

## **NCERT Solution for Class 12**

## Chemistry

## **Chapter 3 - Chemical Kinetics**

**Intext Exercise** 

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.

**Ans:** The average rate of the reaction can be calculated by dividing the change in the rate of decreasing the rate of reactant by the time taken. This is given below:

Average rate =  $-\frac{d[R]}{dt}$ This can be written as: Average rate =  $-\frac{[R]_2 - [R]_1}{t_2 - t_1}$   $R_1 = 0.03 \text{ M}$   $R_2 = 0.02 \text{ M}$   $t_2 - t_1 = 25 \text{ min}$ Putting the values, we get: Average rate =  $-\frac{0.02 - 0.03}{25}$ Average rate =  $-\frac{-0.01}{25} = 4 \times 10^{-4} \text{ M min}^{-1}$ So, the average rate in minutes will be  $4 \times 10^{-4} \text{ M min}^{-1}$ Now, to find the average rate in seconds we have to divide the above answer by 60. So, the answer will be:

Average rate = 
$$-\frac{4 \times 10^{-4}}{60} = 6.66 \times 10^{-6} \text{ M s}^{-1}$$

Therefore, the average rate in seconds will be  $\,6.66\times 10^{^{-6}}$  M  $s^{^{-1}}$ 

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2. In a reaction,  $2A \rightarrow$  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.

**Ans:** The average rate of the reaction can be calculated by dividing the change in the rate of decreasing the rate of reactant by the time taken. This is given below:

Average rate =  $-\frac{1}{2} \frac{\Delta[A]}{\Delta t}$ This is due the fact that the reaction given is:  $2A \rightarrow Products$ So, the average rate will be written as:  $Average rate = -\frac{1}{2} \frac{[A]_2 - [A]_1}{t_2 - t_1}$   $A_1 = 0.5 \text{ M}$   $A_2 = 0.4 \text{ M}$   $t_2 - t_1 = 10 \text{ min}$ Putting the values, we get:  $Average rate = -\frac{1}{2} \times \frac{0.4 - 0.5}{10}$   $Average rate = -\frac{1}{2} \times \frac{-0.1}{10} = 5 \times 10^{-3} \text{ M min}^{-1}$ So, the average rate will be  $5 \times 10^{-3} \text{ M min}^{-1}$ 

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

Ans: The order of the reaction can be calculated by adding the stoichiometry coefficients of the reactants in the given rate of the reaction.

Given the rate is  $r = k [A]^{1/2} [B]^2$ 

So, the order will be:

Order = 
$$2 + \frac{1}{2} = 2.5$$

So, the order of the reaction is 2.5

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4. The conversion of the 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?

**Ans:** The reaction will be:

 $X \rightarrow Y$ 

As the question says that this reaction follows the second order reaction, we can write the rate law equation as:

Rate =  $k[X]^2 = ka^2$ 

If  $[X] = a \mod L$ 

It is said that the concentration of X increases by three times, so we can write:

 $[X] = 3a \mod L$ 

Therefore, the rate of reaction will be:

 $Rate = k (3a)^2 = 9 ka^2$ 

Thus, the rate of the reaction will increase by 9 times or the rate formation will increase by 9 times.

# 5. A first order reaction has a rate constant $1.15 \times 10^{-3}$ s<sup>-1</sup>. How long will 5 g reactant take to reduce to 3 g?

**Ans:** The initial amount of the reactant is given as 5 g. We can write:

 $[R]_0 = 5 g$ 

The final amount of the reactant is given as 3 g. We can write:

[R] = 3 g

We are also given the value of rate constant as:

Rate constant =  $1.15 \times 10^{-3}$  s<sup>-1</sup>

We know that the reaction is a 1<sup>st</sup> order reaction, the time can be calculated by:

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

Putting the values in the above formula, we get:

$$t = \frac{2.303}{1.15 \text{ x } 10^{-3}} \log \frac{5}{3}$$



 $t = \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219$ t = 444 seconds So, the time taken will be 444 seconds.

