

## Chapter 12: Chemical Kinetics

### Review Questions

1. In the reaction  $3\text{H}_2 + \text{N}_2 \rightarrow 2\text{NH}_3$ , how does the rate of disappearance of hydrogen compare to the rate of disappearance of nitrogen? How does the rate of appearance of  $\text{NH}_3$  compare to the rate of disappearance of nitrogen?

#### Solution

This is determined by the coefficients of the balanced chemical equation. For every mole of  $\text{N}_2$  that reacts, 3 mol of  $\text{H}_2$  will react. Thus, the rate of disappearance of hydrogen is three times the rate of disappearance of nitrogen. Similarly, the rate of disappearance of  $\text{N}_2$  is half the rate of appearance of  $\text{NH}_3$ , or  $\text{NH}_3$  appears twice as fast as  $\text{N}_2$  disappears.

2. For the reaction  $m\text{M} \rightarrow n\text{N}$ , the rate law is given by  $\text{rate} = k[\text{M}]^x$ . What is the significance of  $k$  and  $x$ ?

#### Solution

In the given rate law,  $k$  is a constant called rate constant and  $x$  represents the order of reaction. Depending upon whether  $x$  is equal to 0, 1, 2, or 3, the reactions are said to be of zero order, first order, second order, and third order, respectively.

3. Express the rates of the following reactions in terms of disappearance of reactants and formation of products:



#### Solution

$$(a) -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{NO}_2]}{dt}$$

$$(b) -\frac{d[\text{H}_2]}{dt} = -\frac{d[\text{I}_2]}{dt} = \frac{1}{2} \frac{d[\text{HI}]}{dt}$$

4. Write Arrhenius equation and explain the significance of all terms in it.

#### Solution

The Arrhenius equation is  $k = Ae^{-E_a/RT}$

where  $k$  is the rate constant,  $A$  is pre-exponential factor,  $E_a$  is the activation energy,  $R$  is the gas constant, and  $T$  is the temperature.

5. What are the important features of collision theory?

#### Solution

(a) It is based on kinetic theory of gases.

(b) Here reactant molecules are assumed to be hard spheres.

(c) The reactions between the reactant molecules occur because of collisions between the reacting molecules.

(d) The number of collisions which results in the formation of product molecules is called effective collisions.

(e) For a reaction to occur, proper orientation as well as steric hindrance is also important.

(f) Rate of reaction =  $PZ_{AB}e^{-E_a/RT}$  where  $P$  is the orientation factor and  $Z_{AB}$  corresponds to collision frequency.

6. Explain why a second-order reaction behaves as a first-order reaction when one of the reactants is present in large excess.

**Solution**

Because in that case rate of a reaction is determined by the concentration of one of the reactants only. Such reactions are called pseudounimolecular reactions.

7. The boiling point of water depends on atmospheric pressure. As a result, water boils at a lower temperature at 3048 m in the mountains than at sea level. Use the Arrhenius equation to describe why it takes longer to cook a hard-boiled egg at the top of a mountain than it does at sea level.

**Solution**

This is because the external pressure is less at the top of a mountain, so the water will boil at a lower temperature than at sea level. Therefore, the egg will not be as hot in the boiling water. Cooking the egg to make it hard-boiled involves a chemical reaction. According to the Arrhenius equation, the rate constant for this reaction will be smaller at the lower temperature of the boiling water at the top of the mountain.

8. Why is collision theory applicable to simple gaseous molecular reaction?

**Solution**

As in the case of complex reactions, the assumptions made by the collision theory do not hold true and also significant deviations are observed in the case of complex molecules.

9. Why is the potential energy of the molecules shown lowered in the energy profile diagram of reactants and products?

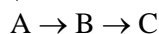
**Solution**

This is because energy is released when reactants are converted into products and also the final heat of reactant depends on the nature of reactants and products.

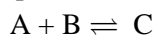
10. Differentiate between consecutive, reversible and parallel reactions by giving examples.

**Solution**

Consecutive reactions: such reactions in which equilibrium constant can be expressed as ratio between two rate coefficients. For example,

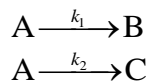


Reversible reactions: These reactions are represented as



In such type of reactions, the net reaction can go in either direction depending upon the concentration of reactants and products.

Parallel reactions: In this type of reactions, a reactant may participate in several reactions. For example,



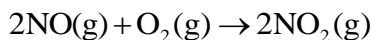
11. Explain the following terms: (a) activated complex; (b) temperature coefficient of a reaction.

**Solution**

(a) It is the intermediate formed when reactant molecules are getting converted into products. It is highly unstable and immediately dissociates to give products.

(b) Temperature coefficient = rate constant at  $t + 10^\circ\text{C}$  / rate constant at  $t^\circ\text{C}$

12. When there are only trace quantities of NO in the atmosphere, it does not react with O<sub>2</sub> to form NO<sub>2</sub>. As the concentration of NO in the atmosphere builds up, however, it reaches a point at which this reaction can and does occur.



The experimentally determined rate law for the reaction is

$$\text{Rate} = k[\text{NO}]^2[\text{O}_2]$$

Classify the order of this reaction.

**Solution**

The reaction is of first-order in  $\text{O}_2$  and second-order in  $\text{NO}$ . The overall reaction is third-order.

**13.** For a second-order reaction with two different reactants, half-life period cannot be determined. Why?

**Solution**

This is because  $t_{1/2} \propto \frac{1}{[\text{A}]^{n-1}}$ , means it depends on the concentration of one of the reactants only.

**14.** According to the Arrhenius relationship between  $E_a$  and  $k$ , is  $k$  large or small when  $E_a$  is large? What does a small  $k$  mean concerning how fast the reaction proceeds? Use this relationship to suggest how catalysts speed up reactions.

**Solution**

The  $E_a$  term is a negative in the Arrhenius equation. Therefore, if  $E_a$  is large,  $k$  will be small. A small  $k$  indicates a slow reaction rate. The use of catalyst provides a different reaction mechanism for which activation energy ( $E_a$ ) is lower, therefore, the value of  $k$  will increase, leading to a faster reaction rate.

**15.** Consider a reaction that was carried out twice, once with an initial concentration of 1 M and then with an initial concentration of 2 M. How will the half-life for the second trial compare to the half-life of the first trial for zero-order and first-order reactions?

**Solution**

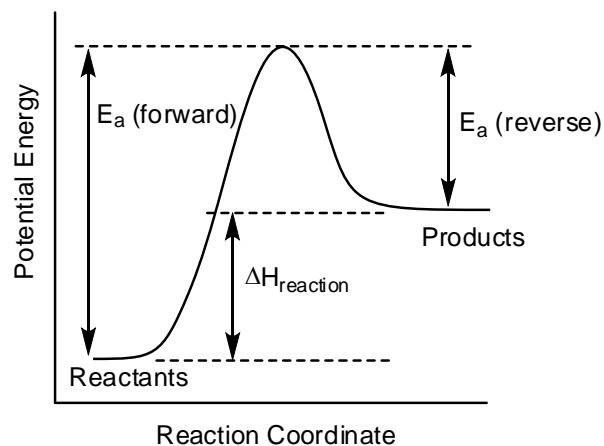
For a zero-order reaction, the half-life for the second reaction will be twice as large as for the first trial. For a first-order reaction, the half-life will not change. It is independent of concentration.

**16.** (a) Draw the potential energy diagram for an endothermic reaction. Indicate on the diagram the activation energy for both the forward and reverse reactions. Also indicate the heat of reaction.

(b) Explain, in terms of the law of conservation of energy, why an endothermic reaction leads to a cooling of the reaction mixture (provided heat cannot enter from outside the system).

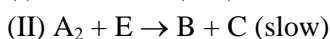
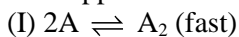
**Solution**

(a) The potential energy diagram for an endothermic reaction is shown below:



(b) The energy that is necessary for the reaction is obtained at the expense of the total kinetic energy of the system. Thus, kinetic energy is lost, being converted into potential energy, and the temperature goes down.

17. Suppose a reaction occurs with the mechanism



In which the first step is a very rapid reversible reaction that can be considered to be essentially an equilibrium (forward and reverse reactions occurring at the same rate) and the second is a slow step.

(a) Write the rate law for the forward reaction in step (I).

(b) Write the rate law for the reverse reaction in step (II).

(c) Write the rate law for the rate-determining step.

(d) What is the chemical equation for the net reaction that occurs in this chemical change?

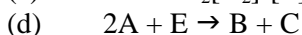
(e) Use the results of parts (a) and (b) to rewrite the rate law of the rate-determining step in terms of the concentrations of the reactants in the overall balanced equation for the reaction.

**Solution**

(a)  $\text{Rate} = k_1[A]^2$

(b)  $\text{Rate} = k_{-1}[A_2]^1$

(c)  $\text{Rate} = k_2[A_2]^1[E]^1$



(e) The rates for the forward and reverse directions of step one are set equal to each other in order to arrive at an expression for the intermediate  $[A_2]$  in terms of the reactant  $[A]$ :

$$k_1[A]^2 = k_{-1}[A_2]$$

$$[A_2] = \frac{k_1}{k_{-1}}[A]^2$$

This is substituted into the rate law for question (c) above, giving a rate expression that is

written using only observable reactants:  $\text{Rate} = k_2 \frac{k_1}{k_{-1}} [A]^2 [E]^1$

18. Explain how a small rise in temperature appreciably increases the rate of reaction.

### Solution

Explained by Arrhenius equation  $k = Ae^{-E_a/RT}$ , on increasing the temperature,  $E_a$  decreases and  $k$  increase.

### Numerical Problems

1. In an experiment, the concentration of a reactant was tripled. The rate increased by a factor of 27. What is the order of the reaction with respect to the reactant?

### Solution

Suppose the reaction is  $A + B \rightarrow C + D$

$$\text{Rate}_1 = k[A]^n[B]^m \quad (1)$$

When [A] is tripled, the rate becomes 27 times. Therefore,

$$27\text{Rate}_1 = k[3A]^n[B]^m \quad (2)$$

Dividing Eq. (2) by Eq. (1), we get

$$\frac{27\text{Rate}_1}{\text{Rate}_1} = \frac{k[3A]^n[B]^m}{k[A]^n[B]^m} \text{ or } 27 = (3)^n \text{ or } n = 3$$

Thus, the order of the reaction with respect to the reactant is 3.

2. The following data were collected for the reaction  $M + N \rightarrow P + Q$ .

Initial concentrations (mol L <sup>-1</sup> )		Initial rate of reaction (mol L <sup>-1</sup> s <sup>-1</sup> )
[M]	[N]	
0.010	0.010	$2.5 \times 10^{-3}$
0.020	0.010	$5.0 \times 10^{-3}$
0.020	0.030	$4.5 \times 10^{-2}$

Use data to obtain the rate law and the rate constant for the reaction.

### Solution

Suppose order with respect to M is  $\alpha$  and with respect to N is  $\beta$ , then the rate law will be

$$\text{Rate} = k[M]^\alpha [N]^\beta$$

From the table, we have

$$(\text{Rate})_1 = 2.5 \times 10^{-3} = (0.010)^\alpha (0.010)^\beta$$

$$(\text{Rate})_2 = 5.0 \times 10^{-3} = (0.020)^\alpha (0.010)^\beta$$

$$(\text{Rate})_3 = 4.5 \times 10^{-2} = (0.020)^\alpha (0.030)^\beta$$

Dividing  $(\text{Rate})_2$  by  $(\text{Rate})_1$ , we have

$$\frac{(\text{Rate})_2}{(\text{Rate})_1} = \frac{5.0 \times 10^{-3}}{2.5 \times 10^{-3}} = \frac{(0.020)^\alpha (0.010)^\beta}{(0.010)^\alpha (0.010)^\beta}$$

$$\text{or } (2)^1 = (2)^\alpha \text{ or } \alpha = 1$$

Dividing  $(\text{Rate})_3$  by  $(\text{Rate})_1$ , we have

$$\frac{(\text{Rate})_3}{(\text{Rate})_2} = \frac{4.5 \times 10^{-2}}{5.0 \times 10^{-3}} = \frac{(0.020)^\alpha (0.030)^\beta}{(0.020)^\alpha (0.010)^\beta}$$

$$\text{or } (3)^2 = (3)^\beta \text{ or } \beta = 2$$

Hence, the rate law expression is

$$\text{Rate} = k[M][N]^2$$

The rate constant can be calculated from the data given above.

$$k = \frac{\text{Rate}}{[\text{M}][\text{N}]^2} = \frac{2.5 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}}{(0.010 \text{ mol L}^{-1})(0.010 \text{ mol L}^{-1})^2} = 2.5 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$$

3. The reaction of sucrose with water was found to be first-order with respect to sucrose. The rate constant under the conditions of the experiments was  $6.17 \times 10^{-4} \text{ s}^{-1}$ . Calculate the value of  $t_{1/2}$  for this reaction in minutes. How many minutes would it take for three-quarters of the sucrose to react? (Hint: What fraction of the sucrose remains?)

**Solution**

For a first-order reaction:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{6.17 \times 10^{-4} \text{ s}^{-1}} = 1.12 \times 10^3 \text{ s} = 1.12 \times 10^3 \text{ s} \times \frac{1 \text{ min}}{60 \text{ s}} = 18.7 \text{ min}$$

Two half-lives will have passed if there is to be only one quarter of the original amount of material remaining. This corresponds to

$$18.7 \text{ min per half-life} \times 2 \text{ half-lives} = 37.4 \text{ min}$$

4. The  $^{14}\text{C}$  content of an ancient piece of wood was found to be one-eighth of that in living trees. How many years old is this piece of wood ( $t_{1/2} = 5730$  years for  $^{14}\text{C}$ )? (Hint: Recall the relationship between the integrated rate equation and half-life.)

**Solution**

For a first-order process,

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

$$k = \frac{0.693}{5730} = 1.21 \times 10^{-4} \text{ y}^{-1}$$

Also,  $\ln \frac{[A]_0}{[A]_t} = kt$ . Therefore,

$$t = \frac{1}{k} \ln \frac{[A]_0}{[A]_t} = \frac{1}{1.21 \times 10^{-4} \text{ y}^{-1}} \ln \frac{8}{1} = 1.72 \times 10^4 \text{ y}$$

5. The rate law for the reaction  $\text{Ester} + \text{H}^+ \rightarrow \text{Acid} + \text{Alcohol}$  is  $\frac{dx}{dt} = k[\text{ester}]$ .

