$  = Collision diameter,  $C_a$  = Average velocity of the molecules,  $N^*$  = number of molecules present per CC,  $E_a$  = Activation Energy,  $N_A$  = Avogadro's Number,  $R$  = Universal Gas Constant,  $-dN^*/dt$  = Rate of the Reaction,  $K$  = Rate Constant,  $A$  = Frequency Factor (in Arrhenius equation)

#### 2.10.39. Limitations of Collision theory:

- (i) This theory cannot explain properly the reason behind the rate constant becomes greater than that is evaluated from Arrhenius equation in such a case of **chain reactions**.
- (ii) This theory cannot explain why sometimes the rate is observed little less than the calculated value from Arrhenius equation. The reason behind that is not considered in this theory and that is the **probability factor** which should be incorporated in this reaction as follows,

$$K = PAe^{-E_a/RT}$$

Where,  $P$  = Probability Factor, and rest have their usual significance.

- (iii) This reaction cannot consider the **entropy change** for a reaction. If for a reversible reaction the forward and backward rate constant is  $K_1$  and  $K_{-1}$ , then,

$$K_{eq} = K_1/K_{-1} = (P_1 A_1 / P_{-1} A_{-1}) e^{-(E_a - E_{-a}/RT)}$$

$$\text{Again, } K_{eq} = \exp(-\Delta G^0/RT) = \exp(-(\Delta H^0 - T\Delta S^0)/RT)$$

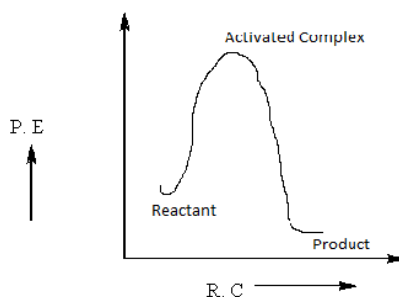
From the above equations, we can conclude as

$$P_1 A_1 / P_{-1} A_{-1} = e^{\Delta S/R}$$

2.10.40. **Transition state theory:** Transition state theory of absolute reaction rate was developed by M. Polanyi and H. Eyring in 1935. According to this theory,

(I) In order of any chemical reaction to take place the reactant molecules possessing sufficient energy must approach each other to form a loose association, known as activated Complex. This complex is in equilibrium with the reactant molecules.

(II) The configuration of the activated complex is such that energetically it corresponds to the top of the Energy barrier separating the reactants from the products shown in the following curve



(III) The activated complex is an aggregate of atoms. It may be thought of being similar to a molecule except that it has one special vibration with respect to which it is unstable. This direction leads to dissociation of the complex into products. The rate in molecules per unit volume per second at which products are formed is

$r = v[A^\ddagger]$  where,  $v$  = frequency of forming activated complex,  $[A^\ddagger]$  = concentration of activated complex

Expression of rate constant through transition state theory

$$K_n = (RT/N_A h) (RT/p_0)^{n-1} e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

Where,  $K_n$  = Rate Constant,  $T$  = reaction temperature,  $N_A$  = Avogadro's number,  $p_0$  = initial total pressure of reactant gas molecules,  $n$  = order of the Reaction or Molecularity of elementary Rate determining step,  $\Delta S^\ddagger$  = Standard Entropy of Activation,  $\Delta H^\ddagger$  = Standard Enthalpy of Activation

Now, for a second order reaction, the rate equation will be

$$K_2 = (R^2 T^2 / N_A h p_0) e^{\Delta S^\ddagger/R} e^{-\Delta H^\ddagger/RT}$$

**2.10.41. Relationship between Standard Internal Energy of Activation and Standard Enthalpy of Activation with Activation Energy:** Relation between Standard internal energy of Activation and Activation Energy is

$$E_a = RT + \Delta U^\#$$

Where,  $\Delta U^\#$  = Standard internal energy change for activation

Relation between standard enthalpy of activation and activation energy

$$\Delta H^\# = E_a + RT(\Delta n - 1)$$

Where,  $\Delta H^\#$  = Standard Enthalpy of Activation

$E_a$  = Activation Energy (from Arrhenius equation)

$\Delta n$  = change in number of molecules or moles in activated complex formation

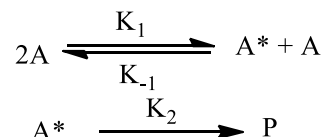
$\Delta n = 1 - n$ , where  $n$  = number of reactants. Hence, for unimolecular reaction  $\Delta n = 0$  and for bimolecular reaction  $\Delta n = -1$ .

**2.10.42. Entropy of activation:** According to transition state theory in any reaction the reactant molecules combine to form an intermediate of higher potential energy which has got a special vibrational degree of freedom that ultimately breaks down to give the products. This intermediate is known as activated Complex. Difference of Entropy between the reactants and the activated complex is known as **entropy of activation**. Entropy of activation values are very much utilized for knowing the mechanism of a reaction. For gaseous unimolecular reactions, the reactant molecules first suffer a structural change to give the intermediate which ultimately breaks down to give the product. Hence the activated complex would most likely to have acquired some of the disorder. That is why, the entropy of activation for gaseous unimolecular reaction is positive. For gaseous bimolecular reaction, two reactant molecules come close to produce the activated Complex; the total translational degrees of freedom are reduced from 6 to 3 and the rotational degrees of freedom also diminished. This is compensated by increasing in vibrational degrees of freedom. But the definite orientation in forming the complex necessarily reduced the entropy. The value of entropy of activation is thus negative.



2.10.43. **Lindemann theory** for the mechanism of Pseudo-unimolecular reaction: Lindemann proposed that for such Unimolecular reactions, the molecules get activated by collision but as the life period of an activated complex is relatively high, thereby some active molecules may become deactivated by collision while others will lead to the reaction. In such a case the two molecules are involved in the collision process but the overall order may be one.

The rate for pseudo-unimolecular reaction



$$r = d[P]/dt = K_1 K_2 [A]^2 / K_{-1} [A] + K_2$$

If during the course of the reaction concentration of A is very high then possibility of deactivation of an active molecule by normal molecule is very high also and hence  $K_{-1}[A] \gg K_2$ . Now the rate becomes

$$r = K_1 K_2 [A] / K_{-1}$$

The reaction becomes Unimolecular and mechanism also be explained by this Theory.

On the contrary if initial concentration of A is very small, then chance of deactivation by collision also becomes low and so  $K_{-1}[A] \ll K_2$ . Now, the rate becomes

$$r = K_1 [A]^2$$

The reaction is now second order.

For gaseous reaction which is first order at high pressure may become second-order at low pressure; this has actually been observed experimentally.

2.10.44. **Chain reaction and its characteristics:** A chain reaction is one in which the products of the reaction carry out the reaction as the part of the reactant molecules and thus a long series of self-repeating step is started.



Some important characteristics of Chain Reaction are as follows:

- A. **Probability factor:** The probability factor for a chain reaction is much greater than 1.
- B. **Uncontrolled velocity of the reaction:** Sometimes chain carrier begins to extrapolate in branches and the speed of the reaction may become beyond the control which ultimately leads to explosion.
- C. **Variation in rate of a chain reaction:** In all non-chain reactions the rate is highest at the beginning and it falls with time. In case of Chain Reaction however rate is zero at the beginning, then rises to maximum and eventually falls with time.
- D. **Influence of foreign substance:** The speed of chain reaction is greatly influenced by the presence of any foreign substances.
- E. **Shape of the vessel:** The speed of Chain Reaction depends on the shape of the vessel.
- F. **Complicated order:** The rate equation for chain reaction is very complicated that cannot be characterized by some order.

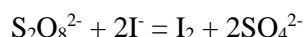
2.10.45. **Primary salt effect:** Due to electrostatic interaction the Kinetics of the reaction between ions deviates from those observed in the reaction between non-electrolytes. The velocity constant of ionic reaction depends on the charges of the reacting ions and also the ionic strength of the solution. The effect of ionic strength on the rate constant is called **primary salt effect**. Primary salt effect exerts due to the change in the values of the activity coefficient of reactants and intermediate complex for the ionic strength of the solution. A very satisfactory treatment of this matter was first made by Bronsted and later Bjerrum. The rate equation for primary salt effect is

$$\log K = \log K_0 + 1.02 Z_a Z_b \sqrt{\mu}$$

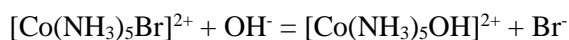
Where,  $K_0$  = rate constant without salt effect,  $Z_a$  and  $Z_b$  are charge on ions A and B,  $\mu$  = ionic strength

2.10.46. There are three cases may be raised when we plot the  $\log(K/K_0)$  vs.  $\sqrt{\mu}$  in dilute solution, three straight lines are raised from three probable cases whenever appeared.

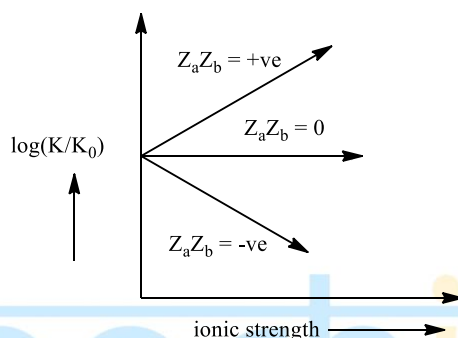
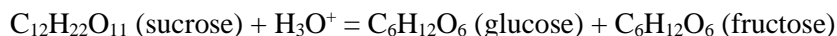
Case 1. When  $Z_a$  and  $Z_b$  are of the same sign that is  $Z_a Z_b$  is positive; the rate constant would increase with ionic strength of the solution. Example is



Case 2. When  $Z_a$  and  $Z_b$  are of opposite sign, i.e.,  $Z_a Z_b$  is negative; the rate constant would decrease with the ionic strength of the solution. Example is



Case 3. When one of the reactants is uncharged, i.e.,  $Z_a Z_b$  is zero; the rate constant would be independent with the ionic strength of the solution. Example is



### Subunit 10B: Catalysis

Text with Technology

2.10.47. **Catalysis:** A catalyst is defined as a foreign substance that enhances the speed of the reaction but itself remains unaltered in mass and in chemical composition after completion of the reaction. This phenomenon is known as catalysis and the reaction is known as catalytic reaction. For example,  $\text{H}^+$  acts as a catalyst in the hydrolysis of Ester or sugar and  $\text{NO}$  acts as a catalyst in the formation of  $\text{SO}_3$  from  $\text{SO}_2$ .