# 6. Time required to decompose SO<sub>2</sub>Cl<sub>2</sub> to half its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Ans: We are given that the decomposition of  $SO_2Cl_2$  is a first order reaction. So, we can write:

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

It is mentioned that the time required for the initial amount to become half is 60 minutes.

$$t_{1/2} = 60 \min$$

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

Putting the value, we get:

$$k = \frac{0.693}{60 \times 60} = 1.925 \times 10^{-4} \text{ s}^{-1}$$

Thus, the rate constant is  $1.925 \times 10^{-4}$  s<sup>-1</sup>.

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

Ans: An increase of 10 degrees in temperature causes a reaction's rate constant to almost double in size. In any case, the Arrhenius equation gives the exact temperature dependency of a chemical reaction rate.

The Arrhenius equation is given below:

 $k = A e^{-E_a/Rt}$ 

Where, A is the Arrhenius factor or the frequency factor,

T is the temperature,

R is the gas constant,

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 $E_a$  is the activation energy.

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>.

Ans: The formula that can be used to solve the question is:

$$\log \frac{\mathbf{k}_1}{\mathbf{k}_2} = \frac{\mathbf{E}_a}{2.303 \mathrm{R}} \left[ \frac{\mathbf{T}_2 - \mathbf{T}_1}{\mathbf{T}_1 \mathbf{T}_2} \right]$$

 $T_1$  temperature given is absolute temperature and it is equal to 298 K.

 $T_2 = 298 + 10 = 308 \text{ K}$ 

It is given that the rate of the chemical reaction double for an increase of 10 K, therefore, we can write the values of rate constant as:

 $\mathbf{k}_1 = \mathbf{x}$ 

 $k_{2} = 2x$ 

Also,  $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$ 

Now, putting all the values in the formula, we get:

$$\log \frac{2x}{x} = \frac{E_{a}}{2.303 \times 8.314} \left[ \frac{10}{298 \times 308} \right]$$
$$\log 2 = \frac{E_{a}}{2.303 \times 8.314} \left[ \frac{10}{298 \times 308} \right]$$
$$E_{a} = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$
$$E_{a} = 52897.78 \text{ J mol}^{-1}$$
$$E_{a} = 52.89 \text{ kJ mol}^{-1}$$

9. The activation energy for the reaction  $2HI_{(g)} \rightarrow H_{2_{(g)}} + I_{2_{(g)}}$  is 209.5 kJ mol<sup>-1</sup> at

581 K. Calculate the fraction of molecules of molecules having energy equal to or greater than activation energy.

Ans: We are given the activation energy as 209.5 kJ mol<sup>-1</sup> T = 581 K

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 $R = 8.314 \; J \; K^{\text{--1}} \; mol^{\text{--1}}$ 

Now, the fraction of molecules of reactants having energy equal to or greater than activation energy is given as:

 $x = e^{E_a/RT}$   $\ln x = \frac{-E_a}{RT}$   $\log x = \frac{-E_a}{2.303 \text{ RT}}$   $\log x = \frac{209500}{2.303 \times 8.314 \times 581} = 18.8323$ Now, taking the antilog: x = Antilog (18.8323) x = 1.471 × 10<sup>-19</sup>

## **NCERT Exercise**

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

(i) 3 NO(g)  $\rightarrow$  N<sub>2</sub>O(g) Rate = k[NO]<sup>2</sup>

Ans: We are given:

Rate =  $k[NO]^2$ 

From this we can see that the order of the reaction = 2

$$k = \frac{rate}{[No]^2}$$

Dimensions will be:

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

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## (ii) $H_2O_2(aq)+3I^{-}(aq)+2H^{+} \rightarrow 2H_2O(l)+I_3^{-}$ Rate=k[ $H_2O_2$ ][ $I^{-}$ ]

**Ans:** Rate =  $k[H_2O_2][I^-]$ 

From this we can see that the order of the reaction = 2

 $k = \frac{\text{rate}}{[H_2O_2][I^-]}$ Dimensions will be:  $k = \frac{\text{mol } L^{-1} \text{ s}^{-1}}{(\text{mol } L^{-1})^2}$  $= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\text{mol}^2 L^2}$  $= L \text{ mol}^{-1} \text{ s}^{-1}$ 