What would be the effect on rate if (a) concentration of ester is doubled and (b) concentration of  $\text{H}^+$  ion is doubled?

**Solution .**

- (a) As rate is directly proportional to the concentration of ester, so on doubling the concentration of ester rate also gets doubled.
- (b) As rate is independent of the concentration of  $[\text{H}^+]$  ions, so on doubling the concentration of  $[\text{H}^+]$  ions, there will be no effect on rate.

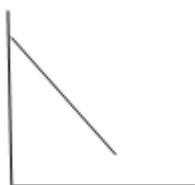
6. For the reaction  $\text{A} \rightarrow \text{B}$ , the rate law expression is  $-\frac{d[\text{A}]}{dt} = k[\text{A}]^{1/2}$ . If initial concentration of A is  $[\text{A}]_0$ , calculate (a) integrated form of the rate expression, (b) nature of plot of  $[\text{A}]^{1/2}$  versus time and (c) half-life period.

**Solution**

(a)  $-d[A]/[A]^{1/2} = kdt$ . On integrating we get  

$$-2[A]^{1/2} = kt + C$$

(b)



$[A]^{1/2}$   $m = -k/2$  and intercept =  $[A]_0$

(c)  $t_{1/2} = \frac{\sqrt{2}(\sqrt{2}-1)}{k} [A]_0^{1/2}$

7. For a homogeneous gaseous phase reaction:  $2A \rightarrow 3B + C$ , the initial pressure of reactant was  $p^\circ$  while pressure at time  $t$  was  $p$ . Find the pressure after time  $2t$ . Assume first-order reaction.

**Solution**

8. The vapor phase decomposition of ethylene oxide into methane and CO at  $414.5^\circ\text{C}$ . Calculate  $k$  for first-order reaction:

Time (min)	0	5	7	12	18
Pressure (mm Hg)	116.51	122.72	125.72	133.23	141.37

**Solution**

The reaction involved is  $\text{C}_2\text{H}_4\text{O} \rightleftharpoons \text{CH}_4 + \text{CO}$

$$k = \frac{2.303}{t} \log \frac{p^\circ}{2p^\circ - p_t}$$

Given that  $p^\circ = 116.51$  mm Hg. When  $t = 5$ ,  $p_t = 122.72$  mm Hg, so

$$k_1 = \frac{2.303}{5} \log \frac{116.51}{2(116.51) - 122.72} = 1.08 \times 10^{-2} \text{ min}^{-1}$$

When  $t = 7$ ,  $p_t = 125.72$  mm Hg, so

$$k_2 = \frac{2.303}{7} \log \frac{116.51}{2(116.51) - 125.72} = 1.17 \times 10^{-2} \text{ min}^{-1}$$

When  $t = 12$ ,  $p_t = 133.23$  mm Hg, so

$$k_3 = \frac{2.303}{12} \log \frac{116.51}{2(116.51) - 133.23} = 1.29 \times 10^{-2} \text{ min}^{-1}$$

When  $t = 18$ ,  $p_t = 141.37$  mm Hg, so

$$k_4 = \frac{2.303}{18} \log \frac{116.51}{2(116.51) - 141.37} = 1.33 \times 10^{-2} \text{ min}^{-1}$$

Average  $k = 1.21 \times 10^{-2} \text{ min}^{-1}$

9. Decomposition of diazobenzene chloride was followed at constant temperature by measuring volume of N<sub>2</sub> evolved at definite intervals of time. Calculate order and rate constant.

Time (min)	0	2.0	5.5	7.0	∞
Volume of N <sub>2</sub> (mL)	0	10	25	35	163

**Solution**

The rate constant is given by

$$k = \frac{2.303}{t} \log \frac{V_{\infty} - V_0}{V_{\infty} - V_t}$$

Given that  $V_0 = 0$  mL and  $V_{\infty} = 163$  mL. Thus,

$$k_1 = \frac{2.303}{2} \log \frac{163 - 0}{163 - 10} = 3.15 \times 10^{-2} \text{ min}^{-1}$$

$$k_2 = \frac{2.303}{5.5} \log \frac{163 - 0}{163 - 25} = 3.01 \times 10^{-2} \text{ min}^{-1}$$

$$k_3 = \frac{2.303}{7.0} \log \frac{163 - 0}{163 - 35} = 3.41 \times 10^{-2} \text{ min}^{-1}$$

Average  $k = 3.2 \times 10^{-2} \text{ min}^{-1}$ .

10. A freshly cut piece of wood gives 16100 counts of  $\beta$ -ray emission per minute per kg and an old wooden bowl gives 13200 counts per minute per kg. Calculate the age of the wooden bowl. The half-life period of <sup>14</sup>C is 5568 years.

**Solution**

Given that  $t_{1/2} = 5568$  years, so  $k_1 = \frac{0.693}{5568} = 0.0001245 \text{ years}^{-1}$

Hence,  $t = \frac{2.303}{0.0001245} \log \frac{16100}{13200} = 1597.4 \text{ years}^{-1}$

11. Two reactions of same order have equal exponential factors but their activation energy differ by 24.9 kJ mol<sup>-1</sup>. Calculate the ratio between the rate constants of these reactions at 27°C. ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ )

**Solution**

We have  $\log k_1 = \log A - \frac{E_a}{RT}$

$$\log k_2 = \log A - \frac{(E_a + 24.9)}{RT}$$

Subtracting both the equations

$$\log \frac{k_2}{k_1} = \frac{24.9 \times 10^3}{RT} \Rightarrow \frac{k_2}{k_1} = 2.159 \times 10^4$$

12. In a second-order reaction, where the initial concentration of the reactants is the same, half of the reactants are consumed in 30 min. If the rate constant is  $3.6 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}$ , what is the initial concentration of the reactants?

**Solution**

Let the initial concentration of reactants be  $a$ .



In a second-order reaction, when both the reactants are taken in equal concentrations, the half-life period is given by

$$t_{1/2} = \frac{1}{ka}$$

Given that  $t_{1/2} = 30$  min and  $k = 3.6 \times 10^{-2} \text{ L mol}^{-1} \text{ min}^{-1}$ . Substituting values in the above equation, we get

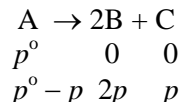
$$30 = \frac{1}{3.6 \times 10^{-2} \times a}$$

or 
$$a = \frac{1}{3.6 \times 10^{-2} \times 30} = \frac{1}{1.08} = 0.926 \text{ mol L}^{-1}$$

**13.** For the reaction,  $A(g) \rightarrow 2B(g) + C(g)$ , pressure of A at  $t = 0$  is 380 mm Hg and pressure of A after 30 s is 190 mm Hg. Calculate total pressure in mm of Hg after 60 s.

**Solution**

The reaction is



Given that  $p^\circ = 380$  mm Hg

Pressure of A after 30 s =  $p^\circ - p = 190$  mm Hg

This means  $p = p^\circ - 190 = 380 - 190 = 190$  mm Hg

$$k = \frac{2.303}{30} \log \frac{380}{190} = 0.0231 \text{ s}^{-1}$$

After 60 s,  $p_t = p^\circ - p + 2p + p = p^\circ + 2p$

Therefore,  $p_t = 190 + 2 \cdot 190 = 760$  mm Hg

**14.** In a reaction,  $aA \rightarrow \text{Products}$ , the rate is doubled when the concentration of A is increased 4 times. If 50% of the reaction occurs in 1414 s, how many seconds would it take for the completion of 75% reaction?

**Solution**

We know that  $t_{1/2} = 2^{n-1} - 1$  and  $t_{3/4} = 4^{n-1} - 1$

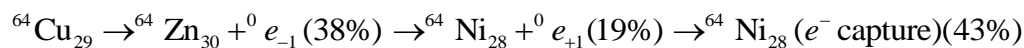
Given that rate is doubled when [A] is increased four times means the order of the reaction is half so putting  $n = 1/2$ , we get

$$\frac{1414}{t_{3/4}} = \frac{2^{1/2} - 1}{4^{1/2} - 1}$$

Solving we get  $t_{3/4} = 2412.97$  s.

**15.**  $^{64}\text{Cu}$  (half-life = 12.8 h) decays by  $\beta^-$ -emission (38%),  $\beta^+$ -emission (19%) and electron capture (43%). Write the decay products and calculate partial half-lives for each of the decay processes.

**Solution**



$$k_{av} = 0.693/12.8 = 5.41 \times 10^{-2} = k_1 + k_2 + k_3$$

Also,  $k_1/k_2 = 38/19$  and  $k_1/k_3 = 38/43$

Solving we get  $k_1 = 2.056 \times 10^{-2} \text{ h}^{-1}$ ,  $k_2 = 1.028 \times 10^{-2} \text{ h}^{-1}$  and  $k_3 = 2.327 \times 10^{-2} \text{ h}^{-1}$   
Therefore,

$$\begin{aligned}t_{1/2}(\beta^- \text{-emission}) &= 0.693/k_1 = 33.70 \text{ h} \\t_{1/2}(\beta^+ \text{-emission}) &= 0.693/k_2 = 67.41 \text{ h} \\t_{1/2}(e^- \text{ capture}) &= 0.693/k_3 = 29.78 \text{ h}\end{aligned}$$

**16.** In a second-order reaction, the initial concentration of the reactant is  $0.2 \text{ mol L}^{-1}$ . The reaction was 40% complete in 20 min. Calculate (a) rate constant, (b) time required for 75% completion of reaction, and (c) half-life period.

**Solution**

In a second-order reaction, with one reactant, the integrated rate law equation is given by

$$k = \frac{1}{t} \left[ \frac{x}{a(a-x)} \right]$$

where  $a$  = initial concentration of reactant at time = 0;  $x$  = number of moles of reactant reacted at time =  $t$ ;  $a - x$  = concentration of reactant after time  $t$ .

Given that  $a = 0.2 \text{ mol L}^{-1}$ ,  $t = 20 \text{ min}$ . At 40% completion of reaction,

$$a - x = a - \frac{40}{100}a = 0.6a$$

$$\text{or } x = a - 0.6a = 0.4a$$

(a) The rate constant may be obtained by substituting values in the above equation

$$k = \frac{1}{20} \left[ \frac{0.4a}{a(0.6a)} \right] = \frac{1}{20} \left[ \frac{2}{3 \times 0.2} \right] = 0.1667 \text{ L mol}^{-1} \text{ min}^{-1}$$

(b) At 75% completion of reaction,

$$a - x = a - \frac{75}{100}a = 0.25a \text{ or } x = 0.75a$$

Substituting values in integrated rate law equation, we get

$$\begin{aligned}k &= \frac{1}{t} \left[ \frac{x}{a(a-x)} \right] \\t &= \frac{1}{0.1667} \left[ \frac{0.75a}{a(0.25a)} \right] = \frac{1}{0.1667} \times \frac{3}{a} = 6 \times \frac{3}{0.2} = 90 \text{ min}\end{aligned}$$

(c) Half-life period for second-order reaction is given by

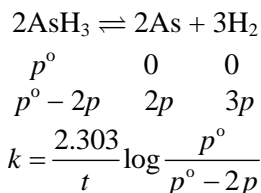
$$t_{1/2} = \frac{1}{k \times a}$$

Substituting values in the equation, we get

$$t_{1/2} = \frac{1}{0.1667 \times 0.2} = 30 \text{ min}$$

**17.** Arsine decomposes on heating to give As and  $\text{H}_2$ . The decomposition studied at constant volume and temperature gives the following data. Calculate velocity constant, assuming first-order reaction.

<b>Time (h)</b>	0	5.5	6.5	8
<b>Pressure (atm)</b>	0.9654	1.06	1.1	1.076

**Solution**

Given that  $p^\circ = 0.9654$  atm. When  $t = 5.5$ ,  $p_t = 1.06$  atm, so

$$k_1 = \frac{2.303}{5.5} \log \frac{0.9654}{0.9654 - 2(1.06)} = 3.25 \times 10^{-2} \text{ h}^{-1}$$

When  $t = 6.5$ ,  $p_t = 1.1$  atm, so

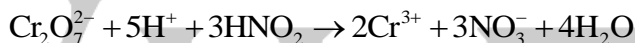
$$k_2 = \frac{2.303}{6.5} \log \frac{0.9654}{0.9654 - 2(1.1)} = 3.78 \times 10^{-2} \text{ h}^{-1}$$

When  $t = 8$ ,  $p_t = 1.076$  atm, so

$$k_3 = \frac{2.303}{8} \log \frac{0.9654}{0.9654 - 2(1.076)} = 2.75 \times 10^{-2} \text{ h}^{-1}$$

Average  $k = 3.2 \times 10^{-2} \text{ h}^{-1}$ .

18. According to the reaction



The rate of disappearance of  $\text{Cr}_2\text{O}_7^{2-}$  is found to be  $2.4 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . Find the rate of appearance of  $\text{Cr}^{3+}$  during given time interval

**Solution**

From the reaction,

$$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = \frac{1}{2} \frac{d[\text{Cr}^{3+}]}{dt} \Rightarrow \frac{d[\text{Cr}^{3+}]}{dt} = 2 \times 2.4 \times 10^{-4} = 4.8 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$$

19. The half-life of  $\text{Pb}^{12}$  is 10.6 h. It undergoes decay to its daughter (unstable) element  $\text{Bi}^{212}$  of half-life 60.5 min. Calculate the time at which daughter element will have maximum activity.

