

## CBSE NCERT Solutions for Class 12 Chemistry Chapter 4

### Back of Chapter Questions

1. For the reaction  $R \rightarrow P$ , the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and seconds.

**Solution:**

Given  $[R]_1 = 0.03$ ;  $[R]_2 = 0.02$ ; Average rate of reaction =

$$\frac{\text{change in concentration}}{\text{time interval}} = \frac{\Delta[R]}{\Delta t}$$

$$= \frac{[R]_2 - [R]_1}{t_2 - t_1}$$

Average rate of reaction in minutes =  $-\frac{(0.02-0.03)}{25} \text{ M min}^{-1}$

Negative sign indicate the decrease the concentration

$$= -\frac{(-0.01)}{25} \text{ M min}^{-1} = 4 \times 10^{-4} \text{ M min}^{-1}$$

Average rate of reaction in seconds =  $\frac{4 \times 10^{-4}}{60} \text{ M s}^{-1}$

$$= 6.67 \times 10^{-6} \text{ M s}^{-1}$$

**Concept Insight:**

Average rate depends upon the change in concentration of reactants or products and time taken for that change to occur.

Rate of disappearance of R = Decrease in concentration of R/Time taken

Rate of appearance of P = Increase in concentration of P/Time taken

2. In a reaction,  $2A \rightarrow \text{Products}$ , the concentration of A decreases from 0.5 mol L<sup>-1</sup> to 0.4 mol L<sup>-1</sup> in 10 minutes. Calculate the rate during this interval?

**Solution:**

Average rate =  $\frac{1}{2} \frac{\Delta[A]}{\Delta t}$

$$= -\frac{1}{2} \frac{[A]_2 - [A]_1}{t_2 - t_1}$$

$$= -\frac{1}{2} \frac{(0.4 - 0.5)}{10}$$

$$= -\frac{1(-0.1)}{2 \times 10}$$

$$= 0.005 \text{ mol L}^{-1} \text{ min}^{-1}$$

$$= 5 \times 10^{-3} \text{ M min}^{-1}$$

**Concept Insight:**

For expression the rate of reaction where stoichiometric coefficients of reactants or products are not equal to one, rate of disappearance of any of the reactants or rate of appearance of products is divided by their respective stoichiometric coefficients.

3. For a reaction,  $A + B \rightarrow \text{Product}$ ; the rate law is given by,  $r = k[A]^{\frac{1}{2}}[B]^2$ . What is the order of the reaction?

**Solution:**

Sum of power of the concentration of the reactants in the rate law expression is called the order of that chemical reaction.

$$\text{Given } r = k[A]^{\frac{1}{2}}[B]^2.$$

$$\text{Hence the order of the reaction} = \frac{1}{2} + 2 = 2\frac{1}{2} = 2.5$$

Concept Insight: Sum of power of the concentration of the actants in the rate law expression is called the order of the chemical reaction.

4. The conversion of molecules X to Y follows second order kinetics. If concentration of X is increased to three times how will it affect the rate of formation of Y?

**Solution:**

The reaction  $X \rightarrow Y$  follows second order kinetics.

Therefore, the rate equation for this reaction will be:

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

$$\text{Let } [X] = a \text{ mol L}^{-1},$$

then equation (1) can be written as:

$$\text{Rate}_1 = k.(a)^2$$

$$= ka^2$$

If the concentration of X is increased to three times, then  $[X] = 3a \text{ mol L}^{-1}$

Now, the rate equation will be:

$$\text{Rate}_2 = k(3a)^2 = 9(ka^2)$$

$$\text{Rate}_2 = 9 \text{ Rate}_1$$

Hence, the rate of formation will increase by nine times.

5. A first-order reaction has a rate constant  $1.15 \times 10^{-3} \text{ s}^{-1}$ . How long will 5 g of this reactant take to reduce to 3 g?

**Solution:**

Given:

$$\text{Initial amount } [R]_0 = 5 \text{ g}$$

$$\text{Final concentration } [R] = 3 \text{ g}$$

$$\text{Rate constant (k)} = 1.15 \times 10^{-3} \text{ s}^{-1}$$

Formula:

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

Put the values of  $[R]_0$ ,  $[R]$ , Rate constant (k) in above formula

$$\begin{aligned} t &= \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3} \text{ second} \\ &= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219 \text{ seconds} \\ &= 444.196 \text{ second} \\ &= 444 \text{ seconds (approx)} \end{aligned}$$

6. Time required to decompose  $\text{SO}_2\text{Cl}_2$  to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

**Solution:**

Given: Time required to decompose  $\text{SO}_2\text{Cl}_2$  to half of its initial amount ( $t_{1/2}$ ) = 60 minutes

Formula for  $t_{1/2}$  of 1<sup>st</sup> order reaction,

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

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

By putting the value  $t_{1/2}$  in the equation the  $k = \frac{0.693}{60}$

$$k = 0.01155 \text{ min}^{-1}$$

$$k = 0.01155/60 \text{ sec}^{-1} = 1.925 \times 10^{-4} \text{ s}^{-1}$$

7. What will be the effect of temperature on rate constant?

**Solution:**

The rate constant of reaction is doubled or triple with an 10 °C or K rise in temperature.

However, the exact d rate of a chemical reaction on temperature is given by Arrhenius equation,

$$k = Ae^{-\frac{E_a}{RT}}$$

Where,

k = rate constant

A = Arrhenius factor or the frequency factor

T = temperature

R = gas constant

E<sub>a</sub> = activation energy

Concept Insight: The effect of temperature on rate constant is given by Arrhenius equation.

8. The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E<sub>a</sub>.

**Solution:**

Given that

initial temperature (T<sub>1</sub>) = 298 K

final temperature (T<sub>2</sub>) = (298 + 10)K = 308 K

We know that the rate of the reaction doubles when temperature is increased by 10°.

Therefore, let assume value of k<sub>1</sub> = k and that of k<sub>2</sub> = 2k

Also, R = 8.314 J K<sup>-1</sup>mol<sup>-1</sup>

$$\text{Formula: } \ln \frac{k_2}{k_1} = \frac{E}{R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

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

$$\log \frac{2k}{k} = \frac{E}{2.303R} \left[ \frac{308 - 298}{298 \times 308} \right]$$

We get:

$$\log \frac{2k}{k} = \frac{E_a}{2.303 \times 8.314} \left[ \frac{10}{298 \times 308} \right]$$

$$\Rightarrow \log 2 = \frac{E_a}{2.303 \times 8.314} \left[ \frac{10}{298 \times 308} \right]$$

$$\Rightarrow E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

$$= 52897.78 \text{ J mol}^{-1}$$

$$= 52.9 \text{ kJ mol}^{-1}$$

Concept insight: The rate of reaction doubles with  $10^\circ$  rise of temperature.