2.10.48. **Classification of catalysis:** Catalysis is classified into two broad types, viz.,

A. **Homogeneous catalysis:** In homogeneous catalysis reactants and the catalyst form a single phase. Some common examples in the gas phase are

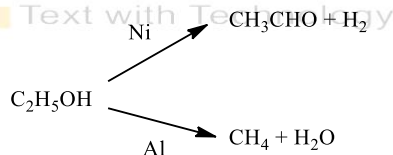


**B. Heterogeneous catalysis:** In heterogeneous catalysis the reactants form one phase but the Catalyst from a different phase usually solid. Some common examples of heterogeneous catalysis are



**2.10.49. General characteristics of catalytic reaction:** The following important characteristics are generally observed in most of the homogeneous and heterogeneous catalytic reactions:

- (i) catalyst remains unchanged in mass and in chemical composition at the end of the reaction.
- (ii) Only a very small amount of the catalyst is generally needed to bring about a considerable extent of reaction.
- (iii) The catalyst does not alter the position of the equilibrium in a reversible reaction.
- (iv) The catalyst will not be able to start a reaction.
- (v) The action of a catalyst on a chemical reaction is specific. The mechanism and the nature of the product depend largely on the nature of the catalyst used, e.g., ethanol vapor at 350°C on Nickel surface gets the hydrogenation while on Alumina surface undergoes dehydration.



- (vi) The effect of temperature on the rate of the reaction remains unaltered even in the presence of catalyst.
- (vii) A catalyst would be poisoned by certain substances; hence the activity of the catalyst becomes reduced. Some catalytic poisons are HCN, CS<sub>2</sub>, H<sub>2</sub>S etc.

**2.10.50. Importance of catalyst:** (i) Catalyst are of tremendous importance in the natural and in technical chemical processes. By selecting a suitable catalyst for a particular reaction in a specific direction can be brought about a desired rate.

(ii) In chemical industry the phenomenon of catalysis is applied in every possible manner of the numerous industrially important catalyzed reactions. Noteworthy mentions are of the production of H<sub>2</sub>SO<sub>4</sub> in both lead chamber and contact process; the synthesis of NH<sub>3</sub>, the oxidation of ammonia to nitric acid and many others.

(iii) All natural chemical processes are catalyzed. One without catalyst life in general would have been impossible. The photosynthesis reaction which is one of the most important natural method for production of carbohydrate is catalyzed by chlorophyll.

(iv) The living cells in plant and in animal body catalyzed the decomposition, synthesis and assimilation of protein, fat, carbohydrate etc. A living cell in effect, is a complete chemical laboratory and it is a catalytic laboratory. Biological processes are catalyzed by special substances is known as enzymes which work totally specifically.

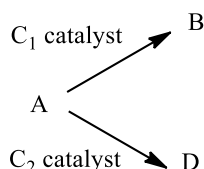
**2.10.51. The catalyst does not alter the position of chemical equilibrium in a reversible reaction.** Since the catalyst remains unchanged in chemical reaction as it contributes no energy to the system. The change in free energy depends on the initial and final state of the system and is independent on the path of the transformation. Hence the change in Gibbs free energy for a reaction at a certain temperature will be same irrespective of whether a catalyst is needed or not. Since in the standard state,

$$\Delta G^0 = -RT \ln K_{eq} \text{ where } K_{eq} = \text{Equilibrium Constant.}$$

It follows that equilibrium constant will be unaffected by the presence of the catalyst. Furthermore, we see that equilibrium constant of a reaction is the ratio of the forward to that of the backward rate constant and since  $K_{eq}$  remains constant and thus the ratio will also remain unaffected as both the forward and backward reaction should be equally influenced by the catalyst.

**2.10.52. The catalyst will not able to start a reaction.** For a reaction to occur the final state should have lower free energy than the initial state and since a catalyst does not contribute to the total free energy of the system. So, a catalyst will not able to start of a reaction. As the rate of the reaction is governed by the activation energy of the process it appears that the reaction which are extremely slow in the absence of a catalyst corresponds to the mechanism involved very high activation energy and the catalyst lowers the activation energy by providing an alternative mechanism; thereby leading the reaction to proceed at an appreciable rate.

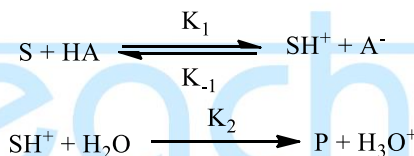
**2.10.53. A catalyst is specific and reduces the activation energy** of a specific path by taking path in the formation of the activated complex of that path. Suppose a substance 'A' decomposes to products 'B' and 'D' into two different paths. If the activation energies are comparable, then 'B' and 'D' will occur together. Let a catalyst  $C_1$  reduce activation energy of A to B pathway. Thus, in presence of  $C_1$  catalyst will be formed first and if collected B will be the sole product. Thus, the catalyst  $C_1$  eliminates the undesirable side product D. Similarly, another catalyst  $C_2$  may eliminate B, and furnish product D solely. **A catalyst eliminates undesirable side products.**



2.10.54. **It is not essential for a catalyst to decrease the activation energy of a reaction.** A catalyst increases the rate by increasing specific rate constant  $K$ . Remembering Arrhenius equation,  $K = Ae^{-E_a/RT}$ , where 'A' is the frequency factor and ' $E_a$ ' is the activation energy. Hence, a catalyst may increase  $K$  by decreasing  $E_a$ . But it also may increase  $K$  by increasing  $A$ , and without decreasing  $E_a$ . It may even increase the rate in spite of increase in  $E_a$ , if  $A$  is sufficiently increased.

2.10.55. **Negative catalysts are not catalysts rather inhibitors.** The negative are substances that retard the rate of the reactions. These substances can do so by increasing the activation energy through altering the mechanistic path. But catalysts are defined as substances that increase the rate of the reactions. Catalysts generally achieve that by reducing activation energy by taking part in activated complex formation. They may do so by another way, i.e., by increasing frequency factor. Hence, the substances having negative impact on reaction kinetics are called inhibitors, e.g.,

2.10.56. **Homogeneous Catalysis:** When catalyst along with other substances all are in same phase in a reaction vessel, then the reaction is known as homogenous catalysis. Most interesting example of homogeneous catalysis is the acid/base catalysis. If the reaction rate directly depends on the concentration of  $H^+$  or  $OH^-$ , then that is known as Specific acid or base catalysis. Again, when the reaction rate is directly proportional to the concentration of acid or base molecules, that kind of catalysis is known as General acid or base catalysis.



The rate of acid catalysis

$$R = d[P]/dt = K_1K_2[S][HA]/(K_{-1}[A^-] + K_2) \dots\dots\dots(i)$$

Now, if we apply boundary conditions

**Case-I:** when  $K_2 \gg K_{-1}[A^-]$ ,  $R = K_1[S][HA] \dots\dots\dots(ii)$

The above equation clearly demonstrates that the rate is first order with respect to each molecule viz., substrate and acid. The reaction for which the rate depends on the concentration of  $HA$ , is said to be General acid catalysis and the complex is called van't Hoff type.

**Case-II:** when  $K_2 \ll K_{-1}[A^-]$ ,  $R = K_1K_2[S][HA]/K_{-1}[A^-] \dots\dots\dots(iii)$

Now, let us consider the dissociation equilibrium of the acid,



If the dissociation constant is  $K_a$ , then

$$K_a = [H^+][A^-]/[HA]$$

Or,  $[HA]/[A^-] = [H^+]/K_a \dots\dots\dots(iv)$

Putting the value of equation (iv) on equation (i), we get,

$$R = d[P]/dt = K_1 K_2 [S][H^+]/K_{-1} K_a \dots\dots\dots (v)$$

From the above equation we can apparently conclude that the rate of the reaction depends on the concentration of  $H^+$ , although the proton is initially transferred from HA. This type of reaction is called Specific acid catalysis and complex is known as Arrhenius type.

Since,  $H^+$  acts as a catalyst, its concentration remains constant; therefore equation (v) becomes

$$R = d[P]/dt = K[S] \quad \text{where, } K = K_1 K_2 [H^+]/K_{-1} K_a = K_{H^+} [H^+] = \text{constant}$$

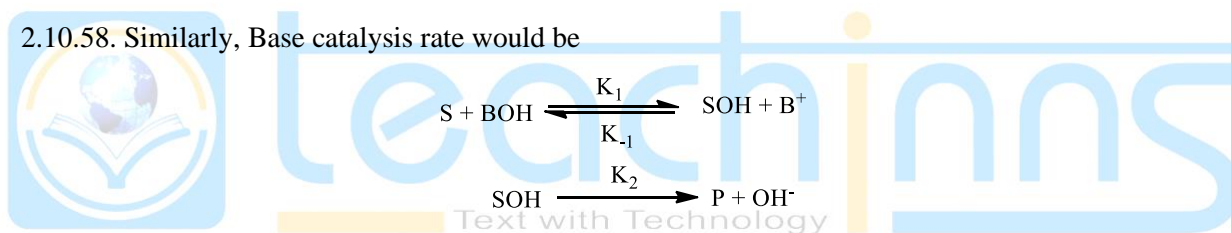
The constant  $K_{H^+}$  is known as Catalytic coefficient of  $H^+$ .

2.10.57. In general, if a reaction is catalyzed by the act of the catalytic species like  $H^+$ ,  $OH^-$ , HA,  $A^-$ , then the first order rate constant K in a buffer mixture containing HA and  $A^-$  is given by,

$$K = K_0 + K_{H^+} [H^+] + K_{OH^-} [OH^-] + K_{HA} [HA] + K_{A^-} [A^-]$$

Where the constants  $K_{H^+}$ ,  $K_{OH^-}$ ,  $K_{HA}$ , and  $K_{A^-}$  are various catalytic coefficients and  $K_0$  is the rate constant for spontaneous reaction or the rate at very low concentration of all the catalytic species.

2.10.58. Similarly, Base catalysis rate would be



$$R = d[P]/dt = K_1 K_2 [S][BOH]/(K_{-1} [B^+] + K_2) \dots\dots\dots (i)$$

General Base catalysis rate is

$$R = d[P]/dt = K_1 [S][BOH] \dots\dots\dots (ii) \quad [\text{when Case-I: } K_2 \gg K_{-1} [B^+]]$$

Specific Base catalysis rate is

$$R = K_1 K_2 [S][BOH]/K_{-1} [B^+] \dots\dots\dots (iii) \quad [\text{when Case-II: } K_2 \ll K_{-1} [B^+]]$$

Now, Now, let us consider the dissociation equilibrium of the base,

If the dissociation constant is  $K_b$ , then

$$K_b = [B^+][OH^-]/[BOH]$$

$$\text{Or, } [BOH]/[B^+] = [OH^-]/K_b \dots\dots\dots (iv)$$

Putting the value of equation (iv) on equation (i), we get,



$$R = d[P]/dt = K_1K_2[S][OH^-]/K_{-1}K_b \dots\dots\dots(v)$$

Since,  $OH^-$  acts as a catalyst, its concentration remains constant; therefore equation (v) becomes

$$R = d[P]/dt = K[S] \quad \text{where, } K = K_1K_2[OH^-]/K_{-1}K_b = K_{OH^-}[OH^-] = \text{constant}$$

The constant  $K_{OH^-}$  is known as Catalytic coefficient of  $OH^-$ .

