## **Reaction Coordinate Diagrams**

It is helpful to visualize energy changes throughout a process on a reaction coordinate diagram like this one for the rearrangement of methyl isonitrile.



It shows the energy of the reactants and products (and, therefore, ∆E).
 The high point on the diagram is the transition state.



The species present at the transition state is called the activated complex.

The energy gap between the reactants and the activated complex is the activation energy barrier.

### Maxwell–Boltzmann Distributions



Temperature is defined as a measure of the average kinetic energy of the molecules in a sample.
 At any temperature there is a wide distribution of kinetic

Kinetic energy

As the temperature increases, the curve flattens and broadens.

energies.

Thus at higher temperatures, a larger population of molecules has higher energy.

## Maxwell–Boltzmann Distributions

If the dotted line represents the activation energy, as the temperature increases, so does the fraction of molecules that can overcome the activation energy barrier.
 As a result, the reaction rate increases.



## Maxwell–Boltzmann Distributions

This fraction of molecules can be found through the expression

 $f = e^{-E_a/RT}$ > where *R* is the gas constant and *T* is the Kelvin temperature Higher temperature Minimum energy needed for reaction,  $E_a$ 

## **Arrhenius Equation**

Svante Arrhenius developed a mathematical relationship between k and  $E_a$ :

 $k = A e^{-E a_{/RT}}$ 

where A is the frequency factor, a number that represents the likelihood that collisions would occur with the proper orientation for reaction.

### **Arrhenius Equation**



Therefore, if k is determined experimentally at several temperatures,  $E_{a}$  can be calculated from the slope of a plot of ln k vs. 1/T.

## **Determining the Activation Energy**

>If we do not have a lot of data, then we recognize

$$\ln k_{1} = -\frac{E_{a}}{RT_{1}} + \ln A \quad \text{and} \quad \ln k_{2} = -\frac{E_{a}}{RT_{2}} + \ln A$$
$$\ln k_{1} - \ln k_{2} = \left(-\frac{E_{a}}{RT_{1}} + \ln A\right) - \left(-\frac{E_{a}}{RT_{2}} + \ln A\right)$$
$$\ln \frac{k_{1}}{k_{2}} = \frac{E_{a}}{R} \left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right)$$

### 8. Effect of temperature on reaction rate

### 8.1 <u>Arrhenius concept</u>

- i) A chemical reaction takes place by collision between the reactant molecules, and for the collision to be effective the colliding molecules must possess some certain minimum energy called threshold energy of the reaction.
- ii) Reactant molecules having energy equal or greater than the threshold are called active molecules and those having energy less than the threshold are called passive molecules.
- iii) At a given temperature there exists a dynamic equilibrium between active and passive molecules. The process of transformation from passive to active molecules being endothermic, increase of temperature increases the number of active molecules and hence the reaction.

Passive molecules Aetive molecules,  $\Delta H = +ve$ 

iv) Concept of energy of  $activation (E_a)$ 

The extra amount of energy which the reactant molecules (having energy less than the threshold) must acquire so that their mutual collision may lead to the breaking of bond(s) and hence the reaction, is known as energy of activation of the reaction. It is denoted by the symbol  $E_a$ . Thus,

 $E_a$  = Threshold energy – Actual average energy

 $E_a$  is expressed in kcals mole<sup>-1</sup> or kJ mole<sup>-1</sup>.

**Arrhenius Equation** 

$$\mathsf{k} = A e^{-E_a/RT}$$

 $T \rightarrow \infty$ ,  $k \rightarrow A$ . Thus, the constant A is the rate constant of reaction at infinity temperature. The rate constant goes on increasing with temperature.

So, when T approaches infinity, k will be maximum. That is to say, A is the maximum rate constant of a reaction.