9. The activation energy for the reaction  $2\text{HI}(\text{g}) \rightarrow \text{H}_2(\text{g}) + \text{I}_2(\text{g})$  is  $209.6 \text{ kJ mol}^{-1}$  of  $581 \text{ K}$ . Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

**Solution:**

Given that

$$\text{Activation energy } (E_a) = 209.6 \text{ kJ mol}^{-1}$$

$$1 \text{ kJ} = 10000 \text{ J}$$

$$E_a = 209500 \text{ J mol}^{-1}$$

$$\text{Temperature } (T) = 581 \text{ K}$$

$$\text{Gas constant } (R) = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

According to Arrhenius equation

$$K = A e^{-E_a/RT}$$

In this formula term  $e^{-E_a/RT}$  represent the number of molecules which have energy equal or more than activation energy

$$\text{Number of molecules} = e^{-E_a/RT}$$

put the values we get number of molecules

$$\text{Number of molecules } (x) = e^{-E_a/RT}$$

$$\Rightarrow \ln x = -E_a/RT$$

$$\Rightarrow \log x = \frac{209500 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 581} = 18.8323$$

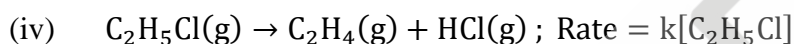
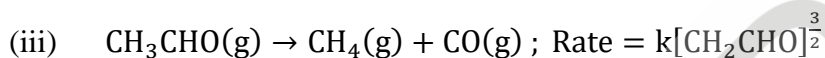
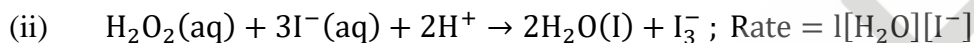
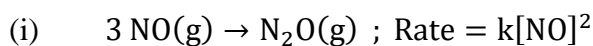
$$\text{Now, } x = \text{Anti log } (18.8323)$$

$$= \text{Anti log } \overline{19.1677}$$

$$= 1.471 \times 10^{-19}$$

### Back of chapter questions

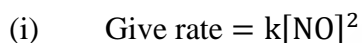
1. From the rate expression for the following reactions, determine their order of reaction and the dimensions of the rate constants.



#### Solution:

Formula used for Dimension of  $k = \frac{\text{Rate}}{[\text{concentration}]^{\text{order of reaction}}} =$

Rate = mole/litre/time



Therefore, order of the reaction = 2

$$\text{Dimension of } k = \frac{\text{Rate}}{[\text{NO}]^2}$$

$$= \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^2}$$

$$= \frac{\text{mol L}^{-1}\text{s}^{-1}}{\text{mol}^2\text{L}^{-2}}$$

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

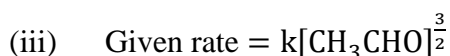


Therefore, order of the reaction = 2

$$\text{Dimension of } k = \frac{\text{Rate}}{[\text{H}_2\text{O}_2][\text{I}^-]}$$

$$= \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})(\text{mol L}^{-1})}$$

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



Therefore, order of reaction =  $\frac{3}{2}$

$$\begin{aligned} \text{Dimension of } k &= \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^{\frac{3}{2}}} \\ &= \frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^{\frac{3}{2}}} \\ &= \frac{\text{mol L}^{-1}\text{s}^{-1}}{\text{mol}^{\frac{3}{2}}\text{L}^{-\frac{3}{2}}} \\ &= \text{L}^{\frac{1}{2}} \text{mol}^{\frac{1}{2}} \text{s}^{-1} \end{aligned}$$

2. For the reaction:

$2\text{A} + \text{B} \rightarrow \text{A}_2\text{B}$  the rate =  $k[\text{A}][\text{B}]^2$  with  $k = 2.0 \times 10^{-6} \text{mol}^{-2}\text{L}^2\text{s}^{-1}$ . Calculate the initial rate of the reaction when  $[\text{A}] = 0.1 \text{mol L}^{-1}$ ,  $[\text{B}] = 0.2 \text{mol L}^{-1}$ . Calculate the initial rate of the reaction when  $[\text{A}] = 0.1 \text{mol L}^{-1}$ ,  $[\text{B}] = 0.2 \text{mol L}^{-1}$ . Calculate the rate of reaction after  $[\text{A}]$  is reduced to  $0.06 \text{mol L}^{-1}$ .

**Solution:**

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

$$\text{rate constant (k)} = 2.0 \times 10^{-6} \text{mol}^{-2}\text{L}^2\text{s}^{-1}.$$

$$[\text{A}]_{\text{initial}} = 0.1 \text{mol L}^{-1},$$

$$[\text{B}]_{\text{initial}} = 0.2 \text{mol L}^{-1}.$$

We know

$$\begin{aligned} \text{The initial rate of the reaction is (r)} &= k[\text{A}][\text{B}]^2 \\ &= (2.0 \times 10^{-6} \text{mol}^{-2}\text{L}^2)(0.1 \text{mol L}^{-1})(0.2 \text{mol L}^{-1})^2 \\ &= 8.0 \times 10^{-9} \text{mol}^{-2}\text{L}^2\text{s}^{-1} \end{aligned}$$

When  $[\text{A}]$  is reduced from  $0.1 \text{mol L}^{-1}$  to  $0.06 \text{mol L}^{-1}$ ,

$$\text{The concentration of A reacted} = (0.1 - 0.06) \text{mol L}^{-1} = 0.04 \text{mol L}^{-1}$$

$$\text{rate of reaction} = \frac{d[\text{A}]}{2dt} = \frac{d[\text{B}]}{dt}$$

$$\text{Therefore, the concentration of B reacted} = \frac{d[\text{A}]}{2dt} = \frac{1}{2} \times 0.04 \text{mol L}^{-1} = 0.02 \text{mol L}^{-1}$$

$$\begin{aligned} \text{Then, the left concentration of B, } [\text{B}] &= (0.2 - 0.02) \text{mol L}^{-1} \\ &= 0.18 \text{mol L}^{-1} \end{aligned}$$

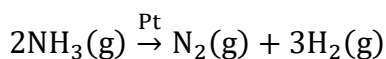
$$\begin{aligned} \text{After } [\text{A}] \text{ is reduced to } 0.06 \text{mol L}^{-1}, \text{ the rate of the reaction} &= k[\text{A}][\text{B}]^2 = \\ (2.0 \times 10^{-6} \text{mol}^{-2}\text{L}^2\text{s}^{-1})(0.06 \text{mol L}^{-1})(0.18 \text{mol L}^{-1})^2 &= 3.89 \text{mol L}^{-1}\text{s}^{-1} \end{aligned}$$

3. The decomposition of  $\text{NH}_3$  on platinum surface is zero order reaction. What are the rates of production of  $\text{N}_2$  and  $\text{H}_2$  if  $k = 2.5 \times 10^{-4} \text{mol}^{-1} \text{Ls}^{-1}$ ?