**Solution**

$$\lambda_{\text{Pb}} = \frac{0.693}{10.6 \times 60} = 1.0896 \times 10^{-3} \text{ min}^{-1}$$

$$\lambda_{\text{Bi}} = \frac{0.693}{60.5} = 11.45 \times 10^{-3} \text{ min}^{-1}$$

$$\begin{aligned}
 t_{\text{max}} &= \frac{2.303}{\lambda_{\text{Bi}} - \lambda_{\text{Pb}}} - \log \frac{\lambda_{\text{Bi}}}{\lambda_{\text{Pb}}} \\
 &= \frac{2.303}{(11.45 \times 10^{-3} - 1.0896 \times 10^{-3})} \times \log \frac{11.45 \times 10^{-3}}{1.0896 \times 10^{-3}} \\
 &= 227.1 \text{ min}
 \end{aligned}$$

20. Ten gram atoms of an  $\alpha$ -active radio isotope are disintegrating in a sealed container. In 1 h, the helium gas collected at STP is  $11.2 \text{ cm}^3$ . Calculate the half-life of the radio-isotope.

**Solution**

Amount of radioactive isotope = 10 g atom

$R_0$  (initial amount) =  $10 \times 6.023 \times 10^{23} = 6.023 \times 10^{24}$  atoms

$22400 \text{ cm}^3$  of He contain =  $6.023 \times 10^{23}$  atoms

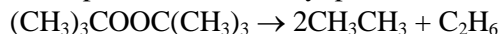
$11.2 \text{ cm}^3$  will contain He atoms =  $\frac{6.023 \times 10^{23}}{22400} \times 11.2 = 3.01 \times 10^{20}$

$R = 6.023 \times 10^{24} - 3.01 \times 10^{20} = 6.0227 \times 10^{24}$

$$k = \frac{2.303}{1} \log \frac{6.023 \times 10^{23}}{6.0227 \times 10^{24}} = 4.982 \times 10^{-5} \text{ h}^{-1}$$

$$t_{1/2} = \frac{0.693}{4.982 \times 10^{-5} \times 24 \times 365} = 1.58 \text{ years}$$

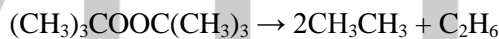
21. At  $155^\circ\text{C}$  the gas phase decomposition of di-*t*-butyl peroxide is a first-order reaction.



The following data were obtained during experiments. Calculate the rate constant for the reaction.

Time (min)	0	12	21
Total pressure (Torr)	170	240	280

**Solution**



$$\begin{array}{ccc} p^\circ & 0 & 0 \\ p^\circ - p & 2p & p \end{array}$$

Now,  $a = p^\circ$

$p_t = p^\circ - p + 2p + p = p^\circ + 2p$

$p = (p_t - p^\circ)/2$

and  $a - x = p^\circ - (p_t - p^\circ/2) = (3p^\circ - p_t)/2$

Therefore,  $k_1 = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{2p^\circ}{3p^\circ - p_t}$

At  $t_1 = 12 \text{ min}$ ,  $p_t = 240 \text{ Torr}$  and  $p^\circ = 170 \text{ Torr}$

$$k_1 = \frac{2.303}{12} \log \frac{2 \times 170}{3 \times 170 - 240} = 0.0185 \text{ min}^{-1}$$

At  $t_2 = 21 \text{ min}$ ,  $p_t = 280 \text{ Torr}$  and  $p^\circ = 170 \text{ Torr}$

$$k_2 = \frac{2.303}{21} \log \frac{2 \times 170}{3 \times 170 - 280} = 0.0186 \text{ min}^{-1}$$

Average  $k = (k_1 + k_2)/2 = 0.0185 \text{ min}^{-1}$ .

22. A wooden door lintel from an excavated site in Mexico would be expected to have what ratio of carbon-14 to carbon-12 atoms if the lintel is  $9.0 \times 10^3$  years old?

**Solution**

From the equation  $\ln \frac{r_0}{r_t} = kt$ , we have

$$\ln\left(\frac{1.2 \times 10^{-12}}{r_t}\right) = (1.21 \times 10^{-4} \text{ y}^{-1})(9.0 \times 10^3 \text{ y})$$

$$\left(\frac{1.2 \times 10^{-12}}{r_t}\right) = \exp[(1.21 \times 10^{-4} \text{ y}^{-1})(9.0 \times 10^3 \text{ y})]$$

$$\left(\frac{1.2 \times 10^{-12}}{2.97}\right) = r_t = 4.0 \times 10^{-13}$$

**23.** Cooking an egg involves the denaturation of a protein called albumen. The time required to achieve a particular degree of denaturation is inversely proportional to the rate constant for the process. This reaction has a high activation energy,  $E_a = 418 \text{ kJ mol}^{-1}$ . Calculate how long it would take to cook a traditional 3-min egg on top of Mt. McKinley in Alaska on a day when the atmospheric pressure there is 355 Torr.

**Solution**

Taking note of the inverse relationship between the reaction rate constant,  $k$ , and the cooking time,  $t$ , we set up Eq. (13.12) in the following manner:

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

$$\ln \left[ \frac{1/t_2}{1/t_1} \right] = \frac{-E_a}{R} \left[ \frac{1}{T_2} - \frac{1}{T_1} \right]$$

We are provided with some subtle but key information about the physical conditions. For instance, the 3-min traditional egg provides a cooking time of 3 min at the normal boiling point of water,  $100^\circ\text{C}$  or  $373 \text{ K}$ . We are also given the atmospheric pressure (355 Torr) on Mt. McKinley where the cooking is to be carried out at a lower temperature. At 355 Torr,  $\text{H}_2\text{O}$  will boil when its vapor pressure equals 355 Torr. The temperature corresponding to this pressure is  $80^\circ\text{C}$  or  $323 \text{ K}$  (see Appendix B “Vapor Pressure of Water at Various Temperatures”). Thus, with the given value of the activation energy, that is,  $E_a = 418 \text{ kJ mol}^{-1}$ , we can proceed with the calculation to obtain  $t_2$ :

$$\ln \left[ \frac{1/t_2}{1/3 \text{ min}} \right] = \frac{-418 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J mol K}} \left[ \frac{1}{353 \text{ K}} - \frac{1}{373 \text{ K}} \right]$$

$$\ln \left[ \frac{3 \text{ min}}{t_2} \right] = -7.64$$

$$\frac{3 \text{ min}}{t_2} = \exp(-7.64)$$

$$t_2 = 3 \text{ min} / \exp(-7.64) = 6.2 \times 10^3 \text{ min} = 104 \text{ h}$$

Thus, to get the same degree of protein denaturation, it would take roughly four days to cook the egg at an atmospheric pressure of 355 Torr as opposed to cooking the egg at normal atmospheric pressure.

**24.** The rate of reaction is doubled when the temperature is changed from 298 K to 308 K. Calculate the energy of activation of the reaction.

**Solution**

The Arrhenius equation can be used to calculate energy of activation, if the rate constant at two different temperatures is known:

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

Given that  $T_1 = 298$  K;  $T_2 = 308$  K;  $k_2 = 2k_1$ ;  $R = 8.314$  J K<sup>-1</sup> mol<sup>-1</sup>. Substituting these in the above equation, we get

$$\begin{aligned} E_a &= 2.303 \times 8.314 \times \left( \frac{298 \times 308}{308 - 298} \right) \log \left( \frac{2k_1}{1k_1} \right) \\ &= 2.303 \times 8.314 \times \left( \frac{91784}{10} \right) \log 2 = 2.303 \times 8.314 \times 9178.4 \times 0.301 \\ &= 52897.78 \text{ J mol}^{-1} = 52.89 \text{ kJ mol}^{-1} \end{aligned}$$

**Additional Objective Questions**

**Single Correct Choice Type**

**1.** For the chemical reaction  $X \rightarrow Y$ , it is found that the rate of reaction increases by 2.25 times when the concentration of X is increased by 1.5 times, what is the order with respect to X?

- (A) zero      (B) one      (C) two      (D) three

**Solution**

(C) As rate varies as  $(1.5 X)^2$  so the order of the reaction is 2.

**2.** A particular reaction increases by a factor of 2 when the temperature is increased from 27°C to 31°C. Hence, the activation energy of the reaction is

- (A) 12.9 kcal mol<sup>-1</sup>      (B) 0.14 kcal mol<sup>-1</sup>      (C) 1.1 kcal mol<sup>-1</sup>      (D) None of these

**Solution**

(A)  $E_a = 2.303R \left( \frac{T_1 T_2}{T_2 - T_1} \right) \log 2$

**3.** For a first-order reaction, the units of Arrhenius factor (A) will be

- (A) J K<sup>-1</sup> s<sup>-1</sup>      (B) s<sup>-1</sup>      (C) mol L<sup>-1</sup> s<sup>-1</sup>      (D) J K<sup>-1</sup> L<sup>-1</sup> s<sup>-1</sup>

**Solution**

(B)  $k = A e^{-E_a/RT} \Rightarrow A = \ln k + \frac{E_a}{RT} \Rightarrow \text{Units of } A = \text{s}^{-1} + \frac{\text{J mol}^{-1}}{\text{J K}^{-1} \text{mol}^{-1} \times \text{K}} = \text{s}^{-1}$

**4.** For an elementary reaction  $2A \xrightleftharpoons[k_2]{k_1} B$  the rate of disappearance of A is equal to

- (A)  $\frac{2k_1}{k_2}[A]^2$       (B)  $-2k_1[A]^2 + 2k_2[B]$       (C)  $2k_1[A]^2 - 2k_2[B]$       (D)  $(2k_1 - k_2)[A]$

**Solution**

(C) From the reactions, we have

Rate of disappearance of A is

$$-\frac{d[A]}{dt} = 2k_1[A]^2 \quad (1)$$

Rate of formation of A from the reverse reaction is

$$-\frac{d[B]}{dt} = +\frac{1}{2} \frac{d[A]}{dt} = k_2[B]$$

$$\Rightarrow \frac{d[A]}{dt} = 2k_2[B] \quad (2)$$

Therefore, Eq (1) – Eq (2) gives the net rate of disappearance of A

$$= 2k_1[A]^2 - k_2[B]$$

**5. Missing**

6. For the reaction,  $3A \rightarrow 2B$ , rate of reaction  $\frac{+d[B]}{dt}$  is equal to

- (A)  $-\frac{3}{2} \frac{d[A]}{dt}$       (B)  $-\frac{2}{3} \frac{d[A]}{dt}$       (C)  $-\frac{1}{3} \frac{d[A]}{dt}$       (D)  $+2 \frac{d[A]}{dt}$

**Solution**

(B) Rate =  $-\frac{1}{3} \frac{d[A]}{dt} = +\frac{1}{2} \frac{d[B]}{dt}$

7. The inversion of cane sugar is represented by  $C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$ . It is a reaction that is

- (A) second-order.      (B) pseudounimolecular.  
(C) unimolecular.      (D) none of these.

**Solution**

(B) Appears to be of higher order, but actually follows first-order kinetics.

8. For the reaction  $H_2(g) + I_2(g) \rightarrow 2HI(g)$ , the rate of disappearance of  $H_2$  is  $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$ . The rate of appearance of HI will be

- (A)  $1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$       (B)  $0.50 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$   
(C)  $2.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$       (D)  $4.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

**Solution**

(C)  $+\frac{1}{2} \frac{d[HI]}{dt} = -\frac{d[H_2]}{dt}$

Therefore,  $\frac{d[HI]}{dt} = 2 \times 1.0 \times 10^{-4} \text{ mol L}^{-1} \text{ s}^{-1}$

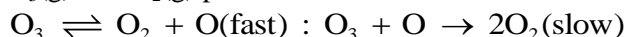
9. The units of rate constant and rate of a reaction are identical for

- (A) zero-order reaction.      (B) first-order reaction.  
(C) second-order reaction.      (D) third-order reaction.

**Solution**

(A) Rate =  $k[A]_0 = k$ .

10. The chemical reaction  $2\text{O}_3(\text{g}) \rightarrow 3\text{O}_2(\text{g})$  proceeds as follows.



The rate law expression is

(A) Rate =  $k[\text{O}_3]^2$

(B) Rate =  $k[\text{O}_3]^2[\text{O}_2]^{-1}$

(C) Rate =  $k[\text{O}_3][\text{O}_2]$

(D) None of these

**Solution**

(D) Rate is determined by the slowest step.

11. For a first-order reaction,

(A)  $t_{0.75} = 3t_{0.5}$

(B)  $t_{0.75} = 2t_{0.5}$

(C)  $t_{0.75} = 1.5t_{0.5}$

(D)  $t_{0.75} = 4t_{0.5}$

**Solution**

(B)

For a first order reaction

$$t_{0.5} = \frac{0.693}{k} \Rightarrow k = \frac{0.693}{t_{0.5}}$$

When the reaction is 75 % complete,

$$t_{0.75} = \frac{2.303}{k} \log \frac{[a]}{[a-x]} = \frac{2.303}{k} \log \frac{[a]}{[a-0.75a]}$$

$$t_{0.75} = \frac{2.303}{k} \log 4 = \frac{2.303}{0.693} \times t_{0.5} \times 0.603 = 2t_{0.5}$$

12. Graph between  $\log k$  and  $(1/T)$  is linear of slope  $S$  (magnitude). Hence,  $E_a$  is

(A)  $R \times S$

(B)  $S/R$

(C)  $R/S$

(D)  $2.303 RS$

**Solution**

(D) According to the Arrhenius equation  $\log k = \log A - \frac{E_a}{2.303RT}$

Given that  $\frac{E_a}{2.303R} = S \Rightarrow E_a = 2.303RS$ .

13. Reaction rates are determined by all of the following factors except the

(A) number of collisions between molecules.

(B) force of collisions between molecules.

(C) orientation of collisions between molecules.

(D) spontaneity of the reaction.

**Solution**

(D) Spontaneity is determined by Gibbs free energy (it should be negative).

14. For the reaction  $\text{A} + 2\text{B} \rightarrow \text{C}$ , rate is given by Rate =  $[\text{A}][\text{B}]^2$ , then the order of the reaction is

(A) 3

(B) 6

(C) 5

(D) 7

**Solution**

(A) Order =  $1 + 2 = 3$

15. For the reaction  $\text{H}_2(\text{g}) + \text{Br}_2(\text{g}) \rightarrow 2\text{HBr}(\text{g})$ , the experimental data suggests Rate =  $k[\text{H}_2][\text{Br}_2]^{1/2}$ . The molecularity and order of reaction for the reaction is, respectively,

(A) 2 and 2

(B) 2 and 3/2

(C) 3/2 and 2

(D) 3/2 and 3/2



**Solution**

(B) Order =  $1 + 1/2 = 3/2$  and molecularity = 2.