# (iii) $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ Rate = k[CH\_3CHO]<sup>3/2</sup>

**Ans:** Rate =  $k[CH_3 CHO]^{3/2}$ 

From this we can see that the order of the reaction =  $\frac{3}{2}$ 

$$k = \frac{\text{rate}}{[CH_3 CHO]^{\frac{3}{2}}}$$
  
Dimensions will be:  
$$k = \frac{\text{mol } L^{-1} \text{ s}^{-1}}{(\text{mol } L^{-1})^{3/2}}$$
$$= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\text{mol}^{\frac{3}{2}} L^{\frac{3}{2}}}$$
$$= L^{\frac{1}{2}} \text{ mol}^{-\frac{1}{2}} \text{ s}^{-1}$$

(iv)  $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$  Rate = k[ $C_2H_5Cl$ ] Ans: Rate = k[ $C_2H_5Cl$ ] From this we can see that the order of the reaction = 1

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 $k = \frac{\text{rate}}{[C_2 H_5 \text{Cl}]}$ Dimensions will be:  $k = \frac{\text{mol } L^{-1} \text{ s}^{-1}}{(\text{mol } L^{-1})}$  $= \text{s}^{-1}$ 

2. For a reaction:

 $2A+B \rightarrow A_2B$ 

The rate =  $k[A][B]^2$  with  $k = 2.0 \times 10^{-6} \text{ mol}^{-2} \text{ L}^2 \text{ s}^{-1}$ .

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Calculate the initial rate of the reaction when [A] = 0.1 \text{ mol } L^{-1},

[B] = 0.2 \text{ mol } L^{-1}Calculate the rate of reaction after [A] is reduced to

0.06 mol L^{-1}.
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**Ans:** We are given the rate of the reaction as:

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

Putting the values in this, we get the rate as:

rate =  $2.0 \times 10^{-6} \times 0.1 \times (0.2)^{2}$ 

 $rate = 8.0 \times 10^{-9} mol L^{-1} s^{-1}$ 

When [A] is reduced from 0.10 mol  $L^{-1}$  to 0.06 mol  $L^{-1}$ . So, the amount of [A] reacted will be:

 $=0.10-0.06=0.04 \text{ mol } L^{-1}$ 

Therefore, the concentration of B reacted will be:

$$=\frac{1}{2} \times 0.04 = 0.02 \text{ mol } \text{L}^{-1}$$

Hence, new [B] =  $0.2 - 0.02 = 0.18 \text{ mol } \text{L}^{-1}$ 

Now, the new rate of the reaction will be:

rate =  $2.0 \times 10^{-6} \times 0.06 \times (0.18)^{2}$ 

 $rate = 3.89 \times 10^{-9} \text{ mol } L^{-1} \text{ s}^{-1}$ 

Therefore, the rate of the reaction is  $3.89 \times 10^{-9} \text{ mol } L^{-1} \text{ s}^{-1}$ .



3. The decomposition of  $NH_3$  on the platinum surface there is zero order reaction. What are the rates of production of  $N_2$  and  $H_2$  if  $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ ?

Ans: The following equation represents the breakdown of Ammonia on the platinum surface.

 $2NH_{3_{(g)}} \xrightarrow{Pt} N_{2_{(g)}} + 3H_{2_{(g)}}$ 

Therefore, we can write the rate of the reaction as:

Rate =  $-\frac{1}{2} \frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3} \frac{d[H_2]}{dt}$ 

But we are given that the reaction is a zero order reaction.