**Solution:**

Given:

The decomposition of  $\text{NH}_3$  on a platinum surface zero order reaction and showing below.



$$\text{We know, Rate of reaction} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt}$$

$$\text{However, } k = 2.5 \times 10^{-4} \text{mol}^{-1} \text{Ls}^{-1}$$

$$\text{For zero order reaction, rate of reaction} = k [\text{NH}_3]^0$$

$$\text{rate of reaction} = k$$

Therefore,

$$\text{Rate of reaction} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = k = 2.5 \times 10^{-4} \text{mol L}^{-1} \text{s}^{-1}$$

Therefore, the rate of production of  $\text{N}_2$  is

$$\frac{d[\text{N}_2]}{dt} = 2.5 \times 10^{-4} \text{mol L}^{-1} \text{s}^{-1}$$

And, the rate of production of  $\text{H}_2$  is

$$\begin{aligned} \frac{d[\text{H}_2]}{dt} &= \frac{3 d[\text{N}_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{mol L}^{-1} \text{s}^{-1} \\ &= 7.5 \times 10^{-4} \text{mol L}^{-1} \text{s}^{-1} \end{aligned}$$

4. The decomposition of dimethyl ether leads to the formation of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  and the reaction rate is given

$$\text{Rate} = k [\text{CH}_3\text{OCH}_3]^{\frac{3}{2}}$$

If the pressure is measured in bar and time in minutes, then what are the units of rate and rate constants ?

**Solution:**

Given:

Mentioned in question the pressure is in bar and time in minutes

$$\text{We know, Rate} = [\text{change in pressure}] / \text{time} = [\text{bar}] / \text{time}$$

$$\text{units of rate} = \text{bar min}^{-1}$$



$$\text{Rate} = k [\text{CH}_3\text{OCH}_3]^{\frac{3}{2}}$$

$$\text{unit of rate constant (k)} = \frac{\text{Rate}}{[\text{p}_{\text{CH}_3\text{OCH}_3}]^{\frac{3}{2}}} = \frac{[\text{bar}]/\text{time}}{[\text{bar}]^{\frac{3}{2}}} =$$

$$\text{bar min}^{-1}/[\text{bar}]^{\frac{3}{2}}$$

$$= \text{bar}^{\frac{1}{2}} \text{min}^{-1}$$

Concept insight: As  $\text{CH}_3\text{OCH}_3 \rightarrow \text{CH}_4 + \text{H}_2 + \text{CO}$  thus the rate = disappearance of diethyl ether

5. Mention the factors that affect the rate of a chemical reaction.

**Solution:**

These are the factors that affect the rate of a chemical reaction

1. Concentration
  2. Temperature
  3. Presence or absence of a catalyst
  4. Nature of reactants and products.
  5. pH of the medium
  6. The pressure inside a reaction container
  7. Dielectric constant
  8. Radiations / light
  9. Electric / magnetic fields (charged / polar species)
6. A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is (i) doubled (ii) reduced to half ?

**Solution:**

$\text{A} \rightarrow \text{product}$

Let the concentration of the reactant  $[\text{A}] = x$

It is mentioned in question reaction is second order with respect to a reactant so rate  $(r_1) = k [\text{A}]^2 = k [\text{x}]^2$

- (i) If the concentration of reactant become double i.e.  $[\text{A}] = 2x$

Then the rate of reaction would be  $(r_2) = k [2x]^2 = 4k[x] = 4r_1$

Therefore the rate become four time increase as concentration become double

- (ii) If the concentration of reactant become half i.e.  $[\text{A}] = \frac{x}{2}$

$$\text{Then the rate of reaction would be } (r_3) = k \left[ \frac{x}{2} \right]^2 = \frac{k[x]}{4} = \frac{r_1}{4}$$

Therefore the rate becomes decrease by  $\frac{1}{4}$  time as concentration becomes half

7. What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on rate constant be represented quantitatively?

**Solution:**

Earlier the rate constant (k) is nearly doubled with a rise in temperature by  $10^\circ$  for a chemical reaction.

The temperature effect on the rate constant (k) can be represented quantitatively by the Arrhenius equation.

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

Where k = the rate constant,

A = Arrhenius factor or the frequency factor,

R = gas constant,

T = Temperature and

$E_a$  = The energy of activation for the reaction

8. In a pseudo first hydrolysis of ester in water, the following results were obtained:

$\frac{t}{s}$	0	30	60	90
[Ester] $\text{mol L}^{-1}$	0.55	0.31	0.17	0.085

- (i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.  
 (ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.

**Solution:**

- (i) At time 30 second to 60-second Average rate of reaction between the time interval,

$$\begin{aligned} &= \frac{d[\text{Ester}]}{dt} \\ &= \frac{0.31 - 0.17}{60 - 30} \\ &= 4.67 \times 10^{-3} \text{mol L}^{-1} \text{s}^{-1} \end{aligned}$$

(ii) The formula used for pseudo-first-order reaction,

$$k = \frac{2.303}{t} \log \frac{[R_0]}{[R]}$$

(i) At  $t = 30\text{s}$ ,  $[R_0] = 0.55$ ;  $[R] = 0.31$  so  $k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.911 \times 10^{-2} \text{s}^{-1}$

(ii) At  $t = 60\text{s}$ ,  $[R_0] = 0.55$ ;  $[R] = 0.17$  so  $k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.957 \times 10^{-2} \text{s}^{-1}$

(iii) At  $t = 90\text{s}$ ,  $[R_0] = 0.085$ ;  $[R] = 0.17$  so  $k_3 = \frac{2.303}{60} \log \frac{0.55}{0.085} = 2.705 \times 10^{-2} \text{s}^{-1}$

Then, the average rate constant ( $k$ ) =  $\frac{k_1+k_2+k_3}{3} = \frac{(1.911 \times 10^{-2}) + (1.957 \times 10^{-2}) + (2.075 \times 10^{-2})}{3} = 1.98 \times 10^{-2} \text{s}^{-1}$

9. A reaction is first order in A and second order in B.

- Write the differential rate equation
- How is the rate affected on increasing the concentration of B three times?
- How is the rate affected when the concentrations of both A and B are doubled?

**Solution:**

(i) The differential rate equation will be

$$r_1 = -\frac{d[R]}{dt} = k[A][B]^2$$

(ii) According to question the concentration of B is increased three times, then

$$r_2 = k[A][3B]^2 = 9k[A][B]^2 = 9r_1$$

Therefore, the rate of reaction ( $r_2$ ) will increase nine times than the initial rate.

(iii) According to the question, the concentrations of both A and B are doubled,

$$r_1 = k[A][B]^2$$

$$r_3 = k[2A][2B]^2$$

$$r_3 = 8k[A][B]^2$$

Therefore, the rate of reaction ( $r_3$ ) will increase 8 times of initial rate ( $r_1$ ).

10. In a reaction between A and B, the initial rate of reaction ( $r_0$ ) was measured for different initial concentration of A and B as given below:

A/mol L <sup>-1</sup>	0.20	0.20	0.40
B. mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0$ / mol L <sup>-1</sup> s <sup>-1</sup>	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

What is the order of the reaction with respect to A and B?

**Solution:**

Assume; The order of the reaction with respect to A is x and with respect to B is y.