16. If the rate of the reaction is equal to the rate constant, the order of the reaction is

- (A) 1 (B) 2 (C) 3 (D) 0

**Solution**

(D) Rate =  $k[A]_0$ .

17. The one which is unimolecular reaction is

- (B)  $2\text{HI} \rightarrow \text{H}_2 + \text{I}_2$  (B)  $\text{N}_2\text{O}_5 \rightarrow \text{N}_2\text{O}_4 + \frac{1}{2} \text{O}_2$   
 (C)  $\text{H}_2 + \text{Cl}_2 \rightarrow 2\text{HCl}$  (D)  $\text{PCl}_3 + \text{Cl}_2 \rightarrow \text{PCl}_5$

**Solution**

(B) As it involves single reactant only.

18. The half-life of a first-order reaction is 10 min. If initial amount is  $0.08 \text{ mol L}^{-1}$  and concentration at some instant is  $0.01 \text{ mol L}^{-1}$ , then  $t$  is

- (A) 10 min. (B) 30 min. (C) 20 min. (D) 40 min.

**Solution**

$$(B) k = \frac{0.693}{t_{1/2}} = \frac{0.693}{10} = 0.0693$$

$$\text{So, } t = \frac{2.303}{0.0693} \log \frac{0.08}{0.01} = 30 \text{ min}$$

19. Suppose  $k$  for a zero-order reaction is  $2 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ . If the concentration of the reactant after 25 s is 0.5 M, the initial concentration must have been

- (a) 0.5 M (b) 1.25 M (C) 12.5 M (D) 1.0 M

**Solution**

$$(D) k = \frac{[\text{R}]_0 - [\text{R}]_t}{t} \Rightarrow 2 \times 10^{-2} = \frac{[\text{R}]_0 - 0.5}{25} \Rightarrow [\text{R}]_0 = 50 \times 10^{-2} + 0.5 = 1.0 \text{ M}$$

20. Velocity constant of a reaction at 290 K was found to be  $3.2 \times 10^{-3}$ . At 300 K, it will be

- (A)  $1.28 \times 10^{-2}$  (B)  $9.6 \times 10^{-3}$  (C)  $6.4 \times 10^{-3}$  (D)  $3.2 \times 10^{-4}$

**Solution**

(C) For a  $10^\circ$  rise in temperature, the velocity constant becomes double. So,  $k$  at 300 K =  $6.4 \times 10^{-3}$ .

21. In the titration between oxalic acid and acidified potassium permanganate, the manganous salt formed catalyzes the reaction. The manganous salt is

- (a) a promoter. (b) a positive catalyst. (c) an autocatalyst. (d) none of these.

**Solution**

(C) It self-catalyzes the reaction.

22. The temperature coefficients of two reactions are 2 and 3, respectively. Which would be correct for these reactions?

(A)  $E_{a_1} < E_{a_2}$

(B)  $E_{a_1} > E_{a_2}$

(C)  $E_{a_1} = E_{a_2}$

(D) Cannot be predicted.

**Solution**

(A) More is the temperature coefficient, more is the activation energy.

23. The formation of gas at the surface tungsten due to adsorption is the reaction of order

(A) 0.

(B) 1.

(C) 2.

(D) Insufficient data.

**Solution**

(A) It does not depend on the concentration of reactants.

24. The rate of a gaseous reaction is given by the expression  $k [A] [B]$ , if the volume of the reaction vessel is suddenly reduced to 1/4th of the initial volume, the reaction rate relating to the original rate will be

(A) 1/10

(B) 1/8

(C) 8

(D) 16

**Solution**

(D)  $(\text{Rate})_{\text{initial}} = k (n/V) \times (n/V)$

$(\text{Rate})_{\text{final}} = k (4n/V) \times (4n/V)$

So,

$$\frac{(\text{Rate})_{\text{initial}}}{(\text{Rate})_{\text{final}}} = \frac{16}{1}$$

25. For a reaction:  $2A + B \rightarrow \text{Products}$ , the active mass of B is kept constant and that of A is doubled. The rate of reaction will then

(A) increase two times.

(B) increase four times.

(C) decrease two times.

(D) decrease four times.

**Solution**

(B)  $\text{Rate} = k[A]^2$ .

26. Diazonium salt decomposes as  $C_6H_5N_2^+Cl^- \rightarrow C_6H_5Cl + N_2$ . At  $0^\circ C$ , the evolution of  $N_2$  becomes two times faster when the initial concentration of the salt is doubled. Therefore, it is

(A) a first-order reaction.

(B) a second-order reaction.

(C) independent of the initial concentration of the salt.

(D) a zero-order reaction.

**Solution**

(A)  $\text{Rate} = k[C_6H_5N_2^+Cl^-]$ .

27. Units of rate constant of first- and zero-order reactions in terms of molarity  $M$  unit are, respectively,

(A)  $s^{-1}, M s^{-1}$

(B)  $s^{-1} M$

(C)  $M s^{-1}, s^{-1}$

(D)  $M, s^{-1}$

**Solution**

(A)  $\text{Rate} = k[A]^1 \Rightarrow M s^{-1} = k[M]^1 \Rightarrow k = s^{-1}$

$\text{Rate} = k[A]^0 \Rightarrow M s^{-1} = k$

28. The rate of reaction is doubled for every  $10^\circ$  rise in temperature. The increase in reaction rate as a result of temperature rise from  $10^\circ$  to  $100^\circ$  is

- (A) 112                      (B) 512                      (C) 400                      (D) 614

**Solution**

(B) The increase would be  $2^9 = 512$  times.

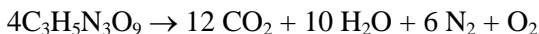
**29.** An example of autocatalytic reaction is

- (A) the decomposition of nitroglycerine.  
 (B) thermal decomposition of  $\text{KClO}_3$  and  $\text{MnO}_2$  mixture.  
 (C) break down of  $^{14}_6\text{C}$ .  
 (D) hydrogenation of vegetable oil using nickel catalyst.

**Solution**

An autocatalysed reaction is catalyzed by one of its products.

(A)



**30.** It takes 10 min for the decomposition of 50%  $\text{H}_2\text{O}_2$ . If the reaction is of first-order, the rate constant will be

- (A) 0.693                      (B) 0.00693                      (C) 0.0693                      (D) 6.93

**Solution**

(C)  $k = 0.693/10 = 0.0693 \text{ min}^{-1}$

**31.** Two substances A and B are present such that  $[\text{A}]_0 = 4[\text{B}]_0$  and half-life of A is 5 min and that of B is 15 min. If they start decaying at the same time following first-order kinetics, how much time later will the concentration of both of them would be same?

- (A) 15 min                      (B) 10 min                      (C) 5 min                      (D) 12 min

**Solution**

(A) Amount of A left in  $n_1$  halves =  $\left(\frac{1}{2}\right)^{n_1} [\text{A}]_0$

Amount of B left in  $n_2$  halves =  $\left(\frac{1}{2}\right)^{n_2} [\text{B}]_0$

At the end, according to the question

$$\frac{[\text{A}]_0}{2^{n_2}} = \frac{[\text{B}]_0}{2^{n_1}} \text{ or } \frac{4}{2^{n_2}} = \frac{1}{2^{n_1}}, [[\text{A}]_0 = 4[\text{B}]_0]$$

Therefore,  $\frac{2^{n_1}}{2^{n_2}} = 4$  or  $2^{n_1-n_2} = (2)^2 \Rightarrow n_1 - n_2 = 2$

Therefore,  $n_2 = (n_1 - 2)$  (1)

Also  $t = n_1 \times t_{1/2(A)}$ ;  $t = n_2 \times t_{1/2(B)}$

(Let concentration of both become equal after time  $t$ )

Therefore,  $\frac{n_1 \times t_{1/2(A)}}{n_2 \times t_{1/2(B)}} = 1$  or  $\frac{n_1 \times 5}{n_2 \times 15} = 1$  or  $\frac{n_1}{n_2} = 3$  (2)

For Eqs. (1) and (2),  $n_1 = 3, n_2 = 1 \Rightarrow t = 3 \times 5 = 15 \text{ min}$ .

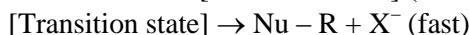
32.  $\text{H}_2\text{O}$  and oxygen atoms react in upper atmospheric level bimolecularly to form two OH radicals having heat of reaction 72 kJ at 400 K and energy of activation being  $77 \text{ kJ mol}^{-1}$ .  $E_a$  for bimolecular combination of two OH radicals to form  $\text{H}_2\text{O}$  and O atom is

- (A)  $-5 \text{ kJ}$                       (B)  $+5 \text{ kJ}$                       (C)  $-10 \text{ kJ}$                       (D)  $+10 \text{ kJ}$

**Solution**

$$(B) \Delta_r H = (E_a)_{\text{forward}} - (E_a)_{\text{reverse}} \Rightarrow (E_a)_{\text{reverse}} = (E_a)_{\text{forward}} - \Delta_r H = 77 - 72 = +5 \text{ kJ mol}^{-1}$$

33. The mechanism of the reaction:  $\text{Nu}^- + \text{R} - \text{X} \rightarrow \text{R} - \text{Nu} + \text{X}^-$  is



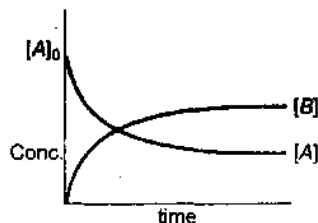
The rate of reaction can be increased by

- (A) increasing the concentration of  $\text{Nu}^-$  only.  
 (B) increasing the concentration of  $\text{R} - \text{X}$  only.  
 (C) Increasing the concentrations of both  $\text{Nu}^-$  and  $\text{R} - \text{X}$ .  
 (D) decreasing the concentrations of both  $\text{Nu}^-$  and  $\text{R} - \text{X}$ .

**Solution**

(C) Rate is determined the slowest step.

34. At the intersection point of two curves  $n\text{A} \rightarrow m\text{B}$  shown in the following figure, the concentration of B can be given by



- (A)  $\frac{m}{m+n}[\text{A}]_0$                       (B)  $\frac{m}{n}[\text{A}]_0$                       (C)  $\frac{m}{m-n}[\text{A}]_0$                       (D)  $\frac{n}{m+n}[\text{A}]_0$

**Solution**

(B)

35. Reaction  $\text{A} + 2\text{B} + \text{C} \rightarrow \text{Product}$ , follows the rate law:

$$-\frac{d[\text{C}]}{dt} = k[\text{A}]^2$$

The false statement regarding the above reaction is

- (A) on doubling the concentrations of B and C the rate of the reaction remains unaffected.  
 (B) on reducing the concentration of A to half, the rate becomes one-fourth.  
 (C) half-life period of the reaction depends upon the concentration of B.  
 (D) half-life period of the reaction is inversely proportional to the first power concentration of A.

**Solution**

(C)

36. The  $t_{1/2}$  of first-order reaction is 10 min. Starting with  $100 \text{ g L}^{-1}$  of the reactant, the amount remaining after one hour is

- (A) 25.0 g                      (B) 3.130 g                      (C) 12.50 g                      (D) 1.563 g

**Solution**

(D)  $k = 0.693/t_{1/2} = 0.693/10 = 0.0693$

Given that  $[R]_0 = 100 \text{ g}$  and  $[R] = ?$

Using the equation

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} \Rightarrow 0.0693 = \frac{2.303}{60} \log \frac{100}{[R]} \Rightarrow \frac{100}{[R]} = \text{antilog}(1.805) = 63.82 \Rightarrow [R] = 1.566 \text{ g L}^{-1}$$

37. The rate of the reaction:  $A + B + C \rightarrow \text{Products}$  is given by

$$\text{Rate} = \frac{d[A]}{dt} = k[A]^{1/2}[B]^{1/4}[C]^0$$

The order of reaction is

- (A) 1/2                      (B) 4                      (C) 3/4                      (D) 3/2

**Solution**

(C) Order =  $1/2 + 1/4 + 0 = 3/4$ .

38. If 8.0 g of a radioactive isotope has a half-life period of 10 h. The half-life period of 2.0 g of the same substance is

- (A) 2.5 h                      (B) 5.0 h                      (C) 10 h                      (D) 40 h

**Solution**

(C) For first order reaction,  $t_{1/2}$  is independent of the concentration of reactant.

39. For the reaction,  $2\text{NO} \rightarrow \text{N}_2 + \text{O}_2$ , the expression  $-\frac{1}{2} \frac{d[\text{NO}]}{dt}$  represents

- (A) the rate of formation of  $\text{NO}$ .                      (B) the average rate of the reaction.  
(C) the instantaneous rate of reaction.                      (D) all of these.

**Solution**

(C) Rate at a particular instant of time.

40. For the system  $\text{A}_2(\text{g}) + \text{B}_2(\text{g}) \rightleftharpoons 2\text{AB}(\text{g})$ ,  $\Delta H = -160 \text{ kJ}$ . If the activation energy for the forward step is  $100 \text{ kcal mol}^{-1}$ , what is the ratio of temperature at which the forward and backward reactions show the same percentage change of rate constant per degree rise of temperature? ( $1 \text{ cal} = 4.2 \text{ J}$ )

- (A)  $\sqrt{0.72}$                       (B)  $\sqrt{0.84}$                       (C)  $\sqrt{0.42}$                       (D)  $\sqrt{1}$

**Solution**

(B)  $E_{af} - E_{ab} = \Delta H$

or  $E_{ab} = E_{af} - \Delta H = 420 + 80 = 500 \text{ kJ mol}^{-1}$

Now, 
$$\frac{d(\ln k)}{dT} = \frac{E_{af}}{RT_f^2} \frac{d(\ln k)}{dT} = \frac{E_{ab}}{RT_b^2} \text{ (here } k_f = k_b = k)$$

$$\text{Therefore } \frac{E_{af}}{T_f^2} = \frac{E_{ab}}{T_b^2} \text{ or } \frac{T}{T_b} = \sqrt{\frac{E_{af}}{E_{ab}}} = \sqrt{\frac{420}{500}} = \sqrt{0.84}$$

41. For the reaction  $R-X + OH^- \rightarrow ROH + X^-$ . The rate is given as

$$\text{Rate} = 5.1 \times 10^{-5} [R-X] [OH^-] + 0.20 \times 10^{-5} [R-X]$$

What percentage of  $R-X$  reacted by  $S_N2$  mechanism when  $[OH^-] = 10^{-2} M$ ?