It is also to be noted that the exponential term i.e.  $e^{-Ea/RT}$  measures the fraction of total number of molecules in the activated state or fraction of the total number of effective collisions. If  $n_{Ea}$  and n be the number of molecules of reactant in the activated state and the total number of molecules of the reactant present in the reaction vessel respectively, then

$$\frac{n_{E_a}}{n} = e^{-E_a / RT}$$

 $k = Ae^{-E_a/RT}$   $logk = \left(-\frac{Ea}{2.303R}\right)\frac{1}{T} + logA$ Since  $\frac{E_a}{2.303R}$  and logA both are constants for a given reaction. So from equation 7 it is evident that a plot of log k vs.  $\frac{1}{T}$  will be a straight line of the slope equal to  $-\frac{E_a}{2.303R}$  and intercept equal to logA as shown below.



$$\frac{-E_{a}}{2.303R} = \tan\theta = -\tan(180 - \theta) = -\frac{0A}{OB}$$
$$\therefore E_{a} = \frac{OA}{OB} \times 2.303R$$
$$\log A = OA$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$

### **Temperature coefficient**

Temperature has very marked effect on the reaction rate. It has been found that the rate of most homogeneous reactions are nearly doubled or tripled by 10° rise in temperature.

$$\frac{k_{t+10}}{k_t} = 2 \text{ to } 3(\text{nearly})$$

### 8.2 Reaction energy profile

### For exothermic reaction:



 $\Sigma H_R$ = Average summation of enthalpies of reactants

 $\Sigma H_P =$  Average summation of enthalpies of products

 $\Delta H$  =Enthalpy change during the reaction

 $Ea_1 = Energy$  of activation of the forward reaction (FR)

Ea<sub>2</sub> = Energy of activation of the backward reaction(BR)



### For endothermic reaction:

### **Notable Points**

- ii) Greater the height of energy barrier, greater will be the energy of activation and more slower will be the reaction at a given temperature.
- iii) Rate = Collision frequency  $\times$  fraction of the total number of collision which is effective.

Collision frequency is the number of collisions per unit volume per unit time. It is denoted by the symbol Z. Z is directly proportional to  $\sqrt{T}$ .

#### Example20:

Two reaction proceed at 25°C at the same rate. The temperature coefficient of the rate of the first reaction is 2 and that of second is 2.5. Find the ratio of the rates of these reactions at 95° C.

**Solution:** At 25°C the rates of the two reactions are same (say R.) Since the temperature coefficient gives the number of times the rate of a reaction increases by a rise in temperature of 10°, we have the following results:

	Rate of		
Temperature	1 <sup>st</sup>	2 <sup>nd</sup>	
	reaction	reaction	
25°	R	R	
35°	2 R	2.5 R	
45°	$2^2 R$	(2.5) <sup>2</sup> R	
55°	2 <sup>3</sup> R	(2.5) <sup>3</sup> R	
65°	2⁴R	(2.5) <sup>4</sup> R	
75°	2⁵R	(2.5) <sup>5</sup> R	
85°	2 <sup>6</sup> R	(2.5) <sup>6</sup> R	
95°	2 <sup>7</sup> R	(2.5) <sup>7</sup> R	

Thus, at 95°,

rateof second reaction	$-2.5^7 R$	_	1 768
rateof first reaction	$=$ $2^7 R$		<b></b> /00

### Example 21 :

What is the energy of activation of a reaction if its rate doubles when the temperature is raised from 290K to 300K?

### Solution:

We have,

$$\log \frac{k_2}{k_1} = \frac{E}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

$$\log 2 = \frac{E}{2.303R} \left( \frac{300 - 290}{290 \times 300} \right) \qquad (R = 2cal \ K^{-1}mole^{-1})$$

$$E = 12062 calories$$

$$\approx 12 kcal$$



### Example22:

The activation energy for the reaction,  $O_3(g) + NO(g) \rightarrow NO_2(g) + O_2(g)$ 

is 9.6kJ/mole. Prepare an activation energy plot if  $\Delta H^{\circ}$  for this reaction is What is the energy of activation for the reverse reaction?

-200kJ/mole .

### Solution :

Energy of activation for reverse reaction

= 9.6 + 200 kJ = 209.6 kJ.