Therefore, the rate of reaction ( $r_0$ ) =  $k[A]^x[B]^y$

$$5.07 \times 10^{-5} = k[0.20]^x[0.30]^y \quad (i)$$

$$5.07 \times 10^{-5} = k[0.20]^x[0.10]^y \quad (ii)$$

$$1.43 \times 10^{-1} = k[0.40]^x[0.05]^y \quad (iii)$$

Dividing equation (i) by (ii), we obtain

$$\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k[0.20]^x[0.30]^y}{k[0.20]^x[0.10]^y}$$

$$\Rightarrow 1 = \frac{[0.30]^y}{[0.10]^y}$$

$$\Rightarrow \left(\frac{0.30}{0.10}\right)^0 = \left(\frac{0.30}{0.10}\right)^y$$

$$\Rightarrow y = 0$$

Dividing equation (iii) by (ii), we obtain

$$\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k[0.40]^x[0.05]^y}{k[0.20]^x[0.30]^y}$$

$$\Rightarrow \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.40]^x}{[0.20]^z} \left[ \begin{array}{l} \text{since } y = 0, \\ [0.05]^3 = [0.30]^3 = 1 \end{array} \right]$$

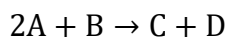
$$\Rightarrow 2.821 = 2^x$$

$$\Rightarrow \log 2.821 = x \log 2 \quad (\text{Taking log on both sides})$$

$$\Rightarrow x = \frac{\log 2.821}{\log 2} = 1.496 = 1.5 = \frac{3}{2}$$

From the above calculation, we get the order of the reaction with respect to A =  $\frac{3}{2}$  and with respect to B = zero.

11. The following results have been obtained during the kinetic studies of the reaction:



Experiment	A (mol L <sup>-1</sup> )	B (mol L <sup>-1</sup> )	Initial rate of formation of D/ mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$6.0 \times 10^{-3}$
II	0.3	0.2	$7.2 \times 10^{-2}$
III	0.3	0.4	$2.88 \times 10^{-1}$
IV	0.4	0.1	$2.40 \times 10^{-2}$

Determine the rate law and the rate constant for the reaction.

**Solution:**

Assume the order of the reaction with respect to A is x and with respect to B is y.

Therefore, rate of the reaction is given by,

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

According to the question,

$$6.0 \times 10^{-3} = k[0.1]^x[0.1]^y \quad \dots \text{(i)}$$

$$7.2 \times 10^{-2} = k[0.3]^x[0.2]^y \quad \dots \text{(ii)}$$

$$2.88 \times 10^{-1} = k[0.3]^x[0.4]^y \quad \dots \text{(iii)}$$

$$2.40 \times 10^{-2} = k[0.4]^x[0.1]^y \quad \dots \text{(iv)}$$

Dividing equation (iv) by (i), we obtain

$$\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k[0.4]^x[0.1]^y}{k[0.1]^x[0.1]^y}$$

$$\Rightarrow 4 \frac{[0.4]^x}{[0.1]^x}$$

$$\Rightarrow 4 = \left(\frac{0.4}{0.1}\right)^x$$

$$\Rightarrow (4)^1 = 4^x$$

$$\Rightarrow x = 1$$

Dividing equation (iii) by (ii), we obtain

$$\frac{2.88 \times 10^{-1}}{7.2 \times 10^{-2}} = \frac{k[0.3]^x[0.4]^y}{k[0.3]^x[0.2]^y}$$

$$\Rightarrow 4 = \left(\frac{0.4}{0.2}\right)^y$$

$$\Rightarrow 4 = 2^y$$

$$\Rightarrow 2^2 = 2^y$$

$$\Rightarrow y = 2$$

Therefore, the rate law is

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

From experiment (I), we get

$$k = \frac{6.0 \times 10^{-3} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.1 \text{ mol L}^{-1})(0.1 \text{ mol L}^{-1})^2}$$

$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

From experiment (II), we get

$$k = \frac{7.2 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol L}^{-1})(0.2 \text{ mol L}^{-1})^2}$$

$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

From experiment (III), we get

$$k = \frac{2.88 \times 10^{-1} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.3 \text{ mol L}^{-1})(0.4 \text{ mol L}^{-1})^2}$$

$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

From experiment (IV) we get

$$k = \frac{2.40 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1}}{(0.4 \text{ mol L}^{-1})(0.1 \text{ mol L}^{-1})^2}$$

$$= 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$$

Therefore, the rate constant,  $k = 6.0 \text{ L}^2 \text{ mol}^{-2} \text{ min}^{-1}$

12. The reaction between A and B is first order with respect to A and zero order with respect to B. Fill in the blanks in the following table:

Experiment	[A] mol L <sup>-1</sup>	[B] mol L <sup>-1</sup>	Initial rate/mol L <sup>-1</sup> min <sup>-1</sup>

I	0.1	0.1	$2.0 \times 10^{-2}$
II	--	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	--
IV	--	0.2	$2.0 \times 10^{-2}$

**Solution:**

According to question the given reaction is of the first order with respect to A and of zero order with respect to B.

Therefore, the rate of the reaction is given by,

$$\text{Rate} = k[A]^1[B]^0$$

$$\text{Rate} = k[A]$$

From experiment II, we get

$$2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = k(0.1 \text{ mol L}^{-1})$$

$$k = 0.2 \text{ min}^{-1}$$

From experiment II, we get

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

$$[A] = 0.2 \text{ mol L}^{-1}$$

From experiment III, we get

$$\text{Rate} = 0.2 \text{ min}^{-1} \times 0.4 \text{ mol L}^{-1}$$

$$= 0.08 \text{ mol L}^{-1} \text{ min}^{-1}$$

From experiment IV, we get

$$2.0 \times 10^{-2} \text{ mol L}^{-1} \text{ min}^{-1} = 0.2 \text{ min}^{-1} [A]$$

$$[A] = 0.1 \text{ mol L}^{-1}$$

Experiment	[A] mol L <sup>-1</sup>	[B] mol L <sup>-1</sup>	Initial rate/mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$2.0 \times 10^{-2}$
II	0.2	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	$8.0 \times 10^{-2}$
IV	0.1	0.2	$2.0 \times 10^{-2}$

Concept Insight: First calculate the Rate constant and then putting each the value in different experiment we can calculate different values.

13. Calculate the half-life of a first order reaction from their rate constants given below:

- (i)  $200 \text{ s}^{-1}$   
 (ii)  $2 \text{ min}^{-1}$   
 (iii)  $4 \text{ years}^{-1}$

**Solution:**

According to question the unit of rate constant is  $\text{time}^{-1}$

(i) Half life  $\left(t_{\frac{1}{2}}\right) = \frac{0.693}{k} = \frac{0.693}{200 \text{ s}^{-1}} = 3.47 \text{ s}$  (approximately)

(ii) Half life,  $\left(t_{\frac{1}{2}}\right) = \frac{0.693}{k} = \frac{0.693}{2 \text{ min}^{-1}}$   
 $= 0.35 \text{ min}$  (approximately)

(iii) Half life  $\left(t_{\frac{1}{2}}\right) = \frac{0.693}{k} = \frac{0.693}{4 \text{ years}^{-1}}$   
 $= 0.173 \text{ years}$  (approximately)

14. The half-life for radioactive decay of  $^{14}\text{C}$  is 5730 years. An archaeological artifact containing wood had only 80% of the  $^{14}\text{C}$  found in a living tree. Estimate the age of the sample.

**Solution:**

Given:  $[R_0] = 100$

$[R] = 80$

half-life for radioactive decay of  $^{14}\text{C} = 5730 \text{ years}$

We know radioactive decay reaction is the first order

Here,  $k = \frac{0.693}{t_{\frac{1}{2}}}$   
 $= \frac{0.693}{5730} \text{ years}^{-1}$

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{\frac{0.693}{5730}} \log \frac{100}{80}$$

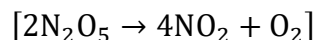
$$= 1845 \text{ years}$$



Hence, the age of the sample is 1845 years.