- (A) 96% (B) 3.9% (C) 80% (D) 20%

**Solution**

$$(D) \text{ Rate}(S_N2) = 5.0 \times 10^5 \times 10^{-2} [R-X] = 5.0 \times 10^{-7} [R-X]$$

$$\text{Rate}(S_N1) = 0.20 \times 10^{-5} [R-X]$$

$$\text{Percentage of } S_N2 = \frac{5 \times 10^{-7} [R-X] \times 100}{5 \times 10^{-7} [R-X] + 0.20 \times 10^{-5} [R-X]} = 20$$

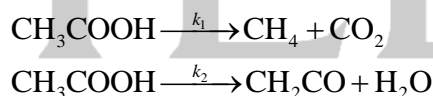
42. The plot of  $\log k$  vs.  $1/T$  is linear with a slope of

- (A)  $\frac{E_a}{R}$  (B)  $\frac{-E_a}{R}$  (C)  $\frac{E_a}{2.303R}$  (D)  $\frac{-E_a}{2.303R}$

**Solution**

(D) This is based on Arrhenius equation which is given as  $\log k = \log A - \frac{E_a}{2.303RT}$

43. The high temperature ( $\approx 1200 K$ ) decomposition of  $CH_3COOH(g)$  occurs as follows as per simultaneous first-order reactions.



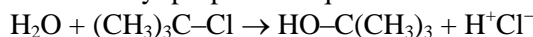
What would be the percentage of  $CH_4$  by mole in the product mixture (excluding  $CH_3COOH$ )?

- (A)  $\frac{50k_1}{(k_1 + k_2)}$  (B)  $\frac{100k_1}{(k_1 + k_2)}$  (C)  $\frac{200k_1}{(k_1 + k_2)}$  (D) It depends on time.

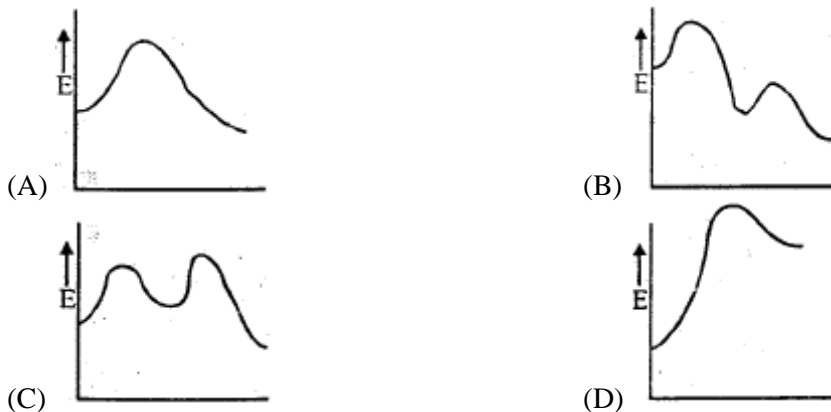
**Solution**

$$\begin{aligned} (A) \frac{n_{CH_4} + n_{CO_2}}{n_{CH_2CO} + n_{H_2O}} &= \frac{k_1}{k_2} \Rightarrow \frac{n_{CH_4} + n_{CO_2}}{n_{CH_4} + n_{CO_2} + n_{CH_2CO} + n_{H_2O}} = \frac{k_1}{k_1 + k_2} \\ \Rightarrow \frac{2n_{CH_4}}{n_{total}} &= \frac{k_1}{(k_1 + k_2)} \text{ OR } \frac{n_{CH_4}}{n_{total}} = \frac{k_1}{2(k_1 + k_2)} \Rightarrow \frac{n_{CH_4}}{n_{total}} \times 100 = \frac{50k_1}{(k_1 + k_2)} \end{aligned}$$

44. The solvolysis of 2-chloro-2-methyl propane in aqueous acetone:



has a rate equation  $\text{Rate} = k[(CH_3)_3C-Cl]$ . From this it may be inferred that the energy profile of the reaction leading from reactants to products is



**Solution**

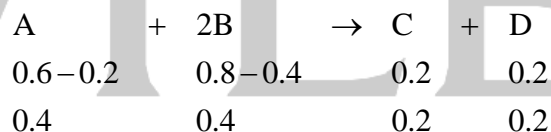
(B) Tertiary butyl halide undergoes solvolysis in a two-step mechanism. Since  $\text{Rate} = k[(\text{CH}_3)_3\text{C}-\text{Cl}]$  step 1 must be rate-determining, that is, it should have a higher activation energy.

**45.** The reaction  $\text{A}(\text{g}) + 2\text{B}(\text{g}) \rightarrow \text{C}(\text{g}) \rightarrow \text{D}(\text{g})$  is an elementary process. In an experiment, the initial partial pressure of A and B are  $p_{\text{A}} = 0.60$  and  $p_{\text{B}} = 0.80$  atm. When  $p_{\text{C}} = 0.2$  atm, the rate of the reaction relative to the initial rate is

- (A)  $1/48$                       (B)  $1/24$                       (C)  $9/16$                       (D)  $1/6$

**Solution**

(D)  $R_1 = k[\text{A}][\text{B}]^2 = k[0.6][0.80]^2$ . The reaction involved is



Comparing the rates, we get

$$\frac{R_2}{R_1} = \frac{(0.4)(0.4)^2}{(0.6)(0.8)^2} = \frac{1}{6}$$

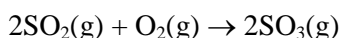
**46.** A zero-order reaction is the one

- (A) in which reactants do not react.  
 (B) in which one of the reactants is in large excess.  
 (C) whose rate does not change with time.  
 (D) whose rate increases with time.

**Solution**

(C)

**47.** The following reaction was carried out at 300 K.



How is the rate of formation of  $\text{SO}_3$  related to the rate of disappearance of  $\text{O}_2$ ?

- (A)  $-\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{SO}_3]}{\Delta t}$                       (B)  $-\frac{\Delta[\text{O}_2]}{\Delta t} = \frac{\Delta[\text{SO}_3]}{\Delta t}$

(C)  $-\frac{\Delta[\text{O}_2]}{\Delta t} = -\frac{1}{2} \frac{\Delta[\text{SO}_3]}{\Delta t}$  (D) None of these

**Solution**

(A) Rate of reaction  $= -\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{SO}_3]}{\Delta t}$

Therefore, rate of disappearance of  $\text{O}_2$  is related to rate of formation of  $\text{SO}_3$  as

$$-\frac{\Delta[\text{O}_2]}{\Delta t} = +\frac{1}{2} \frac{\Delta[\text{SO}_3]}{\Delta t}$$

**48.** According to collision theory of reaction

(A) every collision between reactant molecules leads to a chemical reaction.

(B) rate of reaction is proportional to the velocity of the molecules.

(C) rate of reaction is proportional to the average energy of the molecules.

(D) rate of reaction is proportional to the number of collision per second.

**Solution**

(C) According to Maxwell distribution curve.

**49.** The integrated rate equation is  $Rt = \log C_0 - \log C_t$ . The straight line graph is obtained by plotting

(A) time vs.  $\log C_t$ . (B)  $\frac{1}{\text{time}}$  vs.  $C_t$ . (C) time vs.  $C_t$ . (D)  $\frac{1}{\text{time}}$  vs.  $\frac{1}{C_t}$ .

**Solution**

(A) Comparing it with straight line equation  $y = mx + c$ , if we plot a graph between time vs.  $\log C_t$ , we get slope as  $R$  and intercept as  $\log C_0$ .

**50.** The decomposition of A into product has value of  $k$  as  $4.5 \times 10^3 \text{ s}^{-1}$  at  $10^\circ\text{C}$  and energy of activation  $60 \text{ kJ mol}^{-1}$ . At what temperature, would  $k$  be  $1.5 \times 10^4 \text{ s}^{-1}$ ?

(A)  $12^\circ\text{C}$

(B)  $24^\circ\text{C}$

(C)  $48^\circ\text{C}$

(D)  $36^\circ\text{C}$

**Solution**

(B) Given that  $k_{10} = k_{283} = 4.5 \times 10^3 \text{ s}^{-1}$ ,  $k_T = 1.5 \times 10^4 \text{ s}^{-1}$ ,  $T = ?$ . Also  $E_a = 60 \text{ kJ mol}^{-1} = 60000 \text{ J mol}^{-1}$ . Using Arrhenius equation, one can write

$$\log \frac{k_T}{k_{283}} = \frac{E_a}{2.303R} \left[ \frac{1}{283} - \frac{1}{T} \right]$$

$$\log \frac{1.5 \times 10^4 \text{ s}^{-1}}{4.5 \times 10^3 \text{ s}^{-1}} = \frac{6000 \text{ J mol}^{-1}}{2.303 \times 8.3 \text{ J K}^{-1} \text{ mol}^{-1}} \left[ \frac{T - 283}{283 \times T} \right]$$

On solving, we get  $T = 297 \text{ K} = 24^\circ\text{C}$ .

**51.** If concentrations are measured in  $\text{mol L}^{-1}$  and time in min, the unit for the rate constant of a third-order reaction is

(A)  $\text{mol L}^{-1} \text{ min}^{-1}$

(B)  $\text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$

(C)  $\text{L mol}^{-1} \text{ min}^{-1}$

(D)  $\text{min}^{-1}$

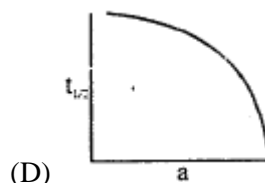
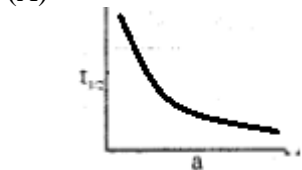
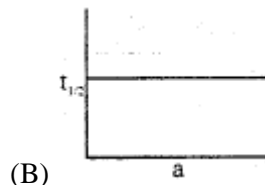
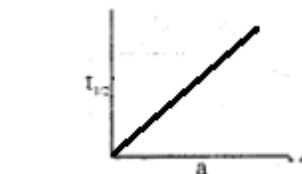
**Solution**

(B) In general,  $k = [\text{conc.}]^{1-n} \text{ min}^{-1}$ .



For third-order reaction =  $[\text{mol L}^{-1}]^{1-3} \text{ min}^{-1}$   
 $= \text{L}^2 \text{ mol}^{-2} \text{ min}^{-1}$

52. Which of the following curves represents a first-order reaction?



**Solution**

(B) Half-life is independent to the initial concentration of the reactant.

53. Calculate the order of the reaction in A and B.

[A] ( $\text{mol L}^{-1}$ )	0.05	0.10	0.05
[B] ( $\text{mol L}^{-1}$ )	0.01	0.05	0.10
Rate ( $\text{mol L}^{-1} \text{ s}^{-1}$ )	$1.2 \times 10^{-3}$	$2.4 \times 10^{-3}$	$1.2 \times 10^{-3}$

(A) 1 and 0

(B) 1 and 1

(C) 0 and 1

(D) None of these

**Solution**

(A) Let Rate =  $k[\text{A}]^x[\text{B}]^y$

$$1.2 \times 10^{-3} = k[0.05]^x \times [0.01]^y \quad (1)$$

$$1.2 \times 10^{-3} = k[0.05]^x \times [0.10]^y \quad (2)$$

Dividing Eq. (1) by Eq. (2), we get

$$1 = (0.1)^y \Rightarrow y = 0$$

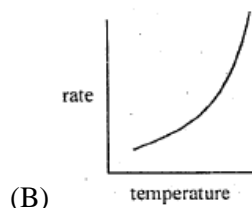
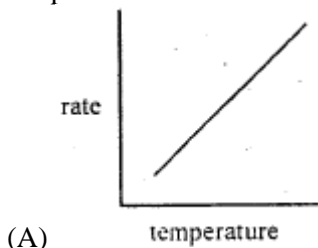
Now,

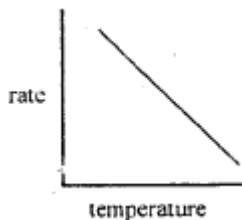
$$2.4 \times 10^{-3} = k[0.10]^x \times [0.05]^y \quad (3)$$

Dividing Eq. (3) by Eq. (2) and substituting  $y = 0$ , we get

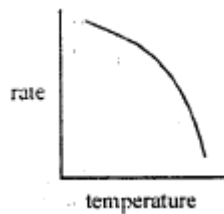
$$2 = (2)^x \Rightarrow x = 1$$

54. Which of the following correctly represents the variation of the rate of the reaction with temperature?





(C)



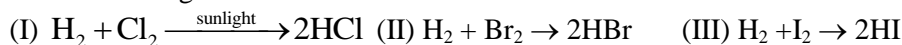
(D)

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**Solution**

(B) The rate increases with temperature but not directly.