**2.10.59. Effect of pH on Acid-Base catalysis:** Homogeneous Acid-Base catalysis depends on pH of the medium as follows

$$pH = (1/2)[\log K_{H^+} - \log K_{OH^-} + pK_w]$$

where  $K_w$  is dissociation constant of water

**2.10.60. Heterogeneous Catalysis:** Most of the heterogeneous catalytic reaction involves the solid surface act as the catalyst. The catalytic effect has been explained on the basis of adsorption of reactant molecules on the active sites available at the surface of the solid catalyst. Invariably, the adsorption is of chemisorption in nature where the adsorbed molecules are held to the surface by valence forces. Thus, in terms, some bonds within the molecule get weaken and thereby the molecule reaches to activation state. The adsorbed molecules are near to the transition state and heterogeneous catalysis primarily functions as tool for lowering the activation energy. In general, a gaseous reaction taking place on the surface of a solid catalyst [According to Langmuir-Hinshelwood theory] involves the following steps,

- (i) Diffusion of reactant molecules to the surface
- (ii) Adsorption of reactant molecules to the surface
- (iii) Chemical reaction on the surface
- (iv) Desorption of product molecules from the surface
- (v) Diffusion of product molecules away from the surface

The rate of overall reaction may depend on any or all the aforementioned steps. It is generally believed that kinetics of surface reactions can be treated successfully on the basis of the following assumptions,

- (i) An equilibrium exists between monolayer adsorption and desorption at the surface of the catalyst.
- (ii) Chemical reaction between adsorbed molecules leads to products.

Now, kinetics of heterogeneous catalysis will be,

Where, R = Reactant molecule, S = heterogeneous catalyst, RS = Adsorbed Activated complex, P = product molecule

$$\Theta = K_1[R]/(K_1[R] + K_{-1} + K_2) \quad \text{where, } \theta = \text{number of Active sites on surface of the catalyst}$$

$$r = K_1K_2[R]/(K_1[R] + K_{-1} + K_2)$$



for gaseous reactants,

$$r = K_1 K_2 P_R / (K_1 P_R + K_{-1} + K_2)$$

where,  $P_R$  = partial pressure of reactant molecule

**Case-I:** when product formation is very fast, i.e.,  $K_2 \gg (K_1 P_R + K_{-1})$ ; at very low pressure,

$$r = K_1 P_R$$

**Case-II:** when product formation is very slow, i.e.,  $K_2 \ll (K_1 P_R + K_{-1})$ ; at very high pressure,

$$\begin{aligned} r &= K_1 K_2 P_R / (K_1 P_R + K_{-1}) \\ &= (K_1 / K_{-1}) K_2 P_R / [(K_1 / K_{-1}) P_R + 1] \\ &= K_{eq} K_2 P_R / [K_{eq} P_R + 1] \end{aligned}$$

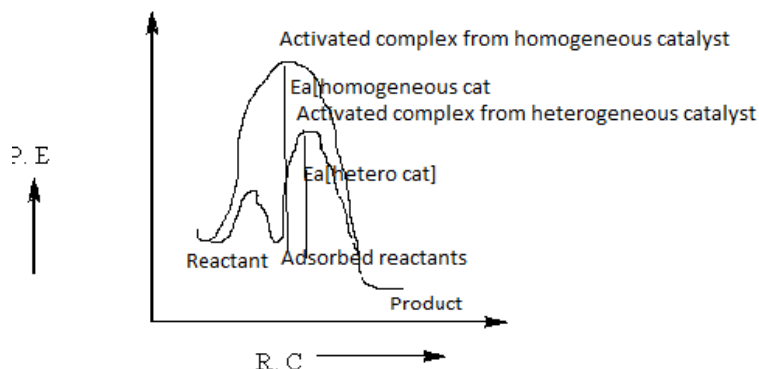
At extreme pressure,

$$r = K_2 \quad [\text{ignoring 1 in the above equation}]$$

**2.10.61. Active Sites:** In addition to the chemical nature of the catalyst, the state of its surface has greater importance in determination of rate of heterogeneous catalysis. Not the whole of the surface but some specific areas or sites chemically active indeed. These sites are called Active sites or centers for the catalyst. The most active sites have high negative heat of adsorption and low activation energy of adsorption. Naturally, if heat of adsorption decreases, then surface coverage increases. But after a certain coverage, the adsorption decreases as available number of active sites decreases.

Ethylene and Hydrogen are adsorbed to some extent by metallic copper. They react to form ethane over copper surface. A trace amount of Mercury reduces the adsorption of ethylene to 80% and Hydrogen to 5% for the clean even surface. But catalytic efficiency reduces only to 0.5%. This observation suggests that the two gases are adsorbed at different centers on the surface. Moreover, a trace of CO is sufficient to suppress the activity of catalyst to a predominant extent by covering a minor fraction of copper surface. This observation reveals that there are some active centers where the hydrogenation occurs and CO inhibits that process. These set of experiments are taken as a apparent proof of existence of active centers or sites.

**2.10.62. Differences between Homogeneous and Heterogeneous catalysis:** In homogeneous catalysis the entire reaction occurs within a single phase, but in heterogeneous catalysis the reaction occurs at the interface between two phases. Both homogeneous and heterogeneous catalysis, a catalyst provides an alternative path having lower activation energy compared to uncatalyzed reaction. But the activation energy of a surface reaction should be less than the corresponding homogeneous catalysis. The reason for that is in heterogeneous catalysis the reactant molecules are absorbed on the solid surface which is chemisorption in nature. The stronger forces of a chemical nature operating in chemisorption tend to bring about a partial loosening of the bonds in adsorbed molecules, the result is that much smaller amount of energy is sufficient to form the activated complex. The way in which the energy of the surface reaction may be less than that of the homogeneous reaction may be considered with reference to the potential energy diagram as shown below,



**2.10.63. Enzyme catalysis:** Enzymes are complex protein substances produced by living cells. They can catalyze numerous chemical reactions by occurring from animal or plant bodies. Some of the common characteristics of enzyme reactions are given below,

(i) Enzymes are highly specific and each enzyme catalyzes a particular. For example, an enzyme called invertase can break up sucrose but fails to break up a very similar disaccharide maltose which requires another enzyme called maltase for this purpose.

(ii) While in general, all chemical reaction shows an increase in the rate on increasing the temperature, for enzyme reaction there exists an optimum temperature at which its efficiency is maximum. Above this temperature enzyme gets denatured and losses its activity and below the optimum temperature the reaction rate is slow because of temperature effect.

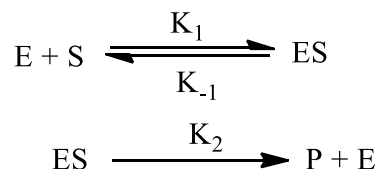
(iii) Enzyme reactions are much sensitive to catalytic poisons, e.g., HCN, CS<sub>2</sub>, H<sub>2</sub>S.

(iv) In certain cases, the activity of an enzyme depends upon certain non-protein substances called co-enzyme. For every enzyme there is only one helper co-enzyme, e.g., vitamin B-2 has coenzyme FAD.

(v) Enzyme losses their activity in presence of electrolytes or expose to UV ray.

(vi) The effect of pH on the rate of enzyme reaction is very complex. The rate usually passes through a maximum value as pH is increased and then decreased.

**2.10.64. Kinetics of Enzyme catalysis:** One of the most important examples of homogeneous catalysis is the enzyme catalysis. The mechanism of enzyme catalyzed reaction was initially proposed by L. Michaelis and M. L. Menten and so this is known after their name. The mechanism involves the following steps,



The rate of the Enzyme catalyzed reaction will be

$$r = K_2[E_0][S_0]/(K_M + [S_0]) \dots\dots\dots(i)$$

Where, [E<sub>0</sub>] = initial concentration of Enzyme, [S<sub>0</sub>] = initial concentration of substrate, K<sub>M</sub> = (K<sub>-1</sub> + K<sub>2</sub>)/K<sub>1</sub> = Michaelis-Menten constant

**Case – I:** At low substrate concentration, i.e.,  $K_M + [S_0] \approx K_M$ , the rate becomes first order w.r.t each enzyme and substrate,

$$r = K_2[E_0][S_0]/K_M \dots\dots\dots(ii)$$

**Case – II:** At very high substrate concentration, i.e.,  $K_M + [S_0] \approx [S_0]$ , the rate becomes zero order w.r.t substrate and first order w.r.t enzyme,

$$r_{\max} = K_2[E_0] \dots\dots\dots(iii)$$

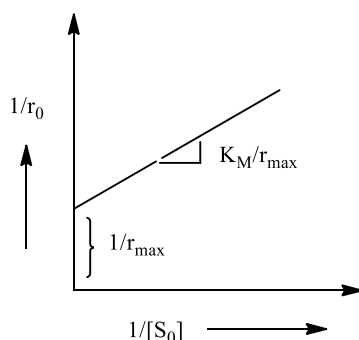
When the rate of an enzyme catalyzed reaction becomes independent on substrate concentration and only depends on initial concentration of the Enzyme, the rate reaches its maximum value.

**2.10.65. Turn Over Number [TON]:** The ‘Turn Over Number’ is the number of reactant molecules converted into product molecules by charging of one molecule of enzyme in unit time interval. In equation (iii),  $r_{\max} = K_2[E_0]$ , the rate constant  $K_2$  is known as “Maximum Turn Over Number”.

**2.10.66. Lineweaver-Burk Equation & Plot:** Lineweaver and Burk had modified the Michaelis-Menten equation as follows,

$$1/r_0 = (1/K_2[E_0]) + (K_M/K_2[E_0][S_0]) = (1/r_{\max}) + (K_M/r_{\max}[S_0]) \dots\dots\dots(iv) \quad [\text{where, } r_0 = \text{initial rate}]$$

The above equation is known as Lineweaver-Burk equation and if we draw a plot of  $1/r_0$  vs.  $1/[S_0]$ , we will obtain a straight-line having slope =  $K_M/r_{\max}$  and intercept =  $1/r_{\max}$ ; this plot is known as Lineweaver-Burk plot of Enzyme catalyzed reactions.