Concept Insight: 80% of carbon found means that the initial value  $[R_0]$  of the C is 100 and that  $[R]$  is 80.

15. The experimental data for decomposition of  $N_2O_5$



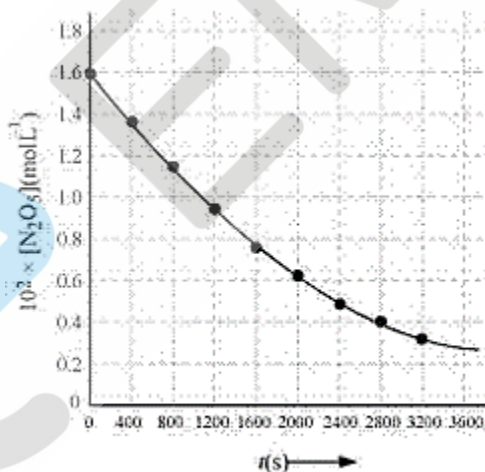
In gas phase at 318 K are given below:

t(s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5] \text{ mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

- Plot  $[N_2O_5]$  against t.
- Find the half-life period for the reaction.
- Draw a graph between  $\log[N_2O_5]$  and t.
- What is the rate law?
- Calculate the rate constant.
- Calculate the half-life period from k and compare it with (ii).

**Solution:**

- (i)

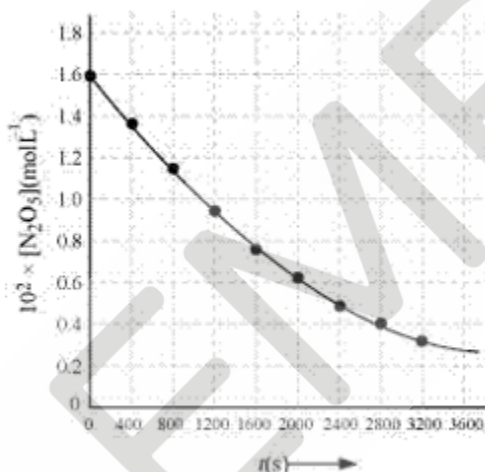


- (ii) half life: time required for a substance to reduce to half of its initial concentration

$$c_t = \frac{C_0}{2} = \frac{1.630 \times 10^2}{2} \text{ mol L}^{-1} = 81.5 \text{ mol L}^{-1}, \text{ is the half life. From the graph, the half life is obtained as 1450 s.}$$

(iii)

t(s)	$10^2 \times [\text{N}_2\text{O}_5]/\text{mol L}^{-1}$	$\log [\text{N}_2\text{O}_5]$
0	1.63	-1.79
400	1.36	-1.87
800	1.14	-1.94
1200	0.93	-2.03
1600	0.78	-2.11
2000	0.64	-2.19
2400	0.43	-2.28
2800	0.43	-2.37
3200	0.35	-2.46



(iv) The given reaction is of the first order as the plot,  $\log[\text{N}_2\text{O}_5]$  v/s t, is straight line. Therefore, the rate law of the reaction is

$$\text{Rate} = k[\text{N}_2\text{O}_5]$$

(v) From the plot,  $\log[\text{N}_2\text{O}_5]$  v/s t, we get

$$\text{Slope} = \frac{-2.46 - (-1.79)}{3200 - 0} = \frac{-0.67}{3200}$$

Again, slope of the line of the plot  $\log[\text{N}_2\text{O}_5]$  v/s time (t) is given by

$$\begin{aligned} \Rightarrow -\frac{k}{2.303} &= -\frac{0.67}{3200} \\ \Rightarrow k &= 4.82 \times 10^{-4} \text{s}^{-1} \end{aligned}$$

(vi) Half-life is given by,

$$\begin{aligned}
 t_{\frac{1}{2}} &= \frac{0.639}{k} \\
 &= \frac{0.693}{4.82 \times 10^{-4} \text{ s}} \\
 &= 1.438 \times 10^3 \text{ s} \\
 &= 1438 \text{ s}
 \end{aligned}$$

This value, 1438 s, is very close to the value that was obtained from the graph.

16. The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the initial concentration of the reactant to its  $\frac{1}{16}$  value?

**Solution:**

Given : rate constant (k) for a first order reaction =  $60 \text{ s}^{-1}$

Let assume: initial concentration  $[R]_0 = x$

Final concentration  $[R] = \frac{x}{16}$ , reduce the initial concentration of the reactant to its  $\frac{1}{16}$  value.

Formula ,

$$\begin{aligned}
 t &= \frac{2.303}{k} \log \frac{[R]_0}{[R]} \text{ for first order reaction} \\
 &= \frac{2.303}{k} \log \frac{x}{\frac{x}{16}} = \frac{2.303}{k} \log \frac{16}{1} = \frac{2.303}{60 \text{ s}^{-1}} \log 16 \\
 &= 4.6 \times 10^{-2} \text{ s (approximately)}
 \end{aligned}$$

Hence, the required time is  $4.6 \times 10^{-2} \text{ s}$ .

Concept Insight: If the initial concentration is one than the final concentration is  $\frac{1}{16}$ .

17. During nuclear explosion, one of the products is  $^{90}\text{Sr}$  with half-life of 28.1 years. If  $1 \mu\text{g}$  of  $^{90}\text{Sr}$  was absorbed in the bones of a newly born baby instead of calcium, how much of it will remain after 10 years and 60 years if it is not lost metabolically.

**Solution:**

Given: half-life = 28.1 years

$^{90}\text{Sr}$  was absorbed in the bones =  $1 \mu\text{g}$

$$\text{Here, } k = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{28.1} \text{ y}^{-1}$$

Formula,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} \text{ for first order reaction}$$

$\Rightarrow$   $^{90}\text{Sr}$  will remain after 10 years

$$t = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow 10 = \frac{2.303}{\frac{0.693}{28.1}} (-\log [R])$$

$$\Rightarrow \log [R] = -\frac{10 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \text{antilog}(-0.1071)$$

$$= \text{antilog}(\bar{1}.8929)$$

$$= 0.7814 \mu\text{g}$$

Therefore, 0.7814  $\mu\text{g}$  of  $^{90}\text{Sr}$  will remain after 10 years.

$\Rightarrow$   $^{90}\text{Sr}$  will remain after 60 years

$$\text{Formula used Again, } t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$

$$\Rightarrow 60 = \frac{2.303}{\frac{0.693}{28.1}} \log \frac{1}{[R]}$$

$$\Rightarrow \log [R] = -\frac{60 \times 0.693}{2.303 \times 28.1}$$

$$\Rightarrow [R] = \text{antilog}(-0.6425)$$

$$= \text{antilog}(\bar{1}.3575)$$

$$= 0.2278 \mu\text{g}$$

Therefore, 0.2278  $\mu\text{g}$  of  $^{90}\text{Sr}$  will remain after 60 years.