#### **Example23:**

The rate constant is giveny by Arrhenius equation

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

Calculate the ratio of the catalysed and uncatalysedrate constant at 25°C if the energy of activation of a catalysed reaction is 162 kJ and for the uncatalysed reaction the value is 350 kJ.

### Solution:

Let k<sub>ca</sub> and k<sub>un</sub> be the rate constants for catalysed and uncatalysed reactions.

2.303  $\log_{10} k_{ca} = 2.303 \log_{10} A - \frac{162 \times 10^3}{RT}$  ...(i) and  $2.303 \log_{10} a_{un} = 2.303 \log_{10} A - \frac{350 \times 10^3}{RT}$  ...(ii) Subtracting Eq. (ii) from Eq. (i)

$$\log_{10} \frac{k}{k_{un}} = \frac{10^3}{2.303RT} (350 - 162)$$
$$= \frac{188 \times 10^3}{2.303 \times 8.314 \times 298} = 32.95$$
$$\frac{k_{ca}}{k_{un}} = 8.8 \times 10^{32}$$

## **Reaction Mechanisms**

What is reaction mechanism?

>This is the sequence of events that describes the actual process by which reactants become products .

- Reactions may occur all at once or through several discrete steps.
- Each of these processes is known as an elementary reaction or elementary process.

### **Reaction Mechanisms**

- The balanced chemical equation provides information about the beginning and end of reaction.
- > The reaction mechanism gives the path of the reaction.
- Mechanisms provide a very detailed picture of which bonds are broken and formed during the course of a reaction.

### **Elementary Steps**

Elementary step: any process that occurs in a single step.

TABLE 14.3         Elementary Reactions and Their Rate Laws					
Molecularity	<b>Elementary Reaction</b>	Rate Law			
<i>Uni</i> molecular <i>Bi</i> molecular <i>Bi</i> molecular <i>Ter</i> molecular <i>Ter</i> molecular <i>Ter</i> molecular	$A \longrightarrow \text{products}$ $A + A \longrightarrow \text{products}$ $A + B \longrightarrow \text{products}$ $A + A + A \longrightarrow \text{products}$ $A + A + B \longrightarrow \text{products}$ $A + B + C \longrightarrow \text{products}$	Rate = $k[A]$ Rate = $k[A]^2$ Rate = $k[A][B]$ Rate = $k[A]^3$ Rate = $k[A]^2[B]$ Rate = $k[A][B][C]$			

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The molecularity of a process tells how many molecules are involved in the process.

## **Rate Laws for Elementary Steps**

### **Rate Laws for Elementary Steps**

- The rate law of an elementary step is determined by its molecularity:
  - Unimolecular processes are first order,
  - Bimolecular processes are second order, and
  - Termolecular processes are third order.

### **Rate Laws for Multistep Mechanisms**

• Rate-determining step: is the slowest of the elementary steps.

## **Multistep Mechanisms**

In a multistep process, one of the steps will be slower than all others.

The overall reaction cannot occur faster than this slowest, rate-determining step.



 $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$ 

The rate law for this reaction is found experimentally to be

Rate =  $k [NO_2]^2$ 

CO is necessary for this reaction to occur, but the rate of the reaction does not depend on its concentration.

This suggests the reaction occurs in two steps.

### **Slow Initial Step**

➤ A proposed mechanism for this reaction is
➤ Step 1: NO<sub>2</sub> + NO<sub>2</sub> → NO<sub>3</sub> + NO (slow)
➤ Step 2: NO<sub>3</sub> + CO → NO<sub>2</sub> + CO<sub>2</sub> (fast)
➤ The NO<sub>3</sub> intermediate is consumed in the second step.
➤ As CO is not involved in the slow, rate-determining step,
it does not appear in the rate law.



Fast Initial Step

2 NO (g) + Br<sub>2</sub> (g) → 2 NOBr (g) > The rate law for this reaction is found to be Rate =  $k [NO]^2 [Br_2]$ > Because the molecular processes are rare, this rate law

suggests a two-step mechanism.