55. Consider the following reactions:



The order of the reactions is

(A) 2, 1, 0

(B) 0, 3/2, 2

(C) 1, 2, 2

(D) 2, 1, 1

**Solution**

(B)

56. If a reaction  $\text{A} + \text{B} \rightarrow \text{C}$  is exothermic to the extent of  $30 \text{ kJ mol}^{-1}$  and the forward reaction has an activation energy  $70 \text{ kJ mol}^{-1}$ , the activation energy in  $\text{kJ mol}^{-1}$  for the reverse reaction is

(A) 30

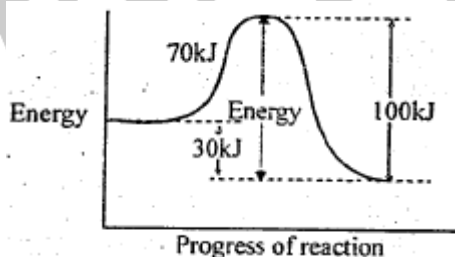
(B) 40

(C) 70

(D) 100

**Solution**

$$(D) \Delta H = E_{\text{af}} - E_{\text{ab}} \Rightarrow E_{\text{ab}} = E_{\text{af}} - \Delta H = 70 - (-30) = 100 \text{ kJ mol}^{-1}$$



57. The rate of a gaseous reaction is generally expressed in terms of  $dp/dt$ . If it were expressed in terms of change in number of moles per unit time ( $dn/dt$ ) or in terms of change in molar concentration per unit time ( $dC/dt$ ), which of the following relationship will hold good?

$$(A) \frac{dC}{dt} = \frac{dn}{dt} = \frac{dp}{dt}$$

$$(B) \frac{dC}{dt} = \frac{1}{V} \left( \frac{dn}{dt} \right) = \frac{1}{RT} \left( \frac{dp}{dt} \right)$$

$$(C) \frac{dC}{dt} = \frac{dn}{dt} = \frac{V}{RT} \left( \frac{dp}{dt} \right)$$

(D) None of these

**Solution**

(B) We know that  $pV = nRT$  or  $p = \frac{n}{V} RT$  or  $\frac{p}{RT} = C$ . On differentiating with respect to  $t$ , we get

$$\frac{1}{RT} \left( \frac{dp}{dt} \right) = \frac{dC}{dt} = \frac{1}{V} \left( \frac{dn}{dt} \right)$$

58. A first-order reaction is carried out starting with  $10 \text{ mol L}^{-1}$  of the reactant. It is 40% complete in 1 h. If the same reaction is carried out with an initial concentration of  $5 \text{ mol L}^{-1}$ , the percentage of the reaction that is completed in 1 h will be

- (A) 40%. (B) 80%. (C) 20%. (D) 60%.

**Solution**

(A) The time taken for completion of the whole reaction is

$$t = \frac{2.303}{k} \log \left( \frac{a_0}{a_0 - x} \right)$$

For 40% completion of the reaction,  $t_1 = \frac{2.303}{k} \log \left( \frac{10}{6} \right) = 1 \text{ h}$

If the initial concentration, that is,  $a = 5 \text{ mol L}^{-1}$ , then

$$t_2 = \frac{2.303}{k} \log \left( \frac{5}{5 - x} \right)$$

Given that  $t_1 = t_2 = 1 \text{ h}$ . So,

$$\log \left( \frac{5}{3} \right) = \log \left( \frac{5}{5 - x} \right)$$

or  $\frac{5}{3} = \frac{5}{5 - x}$  or  $x = 2$

Therefore, the percentage of reaction completed is  $\frac{2}{5} \times 100 = 40\%$

59. A first-order reaction takes 40 min for 30% decomposition. Calculate  $t_{1/2}$ .

- (A) 77.7 min (B) 27.2 min (C) 55.3 min (D) 67.3 min

**Solution**

(A) Extent of reaction = 30% and time taken = 40 min

For a first-order reaction,

$$t = \frac{2.303}{k} \log \frac{a}{a - x} = \frac{2.303}{k} \log \frac{1}{1 - (x/a)}$$

$$40 \text{ min} = \frac{2.303}{k} \log \left( \frac{1}{1 - 0.3} \right)$$

or  $k = \frac{2.303}{40 \text{ min}} \log \frac{1}{0.7} = 8.92 \times 10^{-3} \text{ min}^{-1}$

We know, for a first-order reaction,  $t_{1/2} = \frac{2.303 \log 2}{k}$

Then,  $t_{1/2} = \frac{2.303 \log 2}{8.92 \times 10^{-3} \text{ min}^{-1}} = 77.7 \text{ min}$

60. The number of half-lives ( $t_{1/2}$ ) required to bring the ratio to  $N/N_0 = 0.125$  from  $N/N_0 = 1$  of a radioactive element is

- (A) 2 (B) 4 (C) 3 (D) 1

**Solution**

(C)

61. In the study of inversion of sucrose in the presence of acid, if  $r_0$ ,  $r_t$ , and  $r_\infty$  represent the polarimetric readings at times 0,  $t$ , and  $\infty$ , respectively, then at the 50% inversion, which of the following relationship will hold good?

- (A)  $r_t = r_0 + r_\infty$  (B)  $r_t = \frac{1}{2}(r_0 + r_\infty)$  (C)  $r_t = r_0 - r_\infty$  (D)  $r_t = \frac{1}{2}(r_0 - r_\infty)$

**Solution**

(B) For inversion of sucrose, the rate constant is given by

$$k = \frac{2.303}{t} \log \left( \frac{r_\infty - r_0}{r_\infty - r_t} \right)$$

When  $t = t_{1/2}$ ,

$$k = \frac{2.303 \log 2}{t_{1/2}}$$

Therefore,

$$\frac{2.303(\log 2)}{t_{1/2}} = \frac{2.303}{t_{1/2}} \log \left( \frac{r_\infty - r_0}{r_\infty - r_t} \right)$$

$$2 = \frac{r_\infty - r_0}{r_\infty - r_t} \text{ or } 2r_\infty - 2r_t = r_\infty - r_0$$

or

$$r_t = \frac{1}{2}(r_0 + r_\infty)$$

62. The rate constant, the activation energy, and the Arrhenius parameter of a chemical reaction at 25°C are  $3.0 \times 10^{-4} \text{ s}^{-1}$ , 104.4 kJ mol<sup>-1</sup>, and  $6.0 \times 10^{14} \text{ s}^{-1}$ , respectively. The value of the rate constant as  $t \rightarrow \infty$  is

- (A)  $2.0 \times 10^{18} \text{ s}^{-1}$  (B)  $6.0 \times 10^{14} \text{ s}^{-1}$  (C)  $\infty$  (D)  $3.6 \times 10^{30} \text{ s}^{-1}$

**Solution**

(B)  $k = Ae^{-E_a/RT}$ . When  $T \rightarrow \infty$ ,  $k \rightarrow A$ , so  $A = 6.0 \times 10^{14} \text{ s}^{-1}$ .

63. The half-life for radioactive decay of <sup>14</sup>C is 5730 years. An archaeological artifact containing wood had only 80% of the <sup>14</sup>C found in a living tree. Estimate the age of the sample.

- (A) 1657.3 y (B) 1845.4 y (C) 1512.4 y (D) 1413.1 y

**Solution**

(B) Given that  $t_{1/2} = 5730 \text{ y}$ . If  $a$  is the initial <sup>14</sup>C activity in a living tree, then

$$\text{Activity in the dead wood, } a_t = \frac{80}{100} \times a$$

The nuclear/radioactive decays follow the first-order kinetics. So,

$$t = \frac{2.303}{k} \log \frac{a}{a_t} \text{ and } k = \frac{0.693}{t_{1/2}}$$

Therefore, 
$$t = \frac{2.303}{0.693/t_{1/2}} \log \frac{a}{\frac{80}{100}a} = \frac{2.303 \times 5730 \text{ y}}{0.693} \log \frac{100}{80} = 1845.4 \text{ y}$$

64. Decomposition on  $\text{NH}_3$  on heated tungsten yields the following data:

<b>Initial pressure (mm Hg)</b>	65	105	y	185
<b>Half-life (s)</b>	290	x	670	820

What are the values of x and y in that order?

- (A) 420 s, 110 mm Hg (B) 500 s, 160 mm Hg  
(C) 520 s, 170 mm Hg (D) 460s, 150 mm Hg

**Solution**

(D) 
$$\frac{\text{Half life}}{\text{Initial pressure}} = \frac{290}{65} = 4.46 \text{ and } \frac{820}{185} = 4.43.$$

The values nearly agree. Therefore, the reaction is of zero-order.

$$\frac{x}{105} \approx 4.4 \Rightarrow x \approx 460 \text{ s}$$

$$\frac{670}{y} = 4.4 \Rightarrow y \approx 150 \text{ mm Hg}$$

65. The rate constant of a certain first-order reaction increases by 11.11% per degree rise of temperature at  $27^\circ\text{C}$ . By what percentage will it increase at  $127^\circ\text{C}$ , assuming constancy of activation energy over the given temperature range?

- (A) 5.26% (B) 5.62% (C) 6.25% (D) 7.33%

**Solution**

(C) 
$$\frac{d \ln k}{dT} = \frac{E}{RT^2} \Rightarrow \frac{dk}{k} = \frac{E_a}{RT^2} dT$$

Given that  $\frac{dk}{k} = \frac{11.11}{100}$ ;  $dT = 1^\circ\text{C}$ ;  $T = 27^\circ\text{C} = 300 \text{ K}$

Therefore, 
$$0.111 = \frac{E_a \times 1}{1.987 \times 300 \times 300} \Rightarrow E_a = 0.1111 \times 1.987 \times [300]^2$$

At  $127^\circ\text{C}$ , 
$$\frac{dk}{k} = \frac{E_a}{1.987 \times (400)^2} = \frac{0.111 \times 1.987 \times (300)^2}{1.987 \times (400)^2} = 0.1110 \times \left(\frac{3}{4}\right)^2 = 0.06249$$

Hence, the percentage increase is 6.25%.

**Multiple Correct Choice Type**

1. The following statement(s) is (are) correct:

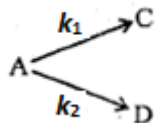
- (A) A plot of  $\log k_p$  vs.  $1/T$  is linear.  
(B) A plot of  $\log [X]$  vs. time is linear for a first-order reaction,  $X \rightarrow P$ .  
(C) A plot of  $\log p$  vs.  $1/T$  is linear at constant volume.

(D) A plot of  $p$  vs.  $1/V$  is linear at constant temperature.

**Solution**

(A, B, D)

2. Consider the following case of competing first-order reactions.



After the start of the reaction at  $t = 0$  with only A, [Q] is equal to the [D] at all times. The time in which all the three concentrations will be equal is given by

(A)  $t = \frac{1}{2k_1} \ln 3$       (B)  $t = \frac{1}{2k_2} \ln 3$       (C)  $t = \frac{1}{3k_1} \ln 2$       (D)  $t = \frac{1}{3k_2} \ln 2$

**Solution**

(A, B)  $k_1 = k_2$  or two-third of A has reacted for  $[A] = [C] = [D]$

Therefore,

$$k_1 + k_2 = \frac{1}{t} \ln \frac{[A]_0}{\frac{1}{3}[A]_0}$$

or

$$t - \frac{1}{k_1 + k_2} \ln 3 = \frac{1}{2k_t} \ln 3 = \frac{1}{2k_2} \ln 3$$

3. For a certain reaction  $A \rightarrow$  Products, the  $t_{1/2}$  as a function of  $[A]_0$ , is given as follows:

$[A]_0$ (M)	0.1	0.025
$t_{1/2}$ (min)	100	50

Which of the following is true?

- (A) The order is  $1/2$ .      (B)  $t_{1/2}$  would be  $100\sqrt{10}$  min for  $[A]_0 = 1$  M.  
 (C) The order is 1.      (D)  $t_{1/2}$  would be 100 min for  $[A]_0 = 1$  M.

**Solution**

(A, B) Given that  $100 \propto (0.1)^{1-n}$  and  $50 \propto (0.025)^{1-n}$ .

Dividing, we get  $2 = 4^{1-n}$

or

$$\log 2 = (1-n) \log 4 \text{ or } 1-n = \frac{\log 2}{\log 4}$$

or

$$n = 1 - \frac{\log 2}{\log 4} = 1 - \frac{\log 2}{2 \log 2} = 1 - \frac{1}{2} = \frac{1}{2}$$

We have  $100 \propto (0.1)^{1/2}$  and  $t_{1/2} \propto (1)^{1/2}$ . Dividing these two, we get

$$\frac{t_{1/2}}{100} = \left( \frac{1}{0.1} \right)^{1/2} \text{ or } t_{1/2} = 100\sqrt{10} \text{ min}$$

4. The polarimeter readings in an experiment to measure the rate of inversion of cane sugar (first-order reaction) were as follows

<b>Time (min)</b>	0	30	$\infty$
<b>Angle (degree)</b>	30	20	-15

Identify the true statement(s) [Given that  $\log 2 = 0.3$ ,  $\log 3 = 0.48$ ,  $\log 7 = 0.84$ ,  $\ln 10 = 2.3$ .]

- (A) The half-life of the reaction is 82.71 min.  
 (B) The solution is optically inactive at 131.13 min.  
 (C) The equimolar mixture of the products is dextrorotatory.  
 (D) The angle would be  $7.5^\circ$  at half time.

**Solution**

$$(A, B, D) \quad k = \frac{2.303}{30} \log \frac{30 - (-15)}{20 - (-15)} = \frac{2.303}{30} \log \frac{45}{35} = 8.38 \times 10^{-3} \text{ min}^{-1}$$

Therefore,  $t_{1/2} = 82.17 \text{ min}$ .

$$\text{Now} \quad k = \frac{1}{t} \log \frac{45}{0 - (-15)} \text{ or } t = 131.13 \text{ min}$$

$$\text{Again } \frac{30 - (-15)}{x - (-15)} = 2 \text{ at half time}$$

$$\text{or} \quad \frac{45}{x + 15} = 2 \text{ or } x + 15 = \frac{45}{2} \text{ or } x = 22.5 - 15 = 7.5^\circ$$

5. The rate law for the reaction  $\text{RCl} + \text{NaOH} \rightarrow \text{ROH} + \text{NaCl}$  is given by  $\text{Rate} = k[\text{RCl}]$ . The rate of this reaction is

- (A) doubled by doubling the concentration of NaOH.  
 (B) halved by reducing the concentration of RCl by one half.  
 (C) increased by increasing the temperature of the reaction.  
 (D) unaffected by change in temperature.

**Solution**



The rate expression is  $\text{Rate} = k[\text{RCl}]$ . So, rate of reaction is unaffected by doubling positive concentration of NaOH, because it does not import in rate law equation. The rate of reaction is increased by increase in temperature.