- 18.** For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

**Solution:**

Given: order reaction = first

Reaction complete 99% then

We know  $[R]_0 = 100$ ;  $[R] = 100 - 99$

We know that,  $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

The time required for 99% completion ( $t_1$ ) =  $\frac{2.303}{k} \log \frac{100}{100-99}$

$$= \frac{2.303}{k} \log 100$$

$$= 2 \times \frac{2.303}{k} \text{ equation 1}$$

Reaction Complete 90% then

We know  $[R]_0 = 100$ ;  $[R] = 100 - 90$

The time required for 90% completion is ( $t_2$ ) =  $\frac{2.303}{k} \log \frac{100}{100-90}$

$$= \frac{2.303}{k} \log 10$$

$$= \frac{2.303}{k} \text{ equation 2}$$

Equation 1 divide by equation 2 we get  $t_1 = 2t_2$

Hence, first order reaction the time required for 99% completion of a is twice the time required for the completion of 90%.

Concept Insight: Let initial concentration be 'a' than the final concentration is 'a - x' That is  $[R]_0 = 100$  than  $[R] = 100 - 90$

19. A first order reaction takes 40 min for 30% decomposition. Calculate  $t_{\frac{1}{2}}$ .

**Solution:**

Given: order of reaction = first

$[R]_0 = 100$ ;  $[R] = 100 - 30 = 70$

Formula:  $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$

$$k = \frac{2.303}{40 \text{ min}} \log \frac{100}{70}$$

$$= \frac{2.303}{40 \text{ min}} \log \frac{10}{7}$$

$$= 8.9168 \times 10^{-3} \text{ min}^{-1}$$

$$\text{Formula for } t_{\frac{1}{2}} \text{ of the decomposition reaction for } = \frac{0.693}{k}$$

$$= \frac{0.693}{8.916 \times 10^{-3}} \text{ min} = 77.71 \text{ min}$$

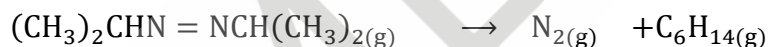
20. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

t(sec)	P(mm of Hg)
0	35.0
360	54.0
720	63.0

Calculate the rate constant.

**Solution:**

The decomposition of azoisopropane to hexane and nitrogen at 543 K is first order reaction which is represented by the following equation.



$$\text{At } t = 0 \quad P_0 \quad 0 \quad 0$$

$$\text{At } t = t \quad P_0 - p \quad p \quad p$$

After time, t, total pressure,  $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

Therefore,  $P_0 - p = P_0 - (P_t - P_0)$

$$= 2P_0 - P_t$$

$$\text{Formula: for a first order reaction } k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

Where  $[R]_0 = P_0$ ;  $[R] = P_0 - p$

$$k = \frac{2.303}{t} \log \frac{P_0}{P_0 - p}$$

$$= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

$$\text{At } t = 360 \text{ s, } k = \frac{2.303}{360 \text{ s}} \log \frac{(35.0)}{(2 \times 35.0 - 54.0)} = 2.175 \times 10^{-3} \text{ s}^{-1}$$

$$\text{At } t = 720 \text{ s, } k = \frac{2.303}{7020 \text{ s}} \log \frac{(35.0)}{(2 \times 35.0 - 63.0)} = 2.235 \times 10^{-3} \text{ s}^{-1}$$

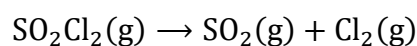
Hence, the average value of rate constant is

$$k = \frac{(2.175 \times 10^{-3}) + (2.235 \times 10^{-3})}{2} \text{ s}^{-1}$$

$$= 2.21 \times 10^{-3} \text{ s}^{-1}$$

Note: There is a slight variation in this answer and the one given in the NCERT text book.

21. The following data were obtained during the first order thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume.



Experiment	Time/s <sup>-1</sup>	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

**Solution:**

The thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume is represented by the following equation.



$$\text{At } t = 0 \quad P_0 \quad 0 \quad 0$$

$$\text{At } t = t \quad P_0 - p \quad p \quad p$$

After time,  $t$ , total pressure,  $P_t = (P_0 - p) + p + p$

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

$$\text{Therefore, } P_0 - p = P_0 - (P_t - P_0)$$

$$= 2P_0 - P_t$$

Formula: for a first order reaction rate constant  $(k) = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

Where  $[R]_0 = P_0$ ;  $[R] = 2P_0 - p$

$$k = \frac{2.303}{t} \log \frac{P_0}{2P_0 - p}$$

$$= \frac{2.303}{t} \log \frac{P_0}{2P_0 - P_t}$$

$$\text{When } t = 100 \text{ s, } k = \frac{2.303}{100} \log \frac{(0.5)}{(2 \times 0.5 - 0.6)}$$

$$= 2.231 \times 10^{-3} \text{ s}^{-1}$$

When  $P_t = 0.65 \text{ atm}$ ,

$$P_0 + p = 0.65$$

$$\Rightarrow p = 0.65 - P_0$$

$$P_0 = 0.5$$

$$p = 0.65 - 0.5$$

$$p = 0.15 \text{ atm}$$

Therefore, when the total pressure is 0.65 atm, pressure of  $\text{SOCl}_2$  ( $P_{\text{SOCl}_2}$ ) =

$$P_0 - p = 0.5 - 0.15$$

$$= 0.35 \text{ atm}$$

when total pressure is 0.65 atm, the rate of equation ( $r$ ) =  $k(P_{\text{SOCl}_2})$

$$= (2.23 \times 10^{-3} \text{ s}^{-1})(0.35 \text{ atm})$$

$$= 7.8 \times 10^{-4} \text{ atm s}^{-1}$$

22. The rate constant for the decomposition of  $\text{N}_2\text{O}_5$  at various temperatures is given below:

$T/^\circ\text{C}$	0	20	40	60	80
$10^5 \times k/\text{s}^{-1}$	0.0787	1.70	25.7	178	2140

Draw a graph between  $\ln k$  and  $1/T$  and calculate the values of  $A$  and  $E_a$ .

Predict the rate constant at  $30^\circ$  and  $50^\circ\text{C}$ .

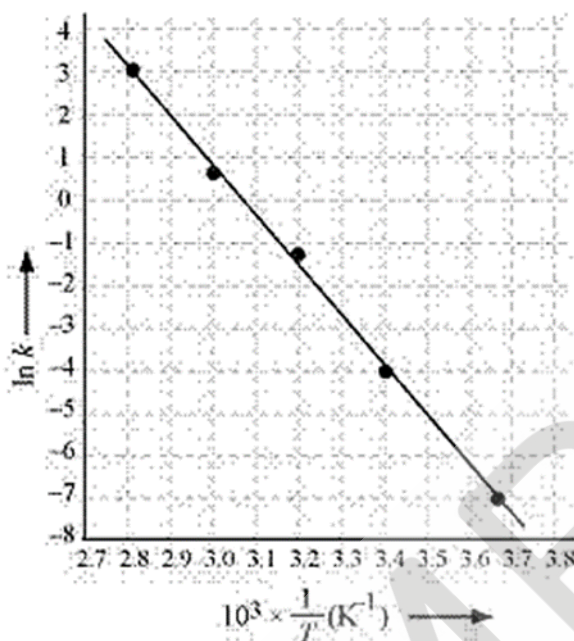
**Solution:**

From the given data, we obtain

$T/^\circ\text{C}$	0	20	40	60	80
$\frac{T}{\text{K}}$	273	293	313	333	353
$\frac{1}{T} \text{K}^{-1}$	$3.66 \times 10^{-3}$	$3.41 \times 10^{-3}$	$3.19 \times 10^{-3}$	$3.0 \times 10^{-3}$	$2.83 \times 10^{-3}$