Step 1 includes the forward and reverse reactions.

## Fast Initial Step

The rate of the overall reaction depends upon the rate of the slow step.

The rate law for that step would be

Rate =  $k_2$  [NOBr<sub>2</sub>] [NO] > But how can we find [NOBr<sub>2</sub>]?

- NOBr<sub>2</sub> can react two ways:
  - With NO to form NOBr
  - By decomposition to reform NO and Br<sub>2</sub>
- The reactants and products of the first step are in equilibrium with each other.
- Therefore: Rate<sub>f</sub> = Rate<sub>r</sub>

```
Fast Initial Step

Secause \text{Rate}_f = \text{Rate}_r,

k_1 [\text{NO}] [\text{Br}_2] = k_{-1} [\text{NOBr}_2]

Solving for [NOBr<sub>2</sub>] gives us
```

$$\frac{k_1}{k_{-1}}$$
 [NO] [Br<sub>2</sub>] = [NOBr<sub>2</sub>]

Substituting this expression for [NOBr<sub>2</sub>] in the rate law for the rate-determining step gives

Rate = 
$$\frac{k_2 k_1}{k_{-1}}$$
 [NO] [Br<sub>2</sub>] [NO]

 $= k [NO]^2 [Br_2]$ 

Nuclear transmutation is a first-order process.
 The kinetics of such a process, you will recall, obey this equation:

$$\ln \frac{N_t}{N_0} = -kt$$

- t: time interval
- k: the decay constant
- N<sub>o</sub>: Initial number of nucleus at time zero
- N<sub>t</sub>:Number remaining after time interval
- Rate at which sample decays is called activity
- Activity is number of disintegrations observed per unit time

>SI unit is the becquerel (Bq) >1 Bg = 1 nuclear disintegration per second Curie (Ci) is 3.7 x10<sup>10</sup> disintegration per second Conversions of Curie to Bq ► E.g. Convert 4.0 mCi to Bq >1 Curie =  $3.7 \times 10^{10}$  disintegration per second >4.0 mCi = 4.0 x 10<sup>-3</sup> x 3.7 x 10<sup>10</sup> disintegration per second =  $1.5 \times 10^8$  disintegration per second =  $1.5 \times 10^8$  Bg Mass of radioactive nuclei and activity are proportional to number of radio active nuclei This means that mass or activity can be substituted for N

The half-life of such a process is:

$$\frac{0.693}{k} = t_{1/2}$$

- Half lives are used to characterize decay of radioactive nuclei
- Each isotope has its own characteristic half life
- Half lives are not affected by external conditions such as temperature, pressure or state of chemical combination
- Radioactive atoms cannot therefore be rendered harmless by chemical reaction or any other practical treatment.

TABLE 21.4       The Half-lives and Type of Decay for Several Radioisotopes						
	Isotope	Half-life (yr)	Type of Decay			
Natural radioisotopes	<sup>238</sup> 92U	$4.5 \times 10^{9}$	Alpha			
	<sup>235</sup> 92U	$7.0 \times 10^{8}$	Alpha			
	<sup>232</sup> <sub>90</sub> Th	$1.4 imes10^{10}$	Alpha			
	40 19K	$1.3 \times 10^{9}$	Beta			
	$^{14}_{6}C$	5715	Beta			
Synthetic radioisotopes	<sup>239</sup> <sub>94</sub> Pu	24,000	Alpha			
	$^{137}_{55}Cs$	30	Beta			
	90 38 Sr	28.8	Beta			
	$^{131}_{53}$ I	0.022	Beta			

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### Dating

Because the half life of particular nuclide is constant, it can be used to determine the age of objects.
 Age can also be done by comparing the amount of a radioactive nuclide present at a given point in time with the amount normally present.
 Carbon 14 is used to determine age of organic materials

### **Practice Exercise:**

A wooden object from an archeological site is subjected to radiocarbon dating. The activity of the sample that is due to <sup>14</sup>C is measured to be 11.6 disintegrations per second. The activity of a carbon sample of equal mass from fresh wood is 15.2 disintegrations per second. The half-life of <sup>14</sup>C is 5715 yr. What is the age of the archeological sample?