So, Rate = 
$$-\frac{1}{2} \frac{d[NH_3]}{dt} = \frac{d[N_2]}{dt} = \frac{1}{3} \frac{d[H_2]}{dt} = 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$$

Thus, the rate of production of  $N_2$  will be:

 $\frac{d[N_2]}{dt} = 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$ 

And the rate of production of  $H_2$  will be:

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1} = 7.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$$

4. The decomposition of dimethyl ether leads to the formation of  $CH_4$ ,  $H_2$ and CO and the reaction rate is given by

Rate =  $k [CH_3OCH_3]^{3/2}$ 

The rate of reaction is followed by increase in pressure in a closed vessel, so the rate can also be expressed in terms of the partial pressure of dimethyl ether, i.e.,

**Rate** = k  $(P_{CH_{1}OCH_{1}})^{3/2}$ 

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

Ans: If the pressure is measured in bar and time in minutes, then unit of rate will be: = bar min<sup>-1</sup>

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We are given the rate of the reaction as: Rate = k  $[CH_3OCH_3]^{3/2}$ 

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

So, we can write the units of rate constant as:

$$k = \frac{bar \min^{-1}}{bar^{3/2}} = bar^{-1/2} \min^{-1}$$

So, the units are bar<sup>-1/2</sup> min<sup>-1</sup>.</sup>

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

Ans: Factors that influence a reaction's speed include.

- (i) Reactant nature: The rate of reaction is affected by the kind of reactant. For example, ionic compound reactions are quicker than covalent compound reactions.
- (ii) The state of the reactants: Solid reactions are sluggish, liquid reactions are rapid, and gas reactions are very quick.
- (iii)Temperature: In addition, temperature has a significant impact on response rate. Every 10 degrees Celsius increase in temperature doubles the pace of reaction.
- (iv)Presence of catalyst: The rate of reaction is also affected by the presence of a catalyst in the reaction. It enhances the pace of reaction by increasing reaction surface area, by generating unstable intermediates with the substrate, and by offering a lower activation energy alternative path.

# 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

**Ans:** Let us assume that the concentration of the reactant be [A] = a

Rate of the reaction will be:

 $\mathbf{R} = \mathbf{k}[\mathbf{A}]^2 = \mathbf{k}\mathbf{a}^2$ 

It is said that the concentration of A increases by two times, so we can write:

 $[A] = 2a \mod L$ 

Therefore, the rate of reaction will be:

Rate =  $k (2a)^2 = 4 ka^2$ 

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Thus, the rate of the reaction will increase by 4 times.

### (ii) Reduced to half

It is said that the concentration of A reduced to half, so we can write:

$$[\mathbf{X}] = \frac{1}{2} \text{ a mol/ } \mathbf{L}$$

Therefore, the rate of reaction will be:

Rate = k 
$$\left[\frac{1}{2}a\right]^2 = \frac{1}{4} ka^2$$

Thus, the rate of the reaction will reduce by 1/4 times.

- 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?
- **Ans:** An increase of 10 degrees in temperature causes a reaction's rate constant to almost double in size. In any case, the Arrhenius equation gives the exact temperature dependency of a chemical reaction rate.

The Arrhenius equation is given below:

 $k = A e^{-E_a/Rt}$ 

Where, A is the Arrhenius factor or the frequency factor,

T is the temperature,

R is the gas constant,

 $E_a$  is the activation energy.

The formula can also be written as:

$$\log \frac{k_{2}}{k_{1}} = \frac{E_{a}}{2.303R} \left[ \frac{T_{2} - T_{1}}{T_{1}T_{2}} \right]$$

Where  $k_2$  is the rate constant at temperature  $T_2$ 

 $k_1$  is the rate constant at temperature  $T_1$ 

# 8. Ina pseudo first order hydrolysis of ester in water, the following results were obtained

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t/s	0	30	60	90
[Ester]mol L <sup>-1</sup>	0.55	0.31	0.17	0.085

(i) Calculate the average rate of reaction between the time interval 30 to 60 seconds.