$10^5 \times k$ $/s^{-1}$	0.0787	1.70	25.7	178	2140
$\ln k$	-7.147	-4.075	-1.359	-0.577	3.063



Slope of the line,

$$\frac{y_2 - y_1}{x_2 - x_1} = 12.301K$$

According to Arrhenius equation,

$$\text{Slope} = -\frac{E_a}{R}$$

$$\Rightarrow E_a = -\text{Slope} \times R$$

$$= -(-12.301 K) \times (8.314 J K^{-1}mol^{-1})$$

$$= 102.27 kJ mol^{-1}$$

Again,

$$\ln k = \ln A - \frac{E_a}{RT}$$

$$\ln A = \ln k + \frac{E_a}{RT}$$

When  $T = 273 K$ ,

$$\ln k = -7.147$$

$$\text{Then, } \ln A = -7.147 + \frac{102.27 \times 10^3}{8.314 \times 273}$$

$$= 37.911$$

$$\text{Therefore, } A = 2.91 \times 10^6$$

$$\text{When } T = 30 + 273 \text{ K} = 303\text{K,}$$

$$\frac{1}{T} = 0.0033 \text{ K} = 3.3 \times 10^{-3}\text{K}$$

$$\text{Then, at } \frac{1}{T} = 3.3 \times 10^{-3}\text{K,}$$

$$\ln k = -2.8$$

$$\text{Therefore, } k = 6.08 \times 10^{-2}\text{s}^{-1}$$

$$\text{Again, when } T = 50 + 273 \text{ K} = 323 \text{ K,}$$

$$\frac{1}{T} = 0.0031 \text{ K} = 3.1 \times 10^{-3}\text{K}$$

$$\text{Then, at } \frac{1}{T} = 3.1 \times 10^{-3}\text{K,}$$

$$\ln k = -0.5$$

$$\text{Therefore, } k = 0.607 \text{ s}^{-1}$$

23. The rate constant for the decomposition of hydrocarbons is  $2.418 \times 10^{-5}\text{s}^{-1}$  at 546 K. If the energy of activation is  $179.9 \frac{\text{kJ}}{\text{mol}}$ , what will be the value of pre-exponential factor.

**Solution:**

Given: rate constant ( $k$ ) =  $2.418 \times 10^{-5}\text{s}^{-1}$  it is first order reaction

$$T = 546 \text{ K}$$

$$E_a = 179.9 \text{ kJ mol}^{-1} = 179.9 \times 10^3 \text{ J mol}^{-1}$$

According to the Arrhenius equation,

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

$$\Rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

$$\Rightarrow \log k = \log A - \frac{E_a}{2.303RT}$$

$$\Rightarrow \log A = \log k + \frac{E_a}{2.303RT}$$

$$= \log(2.418 \times 10^{-5} \text{s}^{-1}) + \frac{179.9 \times 10^3 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ JK}^{-1} \text{ mol}^{-1} \times 546 \text{ K}}$$

$$= (0.3835 - 5) + 17.2082$$

$$= 12.5917$$

Therefore,  $A = \text{antilog}(12.5917)$

$$3.9 \times 10^{12} \text{ s}^{-1}$$

Concept Insight: 'A' is called Arrhenius factor, frequency factor or pre-exponential factor.

24. Consider a certain reaction  $A \rightarrow \text{Products}$  with  $k = 2.0 \times 10^{-2} \text{ s}^{-1}$ . Calculate the concentration of A remaining after 100 s if the initial concentration of A is  $1.0 \text{ mol L}^{-1}$ .

**Solution:**

Given:  $k = 2.0 \times 10^{-2} \text{ s}^{-1}$

$T = 100 \text{ s}$

$[A]_0 = 1.0 \text{ mol L}^{-1}$

Since the unit of  $k$  is  $\text{s}^{-1}$ , the given reaction is a first order reaction.

Formula:  $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$

$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} \log \frac{1.0}{[R]}$$

$$\Rightarrow 2.0 \times 10^{-2} \text{ s}^{-1} = \frac{2.303}{100 \text{ s}} (\log[R])$$

$$= -\log[R] = \frac{2.0 \times 10^{-2} \times 100}{2.303}$$

$$\Rightarrow [R] = \text{antilog} \left( -\frac{2.0 \times 10^{-2} \times 100}{2.303} \right)$$

$$= 0.135 \text{ mol L}^{-1} \text{ (approximately)}$$

Hence the remaining concentration of A is  $0.135 \text{ mol L}^{-1}$ .

Concept insight: since the value of  $k$  is  $\text{s}^{-1}$ . Hence it is a first order reaction. So looking at the units of the rate constant we can find out the order of reaction.

25. Sucrose decomposes in acid solution into glucose and fructose according to the first order rate law, with  $t_{\frac{1}{2}} = 3.00$  hours. What fraction of sample of sucrose remains after 8 hours?

**Solution:**

Given:

Order of reaction: first

Half life  $t_{\frac{1}{2}} = 3.00$  hoursFormula: For a first order reaction rate constant  $(k) = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$ We know rate constant  $(k) = \frac{0.693}{t_{\frac{1}{2}}} = \frac{0.693}{3} \text{ h}^{-1} = 0.231 \text{ h}^{-1}$ Then,  $0.231 \text{ h}^{-1} = \frac{2.303}{8 \text{ h}} \log \frac{[R]_0}{[R]}$ 

$$\Rightarrow \log \frac{[R]_0}{[R]} = \frac{0.231 \text{ h}^{-1} \times 8 \text{ h}}{2.303}$$

$$\Rightarrow \frac{[R]_0}{[R]} = \text{antilog} (0.8024)$$

$$\Rightarrow \frac{[R]_0}{[R]} = 6.3445$$

$$\Rightarrow \frac{[R]_0}{[R]} = 0.158$$

Hence, the fraction of sample of sucrose that remains after 8 hours is 0.158.

26. The decomposition of hydrocarbon follows the equation  $k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K/T}}$

Calculate  $E_a$ .**Solution:**

The given equation is

$$k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000 \text{ K/T}} \quad \text{equation (i)}$$

$$k = A e^{-\frac{E_a}{RT}} \quad \text{equation (ii)}$$

As compare the equation (i) and (ii), we get

$$\frac{E_a}{RT} = \frac{28000 \text{ K}}{T}$$

$$\Rightarrow E_a = R \times 28000 \text{ K}$$

$$= 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 28000 \text{ K}$$

$$= 232792 \text{ J mol}^{-1}$$

$$\begin{aligned}
 &= 232.792 \text{ kJ mol}^{-1} \\
 \text{or } E_a &= R \times 28000 \text{ K} \\
 &= 2 \text{ cal K}^{-1} \text{ mol}^{-1} \times 28000 \text{ K} \\
 &= 56000 \text{ J mol}^{-1} \\
 &= 56 \text{ kJ mol}^{-1}
 \end{aligned}$$

27. The rate constant for the first order decomposition of  $\text{H}_2\text{O}_2$  is given by the following equation:

$$\log k = 14.34 - 1.25 \times 10^4 \text{K/T}$$

Calculate  $E_a$  for this reaction and at what temperature will its half-period be 256 minutes.