**Step1:** First we need to determine the rate constant, *k*, for the process.

**Step 2:** Now we can determine *t*:

### SAMPLE EXERCISE

A rock contains 0.257 mg of lead-206 for every milligram of uranium-238. The half-life for the decay of uranium-238 to lead-206 is  $4.5 \times 10^9$  yr. How old is the rock?

### See solution in textbook on page 913

### SAMPLE EXERCISE

t

If we start with 1.000 g of strontium-90, 0.953 g will remain after 2.00 yr. (a) What is the half-life of strontium-90? (b) How much strontium-90 will remain after 5.00 yr? (c) What is the initial activity of the sample in Bq and in Ci?

### Step 1: Solve k and then calculate half life

$$k = -\frac{1}{t} \ln \frac{N_t}{N_0} = -\frac{1}{2.00 \text{ yr}} \ln \frac{0.953 \text{ g}}{1.000 \text{ g}}$$
$$= -\frac{1}{2.00 \text{ yr}} (-0.0481) = 0.0241 \text{ yr}^{-1}$$
$$_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0241 \text{ yr}^{-1}} = 28.8 \text{ yr}$$

Sample exercise contd

b) How much strontium-90 will remain after 5.00 yr?

$$\ln \frac{N_t}{N_0} = -kt = -(0.0241 \text{ yr}^{-1})(5.00 \text{ yr}) = -0.120$$

>  $N_t/N_0$  is calculated from  $\ln(N_t/N_0) = -0.120$  using the  $e^x$  or INV LN function of a calculator:

>Because  $N_0 = 1.000$  g, we have

$$N_t = (0.887)N_0 = (0.887)(1.000 \text{ g}) = 0.887 \text{ g}$$

(c) What is the initial activity of the sample in Bq and in Ci?

> To obtain the total number of disintegrations per second, calculate number of atoms in the sample. We multiply this quantity by k, where we express k as the number of disintegrations per atom per second, to obtain the number of disintegrations per second:

$$(1.00 \text{ g} {}^{90}\text{Sr}) \left(\frac{1 \text{ mol } {}^{90}\text{Sr}}{90 \text{ g} {}^{90}\text{Sr}}\right) \left(\frac{6.02 \times 10^{23} \text{ atoms } \text{Sr}}{1 \text{ mol } {}^{90}\text{Sr}}\right) = 6.7 \times 10^{21} \text{ atoms } {}^{90}\text{Sr}$$
  
Total disintegrations/s =  $\left(\frac{7.64 \times 10^{-10} \text{ disintegrations}}{\text{ atom } \cdot \text{ s}}\right) (6.7 \times 10^{21} \text{ atoms})$   
=  $5.1 \times 10^{12} \text{ disintegrations/s}$ 

Because a Bq is one disintegration per second, the activity is just 5.1 × 10<sup>12</sup> Bq. The activity in Ci is given by

$$(5.1 \times 10^{12} \text{ disintegrations/s}) \left( \frac{1 \text{ Ci}}{3.7 \times 10^{10} \text{ disintegrations/s}} \right) = 1.4 \times 10^2 \text{ Ci}$$

#### <u>Catalyst</u>

A catalyst is a substance, which increases the rate of a reaction without itself being consumed at the end of the reaction, and the phenomenon is called catalysis. There are some catalysts which decrease the rate of reaction and such catalysts are called negative catalyst. Obviously, the catalyst accelerating the rate will be positive catalyst. However, the term positive is seldom used and catalyst itself implies positive catalyst.