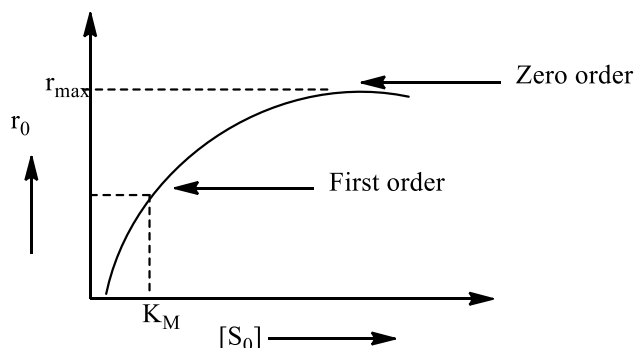


Rearranging the equation (iv), we get,

$$1/r_0 - 1/r_{\max} = K_M/r_{\max}[S_0]$$

$$\text{Or, } (r_{\max} - r_0)/r_0 = K_M/[S_0]$$

It follows that when  $r_0 = r_{\max}/2$ ,  $K_M = [S_0]$ ; i.e., Michaelis-Menten constant is equal to the initial concentration of substrate, when the initial rate is equal to the half of its maximum rate. The variation of initial rate with the initial substrate concentration shown in the diagram below by that we can calculate  $K_M$ .



2.10.67. The physical concept is that each enzyme molecule has one or more active sites at which the substrate must have bound in order that the catalytic action may occur. At low substrate concentration, most of the active sites remain unoccupied at any time. As the substrate concentration is increased, the number of active sites which are occupied increases and hence the reaction rate also increases. However, at very high concentration of the substrate, virtually all the active sites are occupied at any time; so that further increase in substrate concentration can not further increase the formation of enzyme-substrate complex. **Hence, the reaction rate becomes zero order with respect to substrate.**

2.10.68. **Effect of temperature on Enzyme Catalysis:** Like chemical catalysts, the enzyme catalysts also decrease the activation energy of a reaction at a given temperature. In fact, the decrease of activation energy by an enzyme catalyst is far greater than that by a non-enzyme catalyst. While the rate of a reaction generally increases with increase in temperature. This condition is highly unfavorable for a living cell. Enzymes are, in fact, very sensitive to high temperatures. Because of the protein nature of an enzyme, after a certain temperature increment denaturation of enzyme protein is being started. Therefore, efficiency of that enzyme gradually decreases. Rise in temperature up to  $45^\circ\text{C}$ , enzyme can tolerate and so also rate increases; but above of that denaturation becomes predominant. Above  $55^\circ\text{C}$  or so, the denaturation process becomes so rapid that the whole cell gets destroyed and catalytic activity of that enzyme completely ceased.

2.10.69. **Secondary Salt Effect:** The secondary salt effect is the change in the reaction rate by altering the effective concentration of the catalyzing species. If  $\text{H}^+$  and  $\text{OH}^-$  ion produced from a weak acid or weak base acts as the catalyzing agent, then the addition of salts influences the concentration of  $\text{H}^+$  or  $\text{OH}^-$  ion. Since the reaction depends upon the concentration of  $\text{H}^+$  or  $\text{OH}^-$ , it is clear that the reaction rate will be affected by the salt concentration. This phenomenon is quite independent of primary salt effect, known as secondary salt effect.

Expression of secondary salt effect will be,

$$\log K_{\text{exp}} = \log K - (\log \gamma_{\text{HA}} + \log \gamma_{\text{H}^+} - \log \gamma_{\text{A}^-})$$

From Debye-Huckel limiting law,

$$\log \gamma_i = -AZ_i^2 \sqrt{\mu}$$

where,  $K_{\text{exp}}$  = Experimental rate constant with salt effect,  $K$  = rate constant without salt effect,  $\gamma_i$  = activity coefficient,  $\mu$  = ionic strength of the solution.

### 10C: Photochemistry

2.10.70. Many reactions can be initiated by the absorption of radiation lying in the visible and UV region having wavelengths approximately between  $10^4 \text{ \AA}$  to  $10^3 \text{ \AA}$ . These reactions are called **Photochemical Reactions**.

2.10.71. **Differences between Photochemical and Thermal reaction:** (i) In thermal reaction, the energy of activation required is gained by collisions. But in photochemical reaction, the energy of activation required is gained through absorption of quanta in visible or UV region.

(ii) All the thermal reactions proceed with decrease in Gibbs free energy. But photochemical reactions may proceed with increase of the same like as polymerization anthracene, photosynthesis etc.

(iii) the rate of thermal reactions depends on the temperature. Whereas that of the photochemical reactions is independent of temperature, the reaction rate depends on the intensity of radiation used.

(iv) by using monochromatic light of a particular wavelength in the visible and UV region, photochemical reaction permits selectivity. In contrast, thermal reactions do not permit such selectivity.

2.10.72. **Lambert-Beers Law:** when monochromatic light passes through a transparent medium, the rate of decrease in intensity of radiation with thickness of the medium is proportional to the intensity of radiation falling on it; this is known as Lambert's law.

$$-dI/dl \propto I$$

The rate of decrease in intensity with thickness of absorbing material is proportional to the concentration of the light absorbing species.

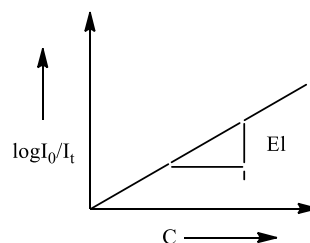
$$-dI/dl \propto c$$

Combining these two equations, we get,

$$-dI/dl \propto Ic$$

$$\text{Or, } -dI/dl = Klc$$

$$\text{Finally, } D = \log I_0/I_t = \epsilon cl$$





Where  $D$  = optical density or absorbance,  $I_0$  = initial intensity of irradiation,  $I_t$  = final intensity of irradiation after passing the light through the sample,  $I_t/I_0$  = Transmittance,  $\epsilon$  = Molar extinction coefficient, defined by reciprocal of the thickness of the medium of 1(M) solution which reduces the intensity of the light to  $1/10^{\text{th}}$  of its initial value. Its value depends on the nature of solute and wave length of the light. It has unit of  $\text{Lmol}^{-1}\text{cm}^{-1}$ ,  $c$  = Concentration of sample solution,  $l$  = pathlength of light i.e., thickness of the cuvette.

2.10.71. Determination of  $\epsilon$  value: Since we know from Lambert-Beer's law,

$$D = \log I_0/I_t = \epsilon cl$$

Now if we plot for  $\log I_0/I_t$  vs  $c$  taken in a column of definite thickness, a straight-line is obtained passing the origin with slope is equal to  $\epsilon l$ .

2.10.73. **Nature of the Absorbance:** Absorbance is an extensive property of a substance whereas molar absorptivity is its intensive property. If there is a change in concentration and the thickness of the cuvette the value remains constant within Beer's law, but the absorbance will change significantly.

2.10.74. **Limitations of Lambert-Beer's law:** The limitations of Lambert-Beer's law are as follows,

- (i) This law is not obeyed except the monochromatic light.
- (ii) This law governs the absorption behaviour of dilute solution. Deviations are observed for concentrated solution.
- (iii) Deviations may also occur, if the coloured solute ionises, dissociates or associates in solution, due to these reasons absorbance will change.

2.10.75. **Applications of Lambert-Beer's law:** The various applications of this law are given below:

- (i) It can be used for the determination of an unknown concentration by comparison with a solution of known concentration by using spectrophotometer.
- (ii) It can be used to determine the colour intensity of the complex.
- (iii) It can be used to determine the composition of the complex.
- (iv) It can be used to determine the stability constant for a given complex.

2.10.76. **Laws of Photochemistry:** The photochemical reactions are governed by two basic laws. These are given below,

1. **Grothus-Draper law:** This law states that only those radiations which are absorbed by the reacting system are effective in producing chemical change.

2. **Einstein's law of photochemical equivalence:** The law of photochemical equivalence was proposed by Starck and Einstein. According to law, each quantum of radiation absorbed by a molecule activates one molecule in the primary step of a photochemical reaction.

$1 \text{ E} = N_A h C / \lambda$  where,  $E = h\nu$  i.e., energy of a quantum measured in Einstein,  $\lambda$  = wave length of radiation,  $h$  = Planck's constant,  $C$  = velocity of light,  $N_A$  = Avogadro's number

2.10.84. **Quantum yield:** The efficiency of a photochemical reaction is often expressed in terms of an important parameter, known as **quantum yield** or **quantum efficiency**. It is defined as the number of light-absorbing molecules reacted per photon of light absorbed and it is represented by  $\Phi$ , i.e.,

$$\Phi = \text{number of molecules reacting / number of quanta absorbed} \\ = \text{number of moles reacting / number of Einstein absorbed}$$

We can convert it into rate if we consider the absorption for a specific period. Thus,

$$\Phi = \text{number of moles reacting per unit time / number of quanta absorbed per unit time} \\ = \text{rate / intensity} = r/I$$

2.10.77. **Frank-Condon principle:** The primary process of a photochemical reaction is the electronic transition of a molecule from lower to higher electronic state following the Frank-Condon principle. According to this principle, the time required for the electronic excitation is so small that the internuclear distance remains unchanged during the excitation.

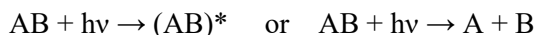
2.10.78. **Secondary Process:** The products of primary process may involve in subsequent thermal reaction. These processes are known as secondary processes. The secondary process may involve more than one step. Sometimes, the secondary process may be represented as chain propagation.

Primary process:  $\text{HI} + h\nu \rightarrow \text{H} + \text{I}$

Secondary process:  $\text{H} + \text{HI} \rightarrow \text{H}_2 + \text{I}$  [propagation]

$\text{I} + \text{I} \rightarrow \text{I}_2$  [termination]

2.10.79. **Difference between Primary and Secondary Process:** (i) Primary process is the process in which each molecule capable of entering into chemical reaction absorbs one quanta of radiation. This absorbed energy may give rise to the formation of excited molecule or the molecule which absorbs light may undergo dissociation to yield free atoms or radicals. However, secondary process which involves the excited atoms or free radicals produced in the primary process; therefore, these processes have no need for light to happen.



(ii) The quantum yield in the primary process is always equal to one, i.e.,  $\phi = 1$ . However, quantum yield may differ from unity when considering the overall reaction due to secondary process.



**2.10.80. Reasons behind low or high quantum yield:** Einstein's law of photochemical equivalence is concerned with the primary process of molecule activation. If every molecule so activated in the primary absorbance directly decomposes, then the number of reactant molecules suffering for chemical change would be equal to the number of quanta absorbed. Thus, according to this law of photochemical equivalence, the quantum yield will always be equal to one. But reactions of low quantum yield ( $\phi = 0.04$ ) and high quantum yield ( $\phi = 10^6$ ) also known.

A. Reasons for low quantum yield of a photochemical reaction:

- (i) The excited molecule is deactivated through fluorescence or phosphorescence.
- (ii) The excited molecule is deactivated by converting its energy into kinetic energy of other molecules.
- (iii) The secondary process may involve a step which produces the reactant molecule as one of the products.
- (iv) The energy absorbed may not be sufficient to cause any fruitful excitation of the molecule.