**Solution:**

Given:  $\log k = 14.34 - 1.25 \times 10^4 \text{K/T}$

Half life = 256 minute

Arrhenius equation is given by,

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

$$\Rightarrow \ln k = \ln A - \frac{E_a}{RT}$$

$$\Rightarrow \log k = \log A - \frac{E_a}{2.303 RT} \quad \text{equation (i)}$$

given in question:  $\log k = 14.34 - 1.25 \times 10^4 \text{K/T}$  equation (ii)

From equation (i) and (ii), we obtain

$$\frac{E_a}{2.303 RT} = \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\Rightarrow E_a = 1.25 \times 10^4 \text{ K} \times 2.303 \times R$$

$$= 1.25 \times 10^4 \text{ K} \times 2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1} = 239.34 \text{ kJ mol}^{-1}$$

Also, when  $t_{\frac{1}{2}} = 256$  minutes,

$$\text{We know rate constant (k)} = \frac{0.693}{t_{1/2}} = \frac{0.693}{256} = 2.707 \times 10^{-3} \text{ min}^{-1}$$

$$= \frac{2.707 \times 10^{-3}}{60} \text{ sec}^{-1}$$

$$= 4.51 \times 10^{-5} \text{ s}^{-1}$$

It is also given that,  $\log k = 14.34 - 1.25 \times 10^4 \text{K/T}$

$$\Rightarrow \log(4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\Rightarrow \log(0.654 - 05) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

$$\Rightarrow \frac{1.25 \times 10^4 \text{ K}}{T} = 18.686$$

$$\Rightarrow T = \frac{1.25 \times 10^4 \text{ K}}{18.686}$$

$$= 668.95 \text{ K}$$

$$= 669 \text{ K (approximately)}$$

28. 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 of  $60 \text{ kJ mol}^{-1}$ . At what temperature would  $k$  be  $1.5 \times 10^4 \text{ s}^{-1}$ ?

**Solution:**

$$\text{Given: } k_1 = 4.5 \times 10^3 \text{ s}^{-1}$$

$$T_1 = 273 + 10 = 283 \text{ K}$$

$$k_2 = 1.5 \times 10^4 \text{ s}^{-1}$$

$$E_a = 60 \text{ kJ mol}^{-1} = 6.0 \times 10^4 \text{ J mol}^{-1}$$

$$\text{Formula: Arrhenius equation, } \log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left( \frac{T_2 - T_1}{T_1 T_2} \right)$$

Put the given values in formula we get

$$\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{6.0 \times 10^4 \text{ J mol}^{-1}}{2.303 \times 8.314 \text{ J K}^{-1} \text{ mol}^{-1}} \left( \frac{T_2 - 283}{283 T_2} \right)$$

$$\Rightarrow 0.5229 = 3133.627 \left( \frac{T_2 - 283}{283 T_2} \right)$$

$$\Rightarrow \frac{0.5229 \times 283 T_2}{3133.627} = T_2 - 283$$

$$\Rightarrow 0.0472 T_2 = T_2 - 283$$

$$\Rightarrow 0.9528 T_2 = 283$$

$$\Rightarrow T_2 = 297.019 \text{ K (approximately)}$$

$$= 297 \text{ K}$$

$$297 \text{ K} - 273 \text{ K} = 24^\circ\text{C}$$

Hence,  $k$  would be  $1.5 \times 10^4 \text{ s}^{-1}$  at  $24^\circ\text{C}$ .

29. The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K. if the value of  $A$  is  $4 \times 10^{10} \text{ s}^{-1}$ . Calculate  $k$  at 318 K and  $E_a$ .

**Solution:**

Given: order of reaction = first

Temperature ( $t$ ) = 298 k; reaction completion = 10%

Temperature ( $t'$ ) = 308 k; reaction completion = 25%

Temperature ( $t_3$ ) = 318 k

$$A = 4 \times 10^{10} \text{ s}^{-1}$$

For a first order reaction,

$$t = \frac{2.303}{k} \log \frac{[R_0]}{[R]}$$

The time required for 10% completion of a first order reaction at 298 K:

$$[R_0] = 100; [R] = 100 - 10 = 90$$

$$\begin{aligned} t &= \frac{2.303}{k} \log \frac{100}{90} \\ &= \frac{0.1054}{k} \end{aligned}$$

The time required for 25% completion of a first order reaction at 398 K:

$$[R_0] = 100; [R] = 100 - 25 = 75$$

$$\begin{aligned} t' &= \frac{2.303}{k'} \log \frac{100}{75} \\ &= \frac{2.2877}{k'} \end{aligned}$$

According to the question

$$t = t'$$

$$\Rightarrow \frac{0.1054}{k} = \frac{0.2877}{k'}$$

$$\Rightarrow \frac{k'}{k} = 2.7296$$

From Arrhenius equation, we obtain

$$\log \frac{k'}{k} = \frac{E_a}{2.303 R} \left( \frac{T' - T}{TT'} \right)$$

$$\log(2.7296) = \frac{E_a}{2.303 \times 8.314} \left( \frac{308 - 298}{298 \times 308} \right)$$

$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log(2.7296)}{308 - 298}$$

$$= 76640.096 \text{ J mol}^{-1}$$

$$= 76.64 \text{ kJ mol}^{-1}$$

To calculate k at 318 K,

It is given that,  $A = 4 \times 10^{10} \text{ s}^{-1}$ ,  $T_3 = 318 \text{ K}$

Again, from Arrhenius equation, we obtain

$$\log k = \log A - \frac{E_a}{2.303RT_3}$$

$$= \log(4 \times 10^{10}) - \frac{76.64 \times 10^3}{2.303 \times 8.314 \times 318}$$

$$= (0.6021 + 10) - 12.5876$$

$$= -1.9855$$

Therefore,  $k = \text{Antilog}(-1.9855)$

$$= 1.034 \times 10^{-2} \text{ s}^{-1}$$

- 30.** The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

**Solution:**

Given:  $k_2 = 4k_1$

$T_1 = 293 \text{ K}$

$T_2 = 313 \text{ K}$

From the Arrhenius equation, we obtain

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

Put all values from given data

$$\text{We get } \log \frac{4k_1}{k_1} = \frac{E_a}{2.303 \times 8.314} \left( \frac{313 - 293}{293 \times 313} \right)$$



$$\Rightarrow 0.6021, = \frac{20 \times E_a}{2.303 \times 8.314 \times 293 \times 313}$$

$$\Rightarrow E_a = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$$

$$= 52863.33 \text{ J mol}^{-1}$$

$$= 52.86 \text{ kJ mol}^{-1}$$

Hence, the required energy of activation is  $52.86 \text{ kJmol}^{-1}$ .