 $2\mathsf{KCIO}_3 + [\mathsf{MnO}_2] \longrightarrow 2\mathsf{KCI} + 3\mathsf{O}_2^{\uparrow} + [\mathsf{MnO}_2]$ 

MnSO<sub>4</sub> is an *"auto catalyst"* for this reaction. This is an example of auto catalysis. 2KMnO<sub>4</sub> +  $3H_2SO_4 + 5H_2C_2O_2 \rightarrow K_2SO_4 + 8H_2O + 10CO_2 + 2MnSO_4$ 

#### **General characteristics of catalyst**

- i) A catalyst does not initiate the reaction. It simply fastens it.
- ii) Only a small amount of catalyst can catalyse the reaction.
- iii) A catalyst does not alter the position of equilibrium i.e. magnitude of equilibrium constant and hence  $\Delta G^0$ . It simply lowers the time needed to attain equilibrium. This means if a reversible reaction in absence of catalyst completes to go to the extent of 75% till attainment of equilibrium, and this state of equilibrium is attained in 20 minutes then in presence of a catalyst also the reaction will go to 75% of completion before the attainment of equilibrium but the time needed for this will be less than 20 minutes.
- iv) A catalyst drives the reaction through a different route for which energy barrier is of short height and hence E<sub>a</sub> is of lower magnitude. That is, the function of the catalyst, to lower down the activation energy.



 $E_a$  = Energy of activation in absence of catalyst.  $E'_a$  = Energy of activation in presence of catalyst.

 $E_a - E'_a$  = lowering of activation energy by catalyst.

If k and  $k_{cat}$  be the rate constant of a reaction at a given temperature T, and  $E_a$  and  $E'_a$  are the activation energies of the reaction in absence and presence of catalyst, respectively, the

$$\frac{k_{cat}}{k} = \frac{Ae^{-E'a/RT}}{Ae^{-E_a/RT}} \quad \frac{k_{cat}}{k} = Ae^{(E_a - E'_a)/RT}$$

Since  $E_a - E_a'$  is +ve so  $k_{cat} > k$ . the ratio  $\frac{k_{cat}}{k}$  gives the number of times the rate of reaction will increase by the use of catalyst at a given temperature and this depends upon  $E_a - E'_a$ . Greater the value of  $E_a - E'_a$ , higher is the value of  $\frac{k_{cat}}{k}$ .

#### Example 25:

The second order rate constant for  $I^- + CIO^- \rightarrow IO^- + CI^-$  is 0.06 (mole/litre)<sup>-1</sup> s<sup>-1</sup>. If a solution initially contains, 1M I<sup>-</sup> and 1.5 × 10<sup>-4</sup> M CIO<sup>-</sup>.Calculate the concentration of CIO<sup>-</sup> after 5 minutes. If no, what additional information is required?

**Solution:** No, rate law is required to calculate [CIO<sup>-</sup>] after 5 minutes because the rate law could be any

of the following forms:

```
Rate = k [I<sup>-</sup>] [CIO<sup>-</sup>]
Rate = k[I<sup>-</sup>]<sup>2</sup>
Rate = k [CIO<sup>-</sup>]<sup>2</sup>
```

#### **Example 26:**

In hypothetical reaction  $A_2 + B_{2\rightarrow}$  2AB follows the mechanism as given below:  $A_2 \rightleftharpoons A + A$  (fast reaction)  $A + B_{2\rightarrow}$  AB + B (slow reaction)  $A + B \rightarrow AB$  (fast reaction) Give the rate law and order of reaction.

**Solution:** 

Sloweset step is rate determining. Rate = k[A][B<sub>2</sub>] ...(1) Here [A] should be eliminated.  $K_{c} = \frac{[A][A]}{[A_{2}]} = \frac{\left[A\right]^{2}}{[A_{2}]}$  $[A] = K_{c}^{1/2} [A_{2}]^{1/2}$ 

From (1). Rate =  $k K_{c}^{1/2} [A_2]^{1/2} [B_2]$ =  $k'[A_2]^{1/2} [B_2] = k' [A_2]^{1/2} [B^2]$ ; [k' = k . K<sub>c</sub>] Order = 1 +  $\frac{1}{2}$  = 3/2