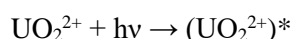
B. Reasons for high quantum yield of a photochemical reaction:

- (i) An intermediate formed during the course of reaction acts a catalyst.
- (ii) One of the steps may be exothermic; so heat generated from that step and deactivated molecules can absorb that energy to get activated.
- (iii) The active molecules by taking extra energy collides with the deactivated ones to pass the energy to activate them and the process subsequently continues.

**2.10.81. Experimental method for determination of quantum yield:** Since the value of Einstein depends on the wavelength of radiation; it is desirable in the photochemical work that light of a definite wavelength, i.e., monochromatic light should be used. The number of photons absorbed are counted either with a thermopile or with an actinometer.

A. **Thermopile:** The thermopile is made of a large number of junctions of two dissimilar metals. When the radiation falling on it, that would be converted into heat and simultaneously emf will be produced due to thermo-electric effect. This observation provides a measure of the energy of radiation falling on the thermopile. The measurements be conducted with and without the reacting system and the difference tells us the actual amount of radiation absorbed by the reacting species.

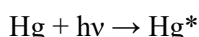
B. **Actinometer:** For many purposes the energy of the absorbed light is determined by means of an actinometer, a device for estimating the absorbed radiation by using a photochemical reaction. One of these which has been used mostly in recent years is Uranyl-Oxalate actinometer. It consists of a dilute solution of oxalic acid containing little amount of uranyl sulphate. When that exposed to UV or visible light within the range of about 254-435 nm, the uranyl ion absorbs the light. The excited uranyl ion transfers the absorbed energy to oxalic acid which is then decomposed. The reaction happens as follows



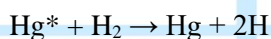
The amount of oxalic acid decomposed can be determined by titrating undecomposed oxalic acid against standard  $\text{KMnO}_4$  solution. The uranyl-oxalate actinometer has been standardized with radiation of various wavelengths and from the amount of decomposed oxalic acid, the amount of photons absorbed can be determined. The measurements be conducted with and without the reacting system and the difference tells us the actual amount of radiation absorbed by the reacting species.

**2.10.82. Photosensitized Reaction:** Certain reactions are known which are not sensitive to light, but can be made sensitive by adding a small amount of foreign material which can absorb light energy and stimulate the reaction without itself taking part into that. Such kind of reactions are called Photosensitized reaction and such added materials are photosensitizers and the phenomenon is known as photosensitization.

Example: If a mixture of  $\text{H}_2$ ,  $\text{O}_2$ , and Hg vapour is exposed to UV light, Hg vapour absorbs strongly at 253.7 nm with the formation of an excited Hg atom [ $\text{Hg}^*$ ], i.e.,



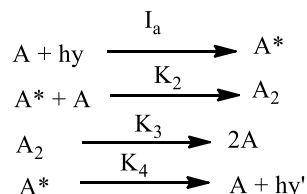
The energy corresponding to this wavelength is  $471.5 \text{ kJmol}^{-1}$ . The energy required to dissociate a molecule of  $\text{H}_2$  in its ground state to two H atoms is  $432 \text{ kJmol}^{-1}$ . The dissociation energy of  $\text{O}_2$  molecule is  $490.2 \text{ kJmol}^{-1}$ . The energy possessed by excited Hg atom is more than enough to dissociate  $\text{H}_2$  molecule but not enough for  $\text{O}_2$  dissociation. The quenching reaction introduces two H atoms into the reaction mixture which can initiate the chain to form  $\text{H}_2\text{O}$  by the usual mechanism. So, Hg vapour is photosensitizer here.



**2.10.83. Photochemical Equilibrium or Photo-stationary state:** Absorption of radiation by reactants of a reaction at thermal equilibrium increases the rate of forward reaction with affecting the rate of reverse reaction. The latter however increases due to increase in the concentration of the product. Thus, a new state is established when the increase in the rate of forward reaction due to absorption of light becomes equal to the increase in the rate of reverse reaction due to the enhanced concentration of the product(s). This new state is called Photo-stationary state or Photochemical Equilibrium. The system at photo-stationary state unlike a thermal equilibrium remains unaffected by temperature of the system. The system reverts back to the normal equilibrium as soon as the source of radiation is removed. One of the well-known examples exhibiting photochemical equilibrium is dimerization of anthracene, another example is formation of  $\text{O}_3$  from  $\text{O}_2$ .

**2.10.84. Dimerization of Anthracene:** When anthracene is dissolved in benzene or other organic solvent and exposed to UV radiation, dimerization occurs. In dilute solution the reaction is accompanied by fluorescence and quantum efficiency becomes small but as the concentration is increased the fluorescence falls off whereas quantum efficiency increases towards a limiting value. In other words, the fluorescence is said to be quenched as the concentration of the light absorbing substance is increased.

The explanation of the above-mentioned phenomenon is very much straight forward. The natural life time of the excited molecule undisturbed by collisions is about  $10^{-8}$  sec. At higher concentration, a molecule experiences a large number of collisions within aforementioned time gap. Consequently, the excited molecule losses its energy by collisions with other molecules before it has a chance to exhibit fluorescence. Therefore, with decrease in concentration the collision frequency also decreases and chance of fluorescence increases.



The rate equation for dimerization of anthracene

$$d[A_2]/dt = K_2[A^*][A] - K_3[A_2] \dots\dots\dots(i)$$

using steady state approximation on  $A^*$ ,

$$[A^*] = I_a/(K_2[A] + K_4) \dots\dots\dots(ii)$$

At photo-stationary state  $d[A_2]/dt = 0$  (as  $[A_2] = \text{constant}$ )

Putting the value of  $[A^*]$  in equation (i),

$$[A_2] = I_a/K_3(1 + K_4/K_2[A])$$

When concentration of monomer is taken very large, then the equation reduces to

$$[A_2] = I_a/K_3$$

That means when the reaction is at photo-stationary state the concentration of dimer is independent of the concentration of monomer. This is in contrast to the reaction at thermal equilibrium, where the concentration of dimer depends on the concentration of monomer through the equilibria constant expression  $[A_2] = K_{eq}[A]^2$ .

**2.10.85. Fluorescence:** When a beam of light is incident on some certain substances, they emit visible light or radiation and that is stopped as soon as the incident light is cut off. This phenomenon is known as Fluorescence. Such substances which emit radiation during the action of stimulating light are called Fluorescent molecules.

Important Characteristics:

- (i) The phenomenon is instantaneous and starts immediately after the absorption of light and stops as soon as the incident light is cut off.
- (ii) It is a general phenomenon and is exhibited by gases, liquids and solids.
- (iii) The extent of fluorescence depends upon the nature of the solvent.
- (iv) During fluorescence, light is absorbed at a certain wavelength and should be emitted at a greater wavelength.
- (v) Fluorescence occurs through the transition always between states having same multiplicity, i.e., singlet (ES)  $\rightarrow$  singlet (GS). Therefore, it is spin allowed process.
- (vi) Excess vibrational energy dissipates through internal conversion (IC).
- (vii) Time scale of fluorescence phenomena is about  $\sim 10^{-8}$  s.
- (viii) There occurs some non-radiative Internal conversion between vibration levels at excited state.

(ix) Atoms having no vibrational level, they will always emit radiation of same wavelength. This is known as Resonance fluorescence.

(x) Various fluorescent substances are Eosin, Fluorescein, Ultramarine.

2.10.86. **Phosphorescence:** When light radiation is incident on certain substances, they emit light continuously even after the incident light is cut off. This type of delayed fluorescence is called Phosphorescence and the substances are called Phosphorescent.

Important Characteristics:

(i) The phenomenon of phosphorescence is chiefly caused by the UV or Violet portion of the spectrum.

(ii) This phenomenon is shown by the solids mainly.

(iii) The time for which the light is emitted from phosphorescent substances depends upon the nature of substances.

(iv) Different colours may be obtained by mixing different phosphorescent substances.

(v) Phosphorescence occurs through the transition always between states having dissimilar multiplicity, i.e., triplet (ES)  $\rightarrow$  singlet (GS). Therefore, it is spin forbidden process.

(vi) Excess vibrational energy dissipates through internal conversion (IC) and especially intersystem crossing (ISC).

(vii) Time scale of phosphorescence phenomena is much more than  $10^{-8}$  s.

(viii) There may occur some non-radiative Internal conversion between vibration levels at excited state and obviously an intersystem crossing from singlet to triplet state at excited electronic level.

(ix) Various fluorescent substances are like ZnS, alkaline earth metal sulphides.

2.10.87. **Chemiluminescence:** Chemiluminescence is the emission of light accompanying by a chemical reaction. In these cases, suppose a reactant 'A' is converted to a product 'B'; again, B gets excited to its excited state  $B^*$  which can cause emission to revert back B. The emission of cold light or cold flame is known as Chemiluminescence. This is actually reverse process of photochemical reaction. The process is depicted as



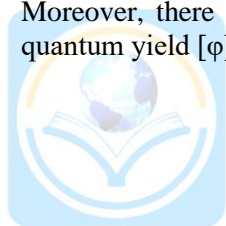
Few examples are

(i) When yellow phosphorus is oxidized in air at low pressure and low temperature between  $-10^\circ\text{C}$  to  $40^\circ\text{C}$ , then phosphorus is converted into  $\text{P}_2\text{O}_5$  with emission of cold greenish-white light.

(ii) Oxidation of certain Grignard reagents are also accompanied by cold visible light emission.

**2.10.88. Temperature effect on photochemical reactions:** The effect of temperature on photochemical reactions is quite different from that of thermal reaction. The temperature coefficients in thermal reactions are generally very large in magnitude. In photochemical reactions temperature coefficients are comparatively lower in magnitude. To explain the fact, it is necessary to consider the primary and secondary reaction separately. The primary process is practically independent of temperature because it is light absorbing process. The secondary processes are thermal in character. These should have temperature coefficients similar to thermal reactions. But it is not so in reality. Most of the secondary processes may involve in interaction between atoms or free radicals generated from primary process. For such reactions, the energy of activation is usually small indeed. As the temperature coefficient is determined by the magnitude of activation energy, the net temperature coefficient of a photochemical reaction will be very low.

**2.10.89. Quantum yield is greater than one for chain reactions.** Generally, the quantum yield ' $\phi$ ' is different from unity if there are secondary processes. If the reaction takes place by a chain mechanism, then the primary process is the chain initiation step and the secondary processes are chain propagation and chain termination step. For large number of chain reactions,  $\phi > 1$ . A classic example is the photochemical combination of  $H_2$  and  $Cl_2$  to form  $HCl$  [ $\phi = 10^6$ ]. Besides, if the chain propagating step is slow, i.e., endothermic, requires high energy for activation, depicts  $\phi < 1$ . A classic example of this type is photochemical combination of  $H_2$  and  $Br_2$  to form  $HBr$  [ $\phi < 1$ ]. The reason behind of that,  $Br + H_2 \rightarrow HBr + H$  step needs  $75 kJ mol^{-1}$  energy to proceed, i.e., high energy involved endoergic process. Moreover, there are other reactions in which chain inhibition step is involved, for those cases the quantum yield [ $\phi$ ] becomes around 0.01.