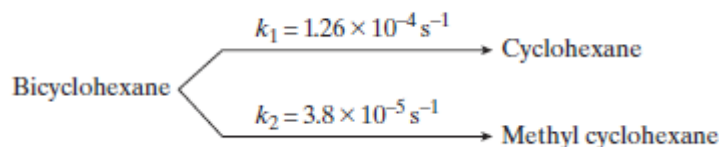
6. According to adsorption theory of catalysis, the speed of the reaction increases because

- (A) the concentration of reactant molecules at the active centers of the catalyst becomes high due to adsorption.  
 (B) in the process of adsorption the activation energy of the molecules becomes small.  
 (C) adsorption produces heat which increases the speed of the reaction.  
 (D) all of these.

**Solution**

(A, B, C)

7. Bicyclohexane was found to undergo two parallel first order rearrangements, as given below:



Choose the correct options:

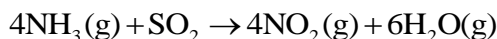
- (A) Percentage of cyclohexane = 77                      (B) Percentage of methylcyclopentane = 23  
 (C) Percentage of methylcyclopentane = 77            (D) Percentage of cyclohexane = 23

**Solution**

$$\text{(A, B) Percentage of cyclohexane} = \frac{k_1 \times 100}{k_1 + k_2} = \frac{1.26 \times 10^{-4}}{1.26 \times 10^{-4} + 3.8 \times 10^{-5}} \times 100 = 77\%$$

Therefore, percentage of methylcyclopentane = 23%.

8. If rate of reaction in terms of disappearance of  $\text{NH}_3$  is  $-\text{d}[\text{NH}_3]/\text{d}t$ , for the reaction:



then which of the following expressions are correct for rate of the reaction?

- (A) Rate =  $-\frac{4 \text{ d}[\text{O}_2]}{5 \text{ dt}}$     (B) Rate =  $\frac{3 \text{ d}[\text{H}_2\text{O}]}{2 \text{ dt}}$   
 (C) Rate =  $\frac{\text{d}[\text{NO}]}{\text{dt}}$     (D) Rate =  $\frac{4 \text{ d}[\text{O}_2]}{5 \text{ dt}}$

**Solution**

(A, C) For the reaction  $4\text{NH}_3(\text{g}) + \text{SO}_2 \rightarrow 4\text{NO}_2(\text{g}) + 6\text{H}_2\text{O}(\text{g})$ ,

$$\begin{aligned}
 -\frac{1 \text{ d}[\text{NH}_3]}{4 \text{ dt}} &= -\frac{1 \text{ d}[\text{O}_2]}{5 \text{ dt}} = \frac{1 \text{ d}[\text{NO}_2]}{4 \text{ dt}} = \frac{1 \text{ d}[\text{H}_2\text{O}]}{6 \text{ dt}} \\
 -\frac{1 \text{ d}[\text{NH}_3]}{4 \text{ dt}} &= -\frac{1 \text{ d}[\text{O}_2]}{5 \text{ dt}} \text{ or } -\frac{\text{d}[\text{NH}_3]}{\text{dt}} = -\frac{4 \text{ d}[\text{O}_2]}{5 \text{ dt}} \text{ or } -\frac{\text{d}[\text{NH}_3]}{\text{dt}} = \frac{\text{d}[\text{NO}]}{\text{dt}}
 \end{aligned}$$

9. Which of the following statements are not true for a catalyst?

- (A) It increases the average kinetic energy of the reacting molecules.  
 (B) It decreases the activation energy.  
 (C) It alters the reaction mechanism.  
 (D) It increases the frequency of collisions of the reacting species.

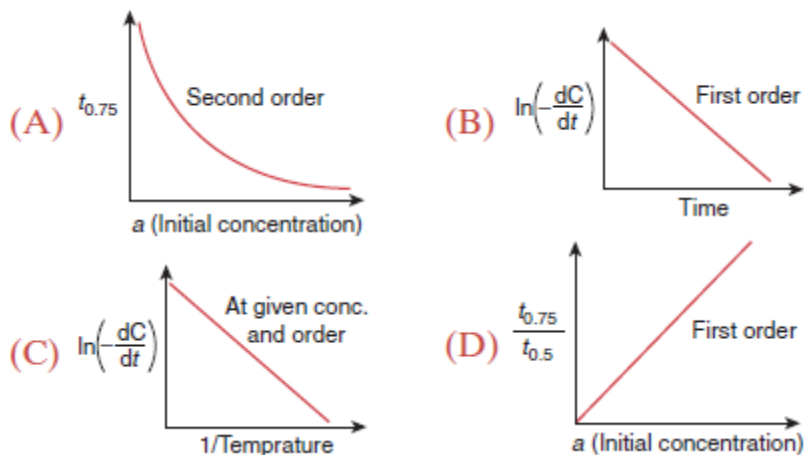
**Solution**

$$\text{(A, D) Rate of reaction} \propto \frac{1}{E_a}$$

Catalyst increases rate of reaction, so, activation energy decreases.  
 Catalyst also alters positive rate of reaction.

10. Which is the correct graph:





### Solution

(A, B, C)

(A)  $t_{x\%} \propto \frac{1}{a}$  for second order

(B) Rate =  $kC_1 = kC_0e^{-kt}$

$$\ln\left(\frac{dc}{dt}\right) = \ln(\text{rate}) = \ln k C_0 - kt$$

Hence, a straight line is observed.

(C)  $k = Ae^{-E_a/RT}$

$$\text{Rate} = k(\text{conc.})^n = Ae^{-E_a/RT} (\text{conc.})^n$$

$$\ln(\text{rate}) = -\frac{E_a}{RT} + \text{constant}$$

Therefore, the slope is  $-E_a/R$ .

(D)  $\frac{t_{0.75}}{t_{0.5}}$  = ratio of time is constant with initial concentration.

**11.** The ozone layer in the Earth's upper atmosphere is important in shielding the earth from very harmful ultraviolet radiation. The ozone,  $O_3$ , decomposes according to the equation  $2O_3(g) \rightarrow 3O_2(g)$ . The mechanism of the reaction is through to proceed through an initial fast, reversible step and then a slow second step.

Step 1: Fast, reversible  $O_3(g) \rightleftharpoons O_2(g)$

Step 2: Slow  $O_3(g) + O(g) \rightarrow 2O_2(g)$

Which of the following is correct?

(A) Step 2 is rate determining step.

(B) The rate expression for Step 2 is  $-\frac{d}{dt}[O_3] = k[O_3][O]$ .

(C) For Step 1, molecularity is 1.

(D) For Step 2, molecularity is 2.

**Solution**

(A, B, C, D) Slow step is rate determining step, from slow step  $-\frac{d}{dt}[\text{O}_3] = k[\text{O}_3][\text{O}]$

Molecularity for Step 1 is 1 and for Step 2 is 2 as shown in above given reaction.

12. Consider the rate law expression for a reaction:

$$\text{Rate} = k[\text{NO}_2^-][\text{I}^-][\text{H}^+]^2$$

Which of the following are not true for the reaction?

- (A) When concentration of each of  $\text{H}^+$ ,  $\text{NO}_2^-$ , and  $\text{I}^-$  are tripled, rate becomes nine times.  
 (B) When concentration of  $\text{NO}_2^-$  is doubled, of  $\text{I}^-$  is halved and of  $\text{H}^+$  is doubled, rate becomes 16 times.  
 (C) When concentration of both  $\text{NO}_2^-$  and  $\text{I}^-$  is doubled, rate becomes four times.  
 (D) When concentration of  $\text{H}^+$  is tripled, rate becomes nine times.

**Solution**

(A, B) The rate expressions are as follows:

(A)  $\text{Rate}_A = k[3\text{NO}_2^-][3\text{I}^-][3\text{H}^+]^2 = 81(\text{Rate})$

(B)  $\text{Rate}_B = k[2\text{NO}_2^-][(1/2)\text{I}^-][2\text{H}^+]^2 = 4(\text{Rate})$

(C)  $\text{Rate}_C = k[2\text{NO}_2^-][2\text{I}^-][\text{H}^+]^2 = 4(\text{Rate})$

(D)  $\text{Rate}_D = k[\text{NO}_2^-][\text{I}^-][3\text{H}^+]^2 = 9(\text{Rate})$

13. The half-period  $T$  for the decomposition of ammonia on tungsten wire was measured for different initial pressures  $p$  of ammonia at  $25^\circ\text{C}$ . Then

$p$ (mm Hg)	11	21	48	73	120
$t$ (s)	48	92	210	320	525

- (A) it is a zero-order reaction. (B) it is a first-order reaction.  
 (C) rate constant for reaction is  $0.114\text{ s}^{-1}$ . (D) rate constant for reaction is  $1.14\text{ s}$ .

**Solution**

(A, C)  $t_{1/2} \propto \frac{1}{p^{n-1}} \Rightarrow \frac{21}{11} = \left(\frac{48}{92}\right)^{n-1} \Rightarrow n = 0$

For zero order,  $t_{1/2} = \frac{p}{2k} \Rightarrow k = \frac{p}{2t_{1/2}} = \frac{11}{2 \times 48} = 0.114\text{ s}^{-1}$

**Assertion–Reasoning Type**

Choose the correct option from the following:

- (A) Statement 1 and Statement 2 are True; Statement 2 is the correct explanation of the Statement 1.  
 (B) Statement 1 and Statement 2 are True; Statement 2 is NOT a correct explanation of the Statement 1.  
 (C) Statement 1 is True, Statement 2 is False.  
 (D) Statement 1 is False, Statement 2 is True.

1. **Statement 1:** For a first order reaction, the degree of dissociation is equal to  $(1 - e^{-kt})$ .

**Statement 2:** For a first order reaction, the pre-exponential factor in the Arrhenius equation has the dimension of time<sup>-1</sup>.

**Solution**

(B) For a first order reaction,

$$[A]_f = [A]_0 \exp(-kt)$$

$$[A]_0 - [A]_f = [A]_0 - [A]_0 \exp(-kt) = [A]_0(1 - \exp(-kt))$$

or

$$\frac{[A]_0 - [A]_f}{[A]_0} = (1 - \exp(-kt))$$

So, degree of dissociation =  $(1 - \exp(-kt))$

For a first order reaction,

$$k = A \exp(-E_a / RT) = A \exp\left(\frac{\text{J mol}^{-1}}{\text{J mol}^{-1} \text{K}^{-1} \text{K}}\right)$$

Thus, the units of A are the same as that for  $k$ . For a first-order reaction, the units of  $k$  are those of time<sup>-1</sup>. So the units of A are also those of time<sup>-1</sup>.

**2. Statement 1:** The reaction  $\text{N}_2(10 \text{ atm}) + 3\text{H}_2(10 \text{ atm}) \rightarrow 2\text{NH}_3(\text{g})$  is faster.

**Statement 2:** Catalyst lowers the activation energy of the reaction.

**Solution**

(B) The reaction,  $\text{N}_2(10 \text{ atm}) + 3\text{H}_2(10 \text{ atm}) \rightarrow 2\text{NH}_3(\text{g})$  is faster because of higher partial pressures of the reactants.

**3. Statement 1:** For a first-order reaction, the concentration of the reactant decreases exponentially with time.

**Statement 2:** Rate of reaction at any time depends upon the concentration of the reactant at that time.

**Solution**

(B) The expression is  $\ln \frac{a}{a-x} = kt$  or  $\frac{a}{a-x} = e^{-kt}$

**4. Statement 1:** For a second-order reaction, graph of  $[A]$  vs.  $t$  is a straight line.

**Statement 2:** For second-order reaction,  $[A] = kt + \frac{1}{[A]_0}$

**Solution**

(C) For second order,  $k = \frac{1}{t} \frac{x}{a(a-x)}$ . This is of the form  $y = mx + c$  and is a straight line.

**5. Statement 1:** The rate constant of a pseudounimolecular reaction has the units of the rate constant of a second-order reaction.

**Statement 2:** A pseudounimolecular reaction is a reaction of second order in which one of the reactants is present in large excess.

**Solution**

(A) Pseudounimolecular reaction is the reaction whose order is one and molecularity is two. So in this reaction, at least two reactants are present.

**6. Statement 1:** Molecularity of a reaction cannot be determined experimentally.

**Statement 2:** Molecularity is assigned to reactions on the basis of mechanism.

**Solution**

(A) Molecularity of a reaction cannot be determined experimentally because molecularity is assigned to the reactions on the basis of mechanism.

**7. Statement 1:** The order of reaction can have a fractional value.

**Statement 2:** The order of reaction cannot be written from the balanced equation of a reaction.

**Solution**

(B) Order is the sum of power of concentration terms which change with time, but molecularity is the sum of stoichiometric coefficients of a balanced equation of reaction.

**8. Statement 1:** If the activation energy of a reaction is zero, temperature will have no effect on the rate of reaction.

**Statement 2:** Lower the activation energy, faster will be the reaction.

**Solution**

(B) Rate of reaction  $\propto \frac{1}{\text{Activation energy}}$

A catalyst decreases the potential energy, due to which rate of reaction increases.

**9. Statement 1:** Molecularity does not influence the rate of reaction.

**Statement 2:** The overall kinetics of a reaction is governed by the slowest step in the reaction scheme.

**Solution**

(B)

**Comprehension Type**

Read the paragraphs and answer the questions that follow.

**Paragraph I**

The reaction between A and B is of first order with respect to A and of zero order with respect to B. The following data were obtained for four experiments:

Experiment	[A] (M)	[B] (M)	Initial Rate (M min <sup>-1</sup> )
I	0.1	0.1	$2.0 \times 10^{-2}$
II	$x$	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	$y$
IV	$z$	0.2	$2.0 \times 10^{-2}$

1. The value of  $x$  is

(A) 0.2

(B) 0.8

(C) 0.1

(D) 0.5

**Solution**

(A) Since the reaction is of zero order with respect to B, hence any change in the concentration of B has no effect on the rate of reaction.