Ans: Between the time interval of 30 to 60 sec the average rate id reaction will be calculated as:

 $= \frac{d[Ester]}{d[Ester]}$ 

dt

Putting the values from the data given in the question, we can write:

$$= \frac{0.31 - 0.17}{60 - 30} = \frac{0.14}{30}$$
$$= 4.67 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$$

(ii) Calculate the pseudo first order rate constant for the hydrolysis of ester.
 Ans: The rate law formula for pseudo first order reaction will be:

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

Now, when t = 30 s, then we rate constant will be:

$$k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31} = 1.91 \times 10^{-2} \text{ s}^{-1}$$

Now, when t = 60 s, then we rate constant will be:

$$k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17} = 1.96 \times 10^{-2} \text{ s}^{-1}$$

Now, when t = 90 s, then we rate constant will be:

$$k_{3} = \frac{2.303}{90} \log \frac{0.55}{0.085} = 2.075 \times 10^{-2} \text{ s}^{-1}$$

So, we can calculate the average rate constant as:

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$$k = \frac{k_1 + k_2 + k_3}{3}$$
$$= 1.98 \times 10^{-2} \text{ s}^{-1}$$

# 9. A reaction is first order in A and second order in B.(i) Write the differential rate equation

Ans: The differential rate equation can be written as:

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

## (ii) How is the rate affected on increasing the concentration of B three times?

**Ans:** The concentration of B is increased by 3 times, then B = 3B

Therefore, the rate will be:

 $-\frac{d[R]}{dt} = k[A][3B]^2 = 9 \times [A][B]^2$ 

Therefore, the rate will increase by 9 times.

# (iii) How is the rate affected when the concentration of both A and B are doubled?

Ans: The concentration of A is doubled, then A = 2A

The concentration of B is doubled, then B = 2B

Therefore, the rate will be:

 $-\frac{d[R]}{dt} = k[2A][2B]^2 = 8 \times [A][B]^2$ 

Therefore, the rate will increase by 8 times.

**10.** In a reaction between A and B the initial rate of reaction (r<sub>0</sub>) was measured for different concentrations of A and B as given below:

A/mol L <sup>-1</sup>	0.20	0.20	0.04
B/mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0/mol L^{-1} s^{-1}$	<b>5.07</b> × 10 <sup>-5</sup>	<b>5.07</b> × 10 <sup>-5</sup>	$1.43 \times 10^{-4}$

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# **Ans:** Let us assume that the order of the reaction with respect to A be x and with respect to B be y. Therefore, we can write: $r_0 = k [A]^x [B]^y$ $5.07 \times 10^{-5} = k [0.20]^{x} [0.30]^{y}$ .....(i) $5.07 \times 10^{-5} = k [0.20]^{x} [0.10]^{y}$ .....(ii) $1.43 \times 10^{-5} = k [0.40]^{x} [0.05]^{y}$ ......(iii) Let us divide (i) by (ii), we get: $\frac{5.07 \times 10^{-5}}{5.07 \times 10^{-5}} = \frac{k [0.20]^{x} [0.30]^{y}}{k [0.20]^{x} [0.10]^{y}}$ $=1=\frac{[0.30]^{y}}{[0.10]^{y}}$ $=\left(\frac{0.30}{0.10}\right)^{x}=\left(\frac{0.30}{0.10}\right)^{y}$ Therefore, y = 0Now, dividing (iii) by (i), we get: $\frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{k \ [0.40]^{x} \ [0.05]^{y}}{k \ [0.20]^{x} \ [0.30]^{y}}$ $\frac{1.43 \times 10^4}{5.07 \times 10^5} = \frac{\text{k} [0.40]^{\text{x}}}{\text{k} [0.20]^{\text{x}}}$ Because y = 0 $= 2.821 = 2^{x}$ Now, taking log on both the sides. $\log 2.821 = x \log 2$ $x = \frac{\log 2.821}{\log 2}$ x = 1.496x = 1.5

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

Thus, the order of the reaction according to A is 1.5 and according to B is 0.

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

$2\mathbf{A} + \mathbf{D} \rightarrow \mathbf{C} + \mathbf{D}$						
Experiment	A/mol L <sup>-1</sup>	<b>B/mol</b> L <sup>-1</sup>	Initial rate of formation	of		
		<b>D/mol</b> $L^{-1}$ min <sup>-1</sup>				
Ι	0.1	0.1	$6.0 \times 10^{-3}$			
II	0.3	0.2	$7.3 \times 10^{-2}$			
ш	0.3	0.4	$2.88 \times 10^{-1}$			
IV	0.4	0.1	$2.40 \times 10^{-2}$			

 $2A + B \rightarrow C + D$ 

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

Ans: Let us assume that the order of the reaction with respect to A be x and with respect to B be y.