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## Previous year solution

### Subunit 10: Chemical Kinetics, Catalysis, Photochemistry

**Q.** If the half-life of a reaction is inversely proportional to the square of the concentration of the reactant, the order of the reaction is

- (a) 0      (b) 1      (c) 2      (d) 3

[NET 2019 June]

**Ans.** Given  $t_{1/2} \propto 1/a^2$  .....(i)

Now, in general form

$t_{1/2} \propto 1/a^{n-1}$  .....(ii)

Therefore comparing equation (i) and (ii), we get,

$$n - 1 = 2$$

or,  $n = 3$ .

Correct answer is **Option (d)**. [Key point 2.10.28]

**Q.** The gas phase decomposition of A at 1000K follows two decomposition paths

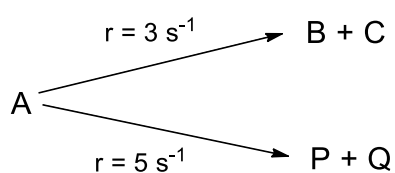
Sl. No.	Elementary Process	Rate Constant
(i)	$A \longrightarrow B + C$	$3 \text{ s}^{-1}$
(ii)	$A \longrightarrow P + Q$	$5 \text{ s}^{-1}$

The maximum theoretical percentage of yield of P at 1000K is

- (a) 62.5      (b) 60      (c) 166      (d) 37.5

[NET 2019 June]

**Ans.**



It's a parallel reaction, so,

$$\text{Yield \% of P} = \frac{K_2}{(K_1 + K_2)} \times 100 = \frac{5}{(3+5)} \times 100 = 62.5\%$$

Correct answer is **Option (a)**. [Key point 2.10.33]



Q. Photochemistry of a molecule, M, is described as by the mechanism

Sl. No.	Elementary Process	Rate
(i)	$M + h\nu \rightarrow M^*$	$I_{\text{abs}}$
(ii)	$M^* + Q \rightarrow M + Q$	$K_Q[Q][M^*]$
(iii)	$M^* \rightarrow M + h\nu_F$	$0.2[M^*]$

The intercept at  $[Q]$  is 4 for the inverse of fluorescence intensity  $[I/I_F]$  vs.  $[Q]$  plot. The value of  $I_{\text{abs}}$  is

- (a) 4      (b) 0.25      (c) 20      (d) 0.8      [NET 2019 June]

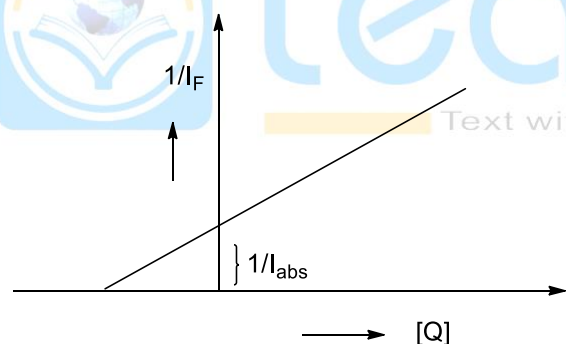
Ans. Fluorescence intensity =  $0.2[M^*]$

Applying steady-state approximation on  $M^*$ , we have,

$$I_{\text{abs}} = K_Q[Q][M^*] + 0.2[M^*]$$

$$\text{Or, } [M^*] = I_{\text{abs}} / K_Q[Q] + 0.2$$

$$\text{So, } I_F = K_Q[Q] / 0.2I_{\text{abs}} + 1/I_{\text{abs}}$$



$$\text{Hence, } I_F/I_{\text{abs}} = 4$$

$$\therefore I_F = 1, \text{ so, } I_{\text{abs}} = 1/4 = 0.25$$

Correct answer is **Option (b)**. [Key point 2.10.85]

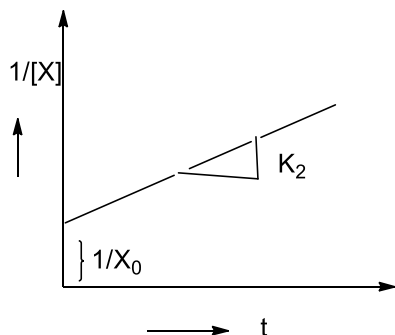


**Q.** For the second order reaction, the straight line among the following plots

- (a)  $[X]$  vs. time (b)  $1/[X]$  vs. time (c)  $\log[X]$  vs.  $1/\text{time}$  (d)  $\log[X]$  vs. time [NET 2018 Dec]

**Ans.** Rate equation for a second order reaction kinetics,

$$K_2 t = 1/X_t - 1/X_0$$



Correct answer is **Option (b)**. [Key point 2.10.17]

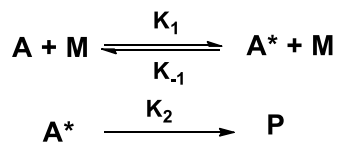
**Q.** The activation energy of a reaction reduces by  $12 \text{ kCal mol}^{-1}$  in presence of an enzyme at  $300\text{K}$ . Assuming pseudo-first order reaction kinetics, calculate the factor by which the reaction rate is increased [given  $R = 2 \text{ Cal K}^{-1} \text{ mol}^{-1}$ ]

- (a)  $2 \times 10^9$  (b) 1.02 (c)  $8.7 \times 10^6$  (d)  $5 \times 10^8$  [NET 2018 Dec]

**Ans.**  $K_e/K_{uc} = e^{(E_{uc} - E_e)/RT} = e^{\Delta E/RT} = \exp\{(12 \times 10^3)/(2 \times 300)\} = \exp 20 = 4.85 \times 10^8 \approx 5 \times 10^8$

Correction answer is **Option (d)**. [Key point 2.10.35]

Q.  $K_{\text{uni}}$  is the effective first order rate constant of the following unimolecular reaction



The slope and the intercept of the plot of  $1/K_{\text{uni}}$  vs.  $1/[\text{M}]$  are  $4 \times 10^6$  and  $8 \times 10^{11}$ , respectively. The value of  $K_{-1}/K_2$  is

- (a)  $2 \times 10^5$       (b)  $0.5 \times 10^5$       (c)  $32 \times 10^5$       (d)  $2 \times 10^{-5}$       [NET 2018 Dec]

Ans.  $R = K_2[\text{A}^*]$  .....(i)

Applying steady-state approximation on  $\text{A}^*$ , we get,

Rate of formation of  $\text{A}^*$  = Rate of deformation of  $\text{A}^*$

$$K_1[\text{A}][\text{M}] = K_{-1}[\text{A}^*][\text{M}] + K_2[\text{A}^*]$$

$$\text{Or, } [\text{A}^*] = K_1[\text{A}][\text{M}] / (K_{-1}[\text{M}] + K_2) \text{ .....(ii)}$$

Putting the value of  $[\text{A}^*]$  on equation (i),

$$R = K_1 K_2 [\text{M}] / (K_{-1}[\text{M}] + K_2) \text{ .....(iii)}$$

$$\text{Again, } K_{\text{uni}} = K_1 K_2 [\text{M}] / (K_{-1}[\text{M}] + K_2)$$

$$\text{Or, } 1/K_{\text{uni}} = (1/K_1[\text{M}]) + (K_{-1}/K_1 K_2) \text{ .....(iv)}$$

Now, equation of a straight line,

$$Y = mX + C$$

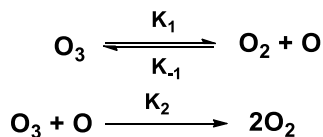
Thereby, slope =  $1/K_1$     intercept =  $K_{-1}/K_1 K_2$  in the plot  $1/K_{\text{uni}}$  vs.  $1/[\text{M}]$ ,

Therefore ratio of intercept and slope will be

$$\text{Intercept/slope} = (K_{-1}/K_1 K_2) \times K_1 = K_{-1}/K_2 = (8 \times 10^{11}) / (4 \times 10^6) = 2 \times 10^5$$

Correct answer is **Option (a)**.      [Key point 2.10.37]

Q. The decomposition mechanism of ozone is



If  $K_{-1}[\text{O}_2] \ll K_2[\text{O}_3]$ , then the order of the reaction with respect to ozone is

- (a) Zero (b) one (c) two (d) complex

[NET 2018 Dec]

Ans.  $R = K_2[\text{O}_3][\text{O}] \dots\dots\dots(i)$

Applying steady-state approximation on O, we have,

Rate of consumption of [O] = Rate of formation of [O]

$$K_{-1}[\text{O}_2][\text{O}] + K_2[\text{O}_3][\text{O}] = K_1[\text{O}_3]$$

$$\text{Or, } [\text{O}] = K_1[\text{O}_3]/(K_{-1}[\text{O}_2] + K_2[\text{O}_3])$$

Putting the value of [O] in equation (i), we get,

$$R = K_2 K_1 [\text{O}_3]^2 / (K_{-1}[\text{O}_2] + K_2[\text{O}_3])$$

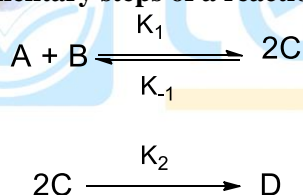
Given  $K_{-1}[\text{O}_2] \ll K_2[\text{O}_3]$ ,

$$\begin{aligned} \text{Thereby, } R &= K_2 K_1 [\text{O}_3]^2 / K_2[\text{O}_3] \quad (\text{ignoring the other term}) \\ &= K_1[\text{O}_3] \end{aligned}$$

Hence, order w.r.t ozone is one.