### **BOOST YOUR LEARNING**

Problem 1: Consider a gaseous reaction, the rate of which is given by K[A] [B], the volume of the reaction vessel containing these gases is suddenly reduced to 1/4<sup>th</sup> of the initial volume. The rate of reaction relative to the original rate would be (A) 16/1 **(B)1/16** (C) 8/1 (D)1/8 Solution: By reducing volume to <sup>1</sup>th the concentration will become 4 times hence rate 16 times. : (A)

Problem 2: The rate of a reaction increases 4-fold when concentration of reactant is increased 16 times. If the rate of reaction is  $4 \times 10^{-6}$  mole L<sup>-1</sup> S<sup>-1</sup> when concentration of the reactant is  $4 \times 10^{-4}$  mole L<sup>-1</sup>, the rate constant of the reaction will be (A)2 × 10<sup>-4</sup> mole<sup>1/2</sup> L<sup>-1/2</sup> S<sup>-1</sup> (B)1 × 10<sup>-2</sup> S<sup>-1</sup> (C) 2 × 10<sup>-4</sup> mole<sup>-1/2</sup>, L<sup>1/2</sup> S<sup>-1</sup> (D)25 mole<sup>-1</sup> L min<sup>-1</sup>

Solution: Rate 
$$\propto \sqrt{\text{concen}}$$
, Rate =  $k \sqrt{\text{conc n}}$   
 $k = \frac{\text{Rate}}{(\text{concen})^{1/2}} = \frac{4 \times 10^{-6}}{(4 \times 10^{-4})^{1/2}} = \frac{4 \times 10^{-6}}{2 \times 10^{-2}} = 2 \times 10^{-4} \text{ mole}^{1/2} \text{ L}^{-1/2} \text{ S}^{-1}$   $\therefore$  (A)

Problem 3: A catalyst lowers the activation energy of a reaction from 20 kJ mole<sup>-1</sup> to 10 kJ mole<sup>-1</sup>. The temperature at which the uncatalysed reaction will have the same rate as that of the catalysed at 27°C is

(A)–123°C (B)327°C (C)327°C (D)+ 23°C

Solution:  $\frac{E'a}{T_1} = \frac{E_a}{T_2} = \frac{10}{300} = \frac{20}{T_2}$   $\therefore T_2 = 600 \text{ K} = 327^{\circ} \text{ C}$   $\therefore$  (B)

# Problem 4: A first order reaction is 87.5% complete in an hour. The rate constant of the reaction is (A)0.0346 min<sup>-1</sup> (B)0.0693 h<sup>-1</sup> (C)0.0693 min<sup>-1</sup> (D)0.0346 h<sup>-1</sup>

**Solution:** 87.5% change takes place in three half lives. Hence half-time of the reaction will be  $\frac{1}{3}$  hour =  $\frac{60}{3}$  = 20 min, since half-time of a first order reaction is a constant independent of initial concentration.  $100\% \xrightarrow{2} \text{ m n} 50\% \xrightarrow{2} \text{ m n} 25\% \xrightarrow{2} \text{ m n} 12.5\%$  (un reacted)

$$k = \frac{0.093}{t_{1/2}} = \frac{0.093}{20} = 0.0346 \text{ min}^{-1}$$
 .: (A)

Problem 5: The half -life of a first order reaction is 24 hours. If we start with 10M initial concentration of the reactant then conc. after 96 hours will be (A) 6.25 M (B) 1.25 M (C) 0.125 M (D) 0.625M 96 Number of half-lives = 24 = 4Solution: 10 Concentration remaining after 96 hrs =  $(2)^4$  = 0.625 M  $\therefore$  (D)

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Problem 6: During a particular reaction 10% of the reactant decomposes in one hour, 20% in two hours, 30% in three hours and so on. The unit of the rate constant is (A) Hour<sup>-1</sup> (B) L mol<sup>-1</sup> hour<sup>-1</sup> (C) mol L<sup>-1</sup> hour<sup>-1</sup> (D) mol hour<sup>-1</sup>

**Solution:** This reaction is a zero order reaction ∴ (C)