From experiment I,  $2.0 \times 10^{-2} \text{ M min}^{-1} = k \times (0.1)^1$

So,

$$k = \frac{2.0 \times 10^{-2} \text{ M min}^{-1}}{0.1 \text{ M}} = 0.2 \text{ min}^{-1}$$

For experiment II,

$$4.0 \times 10^{-2} \text{ M min}^{-1} = 0.2 \text{ min}^{-1} [\text{A}]$$

$$[\text{A}] = \frac{4.0 \times 10^{-2} \text{ M min}^{-1}}{0.2 \text{ min}^{-1}} = 0.2 \text{ M}$$

2. The value of  $y$  is

- (A) 0.2 (B) 0.08 (C) 0.1 (D) 0.5

**Solution**

(B) For experiment III, Rate =  $0.2 \text{ min}^{-1} \times (0.4 \text{ M})^1 = 0.08 \text{ M min}^{-1}$

3. The value of  $z$  is

- (A) 0.2 (B) 0.8 (C) 0.1 (D) 0.5

**Solution**

(C) For experiment IV,  $2.0 \times 10^{-2} \text{ M min}^{-1} = 0.2 \text{ min}^{-1} \times [\text{A}]$

or 
$$[\text{A}] = \frac{2.0 \times 10^{-2} \text{ M min}^{-1}}{0.2 \text{ min}^{-1}} = 0.1 \text{ M}$$

### Paragraph II

In 1889, Svante Arrhenius suggested that the relationship between temperature and the rate constant for a reaction obeyed the following equation:  $k = Ae^{-E_a/RT}$ . For most of the reactions, it was found that the temperature coefficient of the reaction lies between 2 and 3. The activation energy can be calculated from rate constants measured at two temperatures. If the activation energy and the rate constant at a particular temperature are known, the rate constant at another temperature can be calculated. Keeping temperature constant, the effect of catalyst on the activation energy has also been studied by studying how much the rate of reaction changes in the presence of catalyst. Although the catalyst is not part of the overall reaction, it provides a path to the products that has a rate-determining step with a lower activation energy than that of the uncatalyzed reaction.

4. The pre-exponential factor in the Arrhenius equation of a second-order reaction has the units

- (A)  $\text{mol L}^{-1} \text{ s}^{-1}$  (B)  $\text{L mol}^{-1} \text{ s}^{-1}$  (C)  $\text{s}^{-1}$  (D) It is dimensionless.

**Solution**

(B) The equation is  $\log k = \log A - E_a/RT$  where  $k$  for second-order reaction has the units  $\text{L mol}^{-1} \text{ s}^{-1}$ ;  $E_a$  is in J;  $R$  is in  $\text{J K}^{-1} \text{ mol}^{-1}$ ; and  $T$  is in K. So, we get units of  $A$  as  $\text{L mol}^{-1} \text{ s}^{-1}$ .

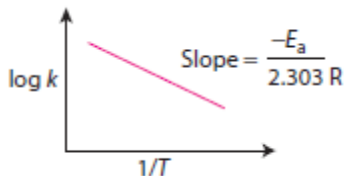
5. The activation energy  $E_a$  of a reaction can be calculated by plotting:

- (A)  $k$  against  $T$  (B)  $k$  against  $1/\log T$  (C)  $\log k$  against  $1/T$  (D)  $\log k$  against  $1/\log T$

**Solution**

(C) According to Arrhenius equation,  $\log k = -E_a/2.303RT + \log A$

Comparing it with straight line equation  $y = mx + c$ , we get slope as  $-E_a/2.303R$  on plotting  $\log k$  vs.  $1/T$  as shown:



6. The activation energy of a certain reaction is  $87 \text{ kJ mol}^{-1}$ . What is the ratio of the rate constants for this reaction when the temperature decreases from  $37^\circ\text{C}$  to  $15^\circ\text{C}$ ?

- (A) 5/1                      (B) 8.3/1                      (C) 13/1                      (D) 24/1

**Solution**

(C) We know that  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$

Putting  $E_a = 87 \times 10^3 \text{ J mol}^{-1}$ , we get

$$T_2 = 37^\circ\text{C} = 37 + 273 = 310 \text{ K}$$

$$T_1 = 15^\circ\text{C} = 15 + 273 = 288 \text{ K}$$

On solving, we get

$$\log \frac{k_2}{k_1} = 1.11 \Rightarrow \frac{k_2}{k_1} = \text{antilog}(1.11) = 12.88 \approx 13/1$$

$$\log k_2/k_1 = 1.11 \text{ or } k_2/k_1 = \text{antilog}(1.11) = 12.88 \approx 13/1.$$

7. The rate of reaction is doubled when the temperature is changed from  $298 \text{ K}$  to  $308 \text{ K}$ . What is the energy of activation of the reaction?

- (A)  $80 \text{ kJ mol}^{-1}$                       (B)  $52.89 \text{ kJ mol}^{-1}$                       (C)  $60.28 \text{ kJ mol}^{-1}$                       (D)  $58.29 \text{ kJ mol}^{-1}$

**Solution**

(B) The expression is  $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$

where  $k_2/k_1 = 2$ ,  $T_1 = 298 \text{ K}$  and  $T_2 = 308 \text{ K}$ .

Substituting the values, we get

$$\log 2 = \frac{E_a}{2.303 \times 8.314} \left( \frac{308 - 298}{308 \times 298} \right)$$

Therefore,  $E_a = \frac{0.3010 \times 2.303 \times 8.314 \times 308 \times 298}{10} = 52897.77 \text{ J mol}^{-1}$  or  $52.89 \text{ kJ mol}^{-1}$

8. If  $x$  is the fraction of molecules having energy greater than  $E_a$ , it will be given by

- (A)  $x = -\frac{E_a}{RT}$                       (B)  $\ln x = -\frac{E_a}{RT}$                       (C)  $x = e^{E_a/RT}$                       (D) any of these.

**Solution**

(B) This is because according to Arrhenius, the fraction of molecules is given by  $e^{E_a/RT}$ .

Let  $x = e^{E_a/RT}$  Taking  $\ln$  on both the sides, we get

$$\ln x = -\frac{E_a}{RT}$$

### Integer Answer Type

The answer to each question is a **non-negative integer**.

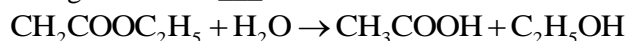
1. If the rate constant for the reaction  $2A + B \rightarrow C$  was found to be  $2.5 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$  after 15 s,  $2.60 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$  after 30 s and  $2.55 \times 10^{-5} \text{ L mol}^{-1} \text{ s}^{-1}$  after 60 s, the order of reaction is \_\_\_\_.

#### Solution

(2) Looking at the units of rate constant we can say that the reaction is of second order. In general,

$$\text{Units of } k = (\text{time})^{-1} \times (\text{conc.})^{n-1}.$$

2. The order of the following reaction is \_\_\_\_.



#### Solution

(4) The order of the reaction is one, it is a pseudounimolecular reaction in which one of the reactant, that is,  $\text{H}_2\text{O}$  is taken in excess.

3. If the half-life of a reaction is inversely proportional to the cube of initial concentration, the order of reaction is \_\_\_\_.

#### Solution

(4) In general,  $t_{1/2} \propto \frac{1}{[\text{A}]_0^{n-1}}$ . Given that  $t_{1/2} \propto \frac{1}{[\text{A}]_0^3}$ , this means  $n - 1 = 3$  or  $n = 4$ .

4. After 24 h, only 0.125 g out of the initial quantity of 1 g of a radioactive isotope remains behind. The half-life period of the radioactive isotope in hours is \_\_\_\_.

#### Solution

$$(8) \text{ We know that } k = \frac{2.303}{t} \log \left[ \frac{a}{a-x} \right]$$

Substituting given values, we get

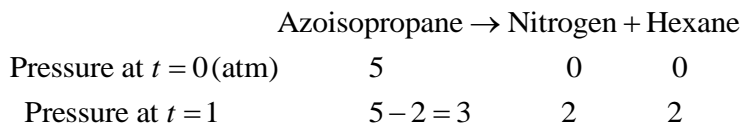
$$k = \frac{2.303}{24} \log \left[ \frac{1}{0.125} \right] \text{ or } k = 0.0867 \text{ h}^{-1}$$

Therefore,  $t_{1/2} = 0.693/k = 7.99 \text{ h} \approx 8 \text{ h}$ .

5. Starting with an initial pressure of 5 atm of azoisopropane, 40% of it decomposes into nitrogen and hexane vapors in 1 h. The pressure in atmospheres exerted by the mixture in atm at this time will be \_\_\_\_.

#### Solution

(7) The reaction can be written as



Total pressure exerted by mixture at this time =  $3 + 2 + 2 = 7 \text{ atm}$ .

6. For a reaction  $2A \rightarrow A_2$ , the rate of reaction becomes 8 times when the concentration of A changes from  $a$  to  $3a$ . The order of reaction is \_\_\_\_.

**Solution**

(3) The reaction is  $2A \rightarrow A_2$ . The expression for rate of reaction is  $\text{Rate} = k[A]$ .

$$\text{Rate} = k[X]^a \quad (1)$$

$$27(\text{Rate}) = k[3X]^a \quad (2)$$

Dividing Eq. (1) by Eq.(2), we get

$$\frac{1}{27} = \left[ \frac{1}{3} \right]^a$$

So,  $a = 3$  or order = 3.

### Matrix–Match Type

1. Match the problem with its numerical solution.

Column I	Column II								
(A) If the activation energy is 65 kJ then how much time faster a reaction proceeds at $25^\circ\text{C}$ than at $0^\circ\text{C}$ ?	(p) 5								
(B) Rate constant of a first-order reaction is $0.0693 \text{ min}^{-1}$ . If we start with $20 \text{ mol L}^{-1}$ , it is reduced to $2.5 \text{ mol L}^{-1}$ , in how many minutes?	(q) 11								
(C) Half-lives of first-order and zero-order reactions are same. Ratio of rates at the start of reaction is how many times of 0.693?	(r) 30								
(D) The half-life periods are given as	(s) 1/4								
<table border="1" style="display: inline-table; vertical-align: middle;"> <tbody> <tr> <td><math>[A]_0 \text{ (M)}</math></td> <td>0.0677</td> <td>0.136</td> <td>0.272</td> </tr> <tr> <td><math>t_{1/2} \text{ (s)}</math></td> <td>240</td> <td>480</td> <td>960</td> </tr> </tbody> </table>	$[A]_0 \text{ (M)}$	0.0677	0.136	0.272	$t_{1/2} \text{ (s)}$	240	480	960	(t) 2
$[A]_0 \text{ (M)}$	0.0677	0.136	0.272						
$t_{1/2} \text{ (s)}$	240	480	960						
What is the order of the reaction?	(u) 0								

**Solution**

(A  $\rightarrow$  (q); (B)  $\rightarrow$  (r); (C)  $\rightarrow$  (t); (D)  $\rightarrow$  (u)

$$(A) 2.303 \log_{10} \frac{k_2}{k_1} = \frac{E_a}{R} \left[ \frac{T_2 - T_1}{T_2 T_1} \right]$$

Putting  $T_2 = 298 \text{ K}$ ;  $T_1 = 273 \text{ K}$ ,  $E_a = 65,000 \text{ J}$ ,  $R = 8.314 \text{ J (mol K)}$ , we get

$$\frac{k_2}{k_1} = 11$$

$$(B) \frac{2.5}{20} = \frac{1}{8} = \left( \frac{1}{2} \right)^n \text{ or } n = 3 \text{ or } t = 3 \times \frac{0.693}{0.0693} = 30$$

$$(C) \text{ Zero order: } t_{1/2} = \frac{a}{2K}, \text{ For first order: } t_{1/2} = \frac{0.693}{K}$$

$$\frac{1}{2k_1} = \frac{0.693}{k_2} \text{ or } \frac{k_2}{k_1} = 2 \times 0.693$$



$$(D) t_{1/2} \propto (a)^{1-n} \quad \text{or} \quad (1-n) = \frac{\log t'_{1/2} - \log t''_{1/2}}{\log a' - \log a''}$$

$$t_{1/2} \propto \frac{1}{a^{n-1}} \quad \text{or} \quad \frac{480}{240} = \left( \frac{0.0677}{0.136} \right)^{n-1}$$

$$\text{or } n = 0$$

2. Kinetics of hydrolysis of ethyl acetate catalyzed by an acid is followed by titrating a fixed volume of reaction mixture with a standard alkali solution at different intervals of time.  $V_0$ ,  $V_1$ , and  $V_\infty$  are the titer values at zero,  $t$  and  $\infty$  time. Match the following:

Column I	Column II
(A) $V_0 \propto$	(p) [Acid] as initially present and that formed at time $t$
(B) $V_1 \propto$	(q) [Acid] present as catalyst
(C) $V_\infty - V_1 \propto$	(r) [Acid] formed after completion reaction
(D) $V_\infty - V_0 \propto$	(s) [Acid] formed after time $t$

**Solution**

(A)  $\rightarrow$  (q); (B)  $\rightarrow$  (p); (C)  $\rightarrow$  (s); (D)  $\rightarrow$  (r)

Concept based

3. Match the quantity with its expression.

Column I	Column II
(A) Half-life of first order reaction	(p) Active mass
(B) Arrhenius equation	(q) $k = Ae^{-E_a/RT}$
(C) Molar concentration	(r) $t_{1/2} = \frac{0.693}{k}$
(D) Half-life period of zero order reaction	(s) $\frac{a}{2k}$

**Solution**

(A)  $\rightarrow$  (r); (B)  $\rightarrow$  (q); (C)  $\rightarrow$  (p); (D)  $\rightarrow$  (s)

4. Match the reaction with its order/molecularity.

Column I	Column II
(A) $\text{RCl} + \text{H}_2\text{O} \rightarrow \text{ROH} + \text{HCl}$	(p) Molecularity 1
(B) $\begin{array}{c} \text{COOH} \\   \\ \text{COOH} \end{array} \longrightarrow \text{CO} + \text{CO}_2 + \text{H}_2\text{O}$	(q) Molecularity 3
(C) $2\text{H}_2\text{O}_2 \rightarrow 2\text{H}_2\text{O} + \text{O}_2$	(r) Molecularity 2
(D) $2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}$	(s) Molecularity 4

**Solution**

(A)  $\rightarrow$  (r); (B)  $\rightarrow$  (p); (C)  $\rightarrow$  (r); (D)  $\rightarrow$  (q)

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