Correct answer is **Option (b).** [Key point 2.10.37]

Q. Elementary steps of a reaction are as follows



If steady state approximation is applicable to C, the rate of product formation in the reaction is

- (a) proportional to  $[\text{A}][\text{B}]$  (b) proportional to  $[\text{A}]^2[\text{B}]^2$   
(c) proportional to  $[\text{A}]^{1/2}[\text{B}]^{1/2}$  (d) independent of  $[\text{A}][\text{B}]$

[NET 2018 June]

Ans.  $d[\text{D}]/dt = K_2[\text{C}]^2$

Steady-state approximation on [C],

$$d[\text{C}]/dt = K_1[\text{A}][\text{B}] - K_{-1}[\text{C}]^2 - K_2[\text{C}]^2$$

$$\text{As } d[\text{C}]/dt = 0, [\text{C}] = (K_1[\text{A}][\text{B}]/K_2 + K_{-1})^{1/2}$$

$$K_{eq} = K_1/K_{-1} = [\text{C}]^2/[\text{A}][\text{B}]$$

$$d[\text{D}]/dt = K_2 \{ (K_1[\text{A}][\text{B}]/K_2 + K_{-1})^{1/2} \}^2 = \text{Constant}[\text{A}][\text{B}]$$

$$d[\text{D}]/dt \propto [\text{A}][\text{B}]$$

Correct answer is **Option (a).**

[Key point 2.10.37]

**Q. If the unit of rate constant of a reaction is  $L^3\text{mol}^{-3}\text{s}^{-1}$ , the order of the reaction is**

- (a) 1                      (b) 2                      (c) 3                      (d) 4                      [NET 2018 June]

**Ans.** Unit of the rate const.  $L^{n-1}\text{M}^{1-n}\text{s}^{-1}$

Now, if we consider  $n = 4$ , then the unit becomes  $L^3\text{mol}^{-3}\text{s}^{-1}$ .

So, order of the reaction = 4.

Correct answer is **Option (d).** [Key point 2.10.28]

**Q. Difference between activation energies of the reverse and forward steps of a reversible reaction is  $9.212RT$ . If the pre-exponential factor of the forward reaction is double that of the reverse reaction at the same temperature, the equilibrium constant for the reaction at that temperature will be [ $\ln 10 = 2.303$ ]**

- (a)  $1 \times 10^4$               (b)  $2 \times 10^4$               (c)  $1 \times 10^{-4}$               (d)  $2 \times 10^{-4}$               [NET 2018 June]

**Ans.** We have,  $\Delta E = E_f - E_b = 9.212RT$  .....(i)

$A_f = 2A$      $A_b = A$

From Arrhenius equation of activation energy,

$$K = Ae^{-E_a/RT}$$

$$\text{Or, } \ln K = \ln A - E_a/RT$$

$$\ln K_f = \ln A_f - E_f/RT \text{ .....(ii)}$$

$$\ln K_b = \ln A_b - E_b/RT \text{ .....(iii)}$$

now, (i) – (ii),

$$\ln K_f - \ln K_b = (\ln A_f - \ln A_b) + (E_b - E_f)/RT$$

$$\text{or, } \ln K_f/K_b = \ln A_f/A_b + \Delta E/RT$$

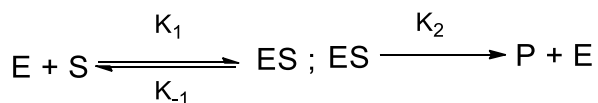
putting all values given in the problem,

$$\log K_{eq} = \log 2 + 9.212/2.303$$

$$\text{so, } K_{eq} = 10^{4.301} = 2 \times 10^4$$

Correct answer is **Option (b).** [Key point 2.10.35]

**Q. For an enzyme-substrate reaction,**



The slope and the intercept of the plot between  $1/r$  and  $1/[S]$  are  $10^{-2}$  s and  $10^2$  M<sup>-1</sup>s, respectively. If  $E_0 = 10^{-6}$  M and  $K_{-1}/K_2 = 1000$ , the value of  $K_1$  will be close to (in units of M<sup>-1</sup>s<sup>-1</sup>) [ $r$  is the rate of reaction and  $E_0$  is the initial concentration of the enzyme].

- (a)  $1 \times 10^{11}$     (b)  $1 \times 10^4$     (c)  $1 \times 10^8$     (d)  $1 \times 10^6$     [NET 2018 June]

**Ans.**  $E_0 = 10^{-6}$  (M),  $K_{-1}/K_2 = 1000$ ,  $K_1 = ?$

Slope =  $10^{-2}$  s, intercept =  $10^2$  M<sup>-1</sup>s,

Lineweaver-Burk plot for Enzyme catalyzed reaction,

$$1/r = 1/r_{\max} + K_M/r_{\max}[E_0] \quad \text{where } r_{\max} = K_2[E_0]$$



Michaelis-Menten Equation shows

$$r = K_2[E_0][S_0]/K_M + [S_0] \quad \text{where } K_M = K_{-1} + K_2/K_1$$

Lineweaver-Burk equation for Enzyme catalyzed reaction,

$$1/r = K_M + [S_0]/K_2[E_0][S_0] = K_M/K_2[E_0][S_0] + 1/K_2[E_0] = 10^{-2} + 1/10^2$$

From this,

$$K_M = 10^{-4} \quad K_2 = 10^4$$

Now, putting the values on equation below,

$$K_{-1} + K_2/K_1 = K_M$$

$$\text{Or, } K_1 = \{(10^3 + 1) \times 10^4\}/10^{-4} = 1.001 \times 10^{11}$$

Correct answer is **Option (a).**    [Key point 2.10.66]

Q. For a sequence of consecutive reactions,  $A \xrightarrow{K_1} I \xrightarrow{K_2} P$  the concentration of I would be, by steady state approximation.

- (a)  $K_1[A]$  (b)  $(K_1 + K_2)[A]$  (c)  $K_1K_2[A]$  (d)  $K_1[A]/K_2$  [NET 2017 Dec]

Ans. From steady-state approximation,

Rate of formation I = Rate of consumption I

$$K_1[A] = K_2[I]$$

$$[I] = K_1[A]/K_2$$

Correct answer is **Option (d)**. [Key point 2.10.37]

Q. The slope and intercept obtained from 1/rate against 1/substrate concentration of an enzyme catalyzed reaction are 300 and  $2 \times 10^5$ , respectively. The Michaelis-Menten constants of the enzyme in this reaction is

- (a)  $5 \times 10^6 \text{ M}$  (b)  $5 \times 10^{-6} \text{ M}$  (c)  $1.5 \times 10^3 \text{ M}$  (d)  $1.5 \times 10^{-3} \text{ M}$  [NET 2017 Dec]

Ans. From Lineweaver-Burk plot for enzyme catalyzed reaction,

$$\text{Slope} = K_M/r_{\max} = 300, \quad \text{intercept} = 1/r_{\max} = 2 \times 10^5$$

$$K_M = 300 \times \frac{1}{2} \times 10^{-5} = 1.5 \times 10^{-3} \text{ M}$$

Correct answer is **Option (d)**. [Key point 2.10.64]



**Q.** Reaction between A & B is carried out for different initial concentrations and the corresponding half-life times are measured. The data listed in the table

Entry	[A] <sub>0</sub> μM	[B] <sub>0</sub> μM	t <sub>1/2</sub> sec
1	500	10	60
2	500	20	60
3	10	500	60
4	20	500	60

The rate can be represented as

- (a)  $K[A][B]$  (b)  $K[A]^2$  (c)  $K[A]^2[B]$  (d)  $K[A][B]^2$  [NET 2017 Dec]

**Ans.** Based on dilution method, when [A] be fixed (excess amount compared to [B]), and then [B] be increased to double, the t<sub>1/2</sub> remains same; so,  $r \propto [B]$ . Overall rate for B is first order.

when [B] be fixed (excess amount compared to [A]), and then [A] be increased to double, the t<sub>1/2</sub> decreases to half of former; so,  $r \propto [A]^2$ . Overall rate for A is second order.

Hence overall rate equation will be

$$R = K[A]^2[B]$$

Correct answer is **Option (c).** [Key point 2.10.10]

**Q.** If the pre-exponential factor in Arrhenius equation is  $1.6 \times 10^{12} \text{ s}^{-1}$ , the value of the rate constant at extremely high temperature will be close to

- (a)  $1.6 \times 10^{12} \text{ s}^{-1}$  (b)  $4.2 \times 10^{12} \text{ s}^{-1}$  (c)  $2.4 \times 10^9 \text{ s}^{-1}$  (d)  $1.2 \times 10^6 \text{ s}^{-1}$  [NET 2017 June]

**Ans.** From Arrhenius equation,

$$K = Ae^{-E_a/RT}$$

At very high temperature,  $T \rightarrow \infty$ , then,

$$K = Ae^{-E_a/R\infty} = Ae^0 = A = 1.6 \times 10^{12} \text{ s}^{-1}$$

Correct answer is **Option (a).** [Key point 2.10.35]

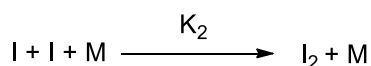
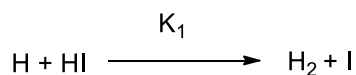
**Q. If kinetic study of a chemical reaction, slopes are shown at different times in the plot concentration of reactants vs. time. The magnitude of slopes with increase of time**

- (a) remains unchanged                      (b) increases  
(c) decreases                      (d) increases & decreases periodically                      [NET 2017 June]

**Ans.** As with elapse of time the concentrations of reactants gradually decrease, so also slopes decrease.

Correct answer is **Option (c).** [Key point 2.10.2]

**Q. Photochemical decomposition of HI takes place with the following mechanism**



**Considering H and I atoms as intermediates, the rate of removal of HI is**

- (a)  $\text{I}_a/2$                       (b)  $\text{I}_a$                       (c)  $2\text{I}_a$                       (d)  $\text{I}_a^2$                       [NET 2017 June]

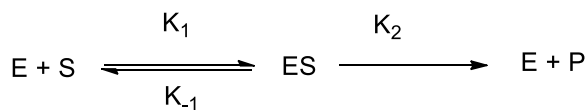
**Ans.** Rate of removal of HI =  $\text{K}_1[\text{H}][\text{HI}] + \text{I}_a$

Steady-state approximation on H,

$$\text{I}_a = \text{K}_1[\text{H}][\text{HI}]; \text{ therefore rate } r = \text{I}_a + \text{I}_a = 2\text{I}_a$$

Correct answer is **Option (c).** [Key point 2.10.76]

**Q. In an enzyme catalyzed reaction**



$K_2 = 3.42 \times 10^4 \text{ s}^{-1}$ , if  $[E]_0 = 1 \times 10^{-2} \text{ moldm}^{-3}$ , the magnitude of maximum velocity and turn over number using Michaelis-Menten kinetics are

- (a)  $3.42 \times 10^2 \text{ moldm}^{-3}\text{s}^{-1}$ ;  $3.42 \times 10^4 \text{ s}^{-1}$   
 (b)  $3.42 \times 10^6 \text{ moldm}^{-3}\text{s}^{-1}$ ;  $3.42 \times 10^4 \text{ s}^{-1}$   
 (c)  $3.42 \times 10^4 \text{ moldm}^{-3}\text{s}^{-1}$ ;  $3.42 \times 10^6 \text{ s}^{-1}$   
 (d)  $3.42 \times 10^4 \text{ moldm}^{-3}\text{s}^{-1}$ ;  $3.42 \times 10^2 \text{ s}^{-1}$

[NET 2017 June]

**Ans.** we know from Michaelis-Menten kinetics for enzyme catalyzed reaction,

$$r_{\max} = K_2[E]_0 = 3.42 \times 10^4 \text{ s}^{-1} \times 1 \times 10^{-2} \text{ moldm}^{-3} = 3.42 \times 10^2 \text{ moldm}^{-3} \text{ s}^{-1}$$

$$\text{Turn Over Number [TON]} = K_2 = 3.42 \times 10^4 \text{ s}^{-1}$$

Correct answer is **Option (a).**

[Key point 2.10.64]

**Q. Arrhenius equations for two chemical reactions are:  $K_1 = A_1 e^{-E_1/RT}$ ;  $K_2 = A_2 e^{-E_2/RT}$ . If  $E_1 > E_2$ , then at a given temperature T,**

- (a)  $K_1/K_2 < A_1/A_2$     (b)  $K_2/K_1 < A_2/A_1$     (c)  $K_1 K_2 > A_1 A_2$     (d)  $K_1 + K_2 > A_1 + A_2$     [NET 2017 JUNE]

**Ans.**  $K_1/A_1 = e^{-E_1/RT}$  .....(i)

$K_2/A_2 = e^{-E_2/RT}$  .....(ii)

Equation (ii) is divided by equation (i),

$$K_2 A_1 / K_1 A_2 = e^{(E_1 - E_2)/RT}$$

So,  $K_2 A_1 / K_1 A_2 > 1$ , as  $E_1 > E_2$

$$A_1/A_2 > K_1/K_2$$

Correction answer is **Option (a).**

[Key point 2.10.35]

**Q. For a reaction with an activation energy of  $49.8 \text{ kJmol}^{-1}$ , the ratio of rate constants at 600K and 300K, ( $K_{600}/K_{300}$ ), is approximately ( $R = 8.3 \text{ Jmol}^{-1}\text{K}^{-1}$ )**

- (a)  $\ln 10$       (b) 10      (c)  $10 + e$       (d)  $e^{10}$       [NET 2016 Dec]

**Ans.** From Arrhenius theory of activation energy,

$$\ln (K_2/K_1) = E_a [T_2 - T_1 / T_1 T_2] / R$$

putting the values from given data,

$$\ln(K_{600}/K_{300}) = 49.8 \times 10^3 [600 - 300 / 300 \times 600] / 8.314$$

$$\text{or, } \ln(K_{600}/K_{300}) = 10$$

$$\text{or, } (K_{600}/K_{300}) = e^{10}$$

Correction answer is **Option (d)**.      [Key point 2.10.35]

**Q. According to the transition state theory, the plot with slope equal to  $-\Delta H^\ddagger/R$  is**

- (a)  $\ln K$  vs  $T$       (b)  $\ln(K/T)$  vs  $T$       (c)  $\ln(K/T)$  vs  $1/T$       (d)  $\ln K$  vs  $1/T$       [NET 2016 Dec]

**Ans.** From Transition State theory,

$$K = K_B T [e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}] / h$$

$$\text{Or, } K/T = K_B [e^{-\Delta H^\ddagger/RT} e^{\Delta S^\ddagger/R}] / h$$

Taking  $\ln$  on both the sides,

$$\ln K/T = K_B/T - \Delta H^\ddagger/RT + \Delta S^\ddagger/R$$

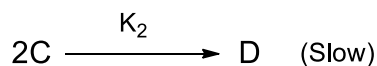
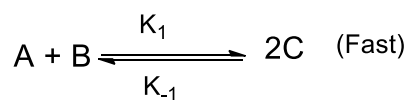
$$\text{or, } \ln K/T = K_B/T - 1/R [(\Delta H^\ddagger - T\Delta S^\ddagger)/T]$$

Straight line equation be  $y = mx + c$

Comparing two above equations, we can say  $\ln(K/T)$  vs  $1/T$  portrays a straight line equation.

Correction answer is **Option (c)**.      [Key point 2.10.40]

**Q. A reaction goes through the following elementary steps**



**Assuming that steady state approximation can be applied to C, on doubling the concentration of A, the rate of production of D will increase by (assuming  $K_2[A] \ll K_{-1}[C]$ )**

- (a) 2 times      (b) 4 times      (c) 8 times      (d)  $2\sqrt{2}$  times      [NET 2016 Dec]

**Ans.** Rate of production of D

$$d[D]/dt = r_D = K_2[A][C]$$

Steady-state approximation on C,

$$2K_1[A][B] = 2K_{-1}[C]^2 + K_2[A][C]$$

$$\text{Or, } [C] = 2K_1[A][B]/(2K_{-1}[C] + K_2[A])$$

$$\text{As, } K_2[A] \ll K_{-1}[C]$$

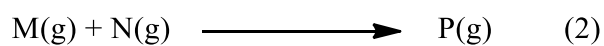
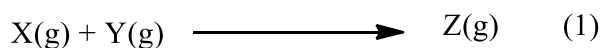
$$\text{So, } [C] = (K_1/K_{-1})^{1/2}[A]^{1/2}[B]^{1/2}$$

$$r_D = K_2(K_1/K_{-1})^{1/2}[A]^{1/2}[B]^{1/2}$$

Correct answer is **Option (d).**

[Key point 2.10.37]

**Q. For two reactions,**



According to the collision theory, the ratio of squares of pre-exponential factors of reaction 2 ( $A_2$ ) and 1 ( $A_1$ ) at the same temperature,  $(A_2/A_1)^2$ , is

Species	Mass (g/mol)	Diameter (nm)
X	5	0.3
Y	20	0.5
M	10	0.4
N	10	0.4

(a) 4/5

(b) 5/5

(c) 5/3

(d) 3/5

[NET 2016 Dec]

Ans. Pre-exponential factor in Collision theory,

$$A \propto \sigma^2 / \sqrt{\mu}$$

$$A_2/A_1 = (\sigma_2/\sigma_1)^2 (\mu_1/\mu_2)^{1/2}$$

$$\text{Or, } (A_2/A_1)^2 = (\sigma_2/\sigma_1)^4 (\mu_1/\mu_2)$$

$$\text{Here, } \sigma_2 = \sigma_1 = 0.4$$

$$\text{So, } (A_2/A_1)^2 = (\mu_1/\mu_2) = \{(5 \times 20)/25\} / \{(10 \times 10)/20\} = 4/5$$

Correct answer is **Option (a).**

[Key point 2.10.38]



**Q. If the rates of a reaction are R1 and R2 at concentration C1 and C2 of a reactant respectively, the order of reaction, 'n' [assuming that the concentrations of all other reactants and temperature remain constant] with respect to that reactant is given by**

[NET 2016 June]

(a)  $n = (\log R1 - \log R2)/(\log C1 - \log C2)$

(b)  $n = (\log C1 - \log C2)/(\log R1 - \log R2)$

(c)  $n = (\log C1 - \log R1)/(\log C2 - \log R2)$

(d)  $n = (\log C2 - \log R2)/(\log C1 - \log R1)$

**Ans.** We know from rate equation,

$$R1/R2 = (C1/C2)^n$$

Taking log on both the sides,

$$\log(R1/R2) = n \log(C1/C2)$$

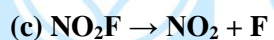
$$\text{or, } n = (\log R1 - \log R2)/(\log C1 - \log C2)$$

Correct answer is **Option (a).**

[Key point 2.10.28]

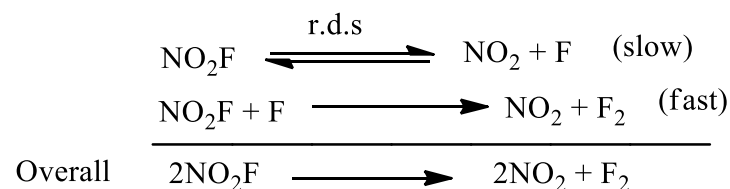
**Q. Experimentally determined rate law for the chemical reaction,  $2\text{NO}_2\text{F} \rightarrow 2\text{NO}_2 + \text{F}_2$  is  $R = K[\text{NO}_2\text{F}]$ .**

**The rate determining step consistent with the rate law is**



[NET 2016 June]

**Ans.**



As,  $r = K[\text{NO}_2\text{F}]$

Hence, in r.d.s only one concentration term of a component, here  $\text{NO}_2\text{F}$  species should be involved.

Correct answer is **Option (c).**

[Key point 2.10.2]

**Q. If experimentally observed rate constant is greater than the maximum value of rate constant obtained using hard-sphere model of collision theory, then relation between the impact parameter (b) and sum of the radii of two reactants is**

- (a)  $b = r_1 + r_2$  (b)  $b < r_1 + r_2$  (c)  $b > r_1 + r_2$  (d)  $b \leq r_1 + r_2$  [NET 2016 June]

**Ans.** If 'n' be the number of molecules per cc and  $\langle c \rangle$  be the average speed and  $\sigma$  be the molecular diameter, then, frequency of activated collision [Z]

$$Z = (1/\sqrt{2}) \prod \sigma^2 \langle c \rangle n^2 e^{-E_a/RT}$$

$$\text{Rate constant } K_{\text{obs}} = \sqrt{2} N_A 10^{-3} \prod \sigma^2 \langle c \rangle n^2 e^{-E_a/RT}$$

$$\text{Again, } K_{\text{obs}} = \sqrt{2} N_A b \prod [(\sigma_1 + \sigma_2)/2]^2 \langle c \rangle n^2 e^{-E_a/RT}$$

Where,  $N_A$  = Avogadro's number,  $\sigma_1$  and  $\sigma_2$  are diameter of reactants

Now, from collision theory, we can conclude that if  $K_{\text{obs}} > K_{\text{max}}$  then there would be fruitful collisions were happened almost every occasion and this is only possible when sum of radii of reactants would be lesser than collision diameter/impact parameter, that means,  $b > r_1 + r_2$ .

Correct answer is **Option (c).** [Key point 2.10.38]

**Q. half-life  $t_{1/2}$  for a third order reaction  $3C \rightarrow \text{Products}$ , where  $C_0$  is the initial concentration of C, will be**

- (a)  $3/2K(C_0)^2$  (b)  $3/K(C_0)$  (c)  $3/2K(C_0)$  (d)  $2/3K(C_0)^2$  [NET 2016 June]

**Ans.** For a third order reaction the rate equation will be

$$K_3 t = (1/2) [1/(a-x)^2 - 1/a^2]$$

$$\text{When, } t = t_{1/2}, a - x = a/2$$

Then, putting the values on rate equation, we have

$$K_3 t_{1/2} = (1/2) [4/a^2 - 1/a^2] = 3/2a^2$$

$$\text{So, } t_{1/2} = 3/2K_3 a^2 \quad \text{here, } K_3 = K \text{ and } a = C_0$$

Correct answer is **Option (a).** [Key point 2.10.23]