Therefore, we can write:

Rate = k [A]<sup>x</sup> [B]<sup>y</sup>  

$$6.0 \times 10^{-3} = k [0.1]^{x} [0.1]^{y}$$
 ......(i)  
 $7.2 \times 10^{-2} = k [0.3]^{x} [0.2]^{y}$  ......(ii)  
 $2.88 \times 10^{-1} = k [0.3]^{x} [0.1]^{y}$  ......(iii)  
 $2.40 \times 10^{-2} = k [0.4]^{x} [0.1]^{y}$  ......(iv)  
Let us divide (iv) by (i), we get:  
 $\frac{2.40 \times 10^{-2}}{6.0 \times 10^{-3}} = \frac{k [0.4]^{x} [0.1]^{y}}{k [0.1]^{x} [0.1]^{y}}$   
 $=4 = \frac{[0.4]^{x}}{[0.1]^{x}}$   
 $=4 = \left(\frac{0.4}{0.1}\right)^{x}$   
Therefore, x = 1  
Now, dividing (iii) by (ii), we get:  
 $2.88 \times 10^{-1} = k [0.3]^{x} [0.4]^{y}$ 

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

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$$= 4 = \left(\frac{0.4}{0.2}\right)^{y}$$
$$= 4 = 2^{y}$$
$$= 2^{2} = 2^{y}$$

y = 2

Thus, the order of the reaction according to A is 1 and according to B is 2.

So, the rate law is:

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

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

Now, putting the values for each experiment, we get: From experiment I:

$$k = \frac{6.0 \times 10^{-3}}{[0.1][0.1]^2}$$
  
= 6.0 L<sup>2</sup> mol<sup>-2</sup> min<sup>-1</sup>  
From experiment II:  
$$k = \frac{7.3 \times 10^{-2}}{[0.3][0.2]^2}$$
  
= 6.0 L<sup>2</sup> mol<sup>-2</sup> min<sup>-1</sup>  
From experiment III:  
$$k = \frac{2.88 \times 10^{-1}}{[0.3][0.4]^2}$$
  
= 6.0 L<sup>2</sup> mol<sup>-2</sup> min<sup>-1</sup>  
From experiment IV:  
$$k = \frac{2.40 \times 10^{-2}}{[0.4][0.1]^2}$$
  
= 6.0 L<sup>2</sup> mol<sup>-2</sup> min<sup>-1</sup>

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

# 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:

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Experiment	A/mol L <sup>1</sup>	<b>B/mol</b> L <sup>-1</sup>	Initial rate D/mol L <sup>1</sup> min <sup>-1</sup>
Ι	0.1	0.1	$2.0 \times 10^{-2}$
II		0.2	$4.0  imes 10^{-2}$
III	0.4	0.4	
IV		0.2	$2.0 \times 10^{-2}$

Ans: We are given that, the reaction between A and B is first order with respect to A and zero order with respect to B.

Therefore, the rate of the reaction is given by:

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

So, we can write:

Rate = k[A]

According to the experiment I we can write:

 $2.0 \times 10^{-2} = k(0.1)$ 

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

According to the experiment II we can write:

 $4.0 \times 10^{-2} = (0.2) [A]$ 

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

According to the experiment III we can write:

Rate =  $0.2 \times 0.4$ 

= 0.08 mol L<sup>-1</sup> min<sup>-1</sup>

According to the experiment III we can write:

 $2.0 \times 10^{-2} = (0.2)$  [A]

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

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

## (i) 200 s<sup>-1</sup>

Ans: Half-life of the reaction can be related with the rate constant of the reaction as:

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

Putting the value of time, we get:

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$$k = \frac{0.693}{200} = 3.46 \times 10^{-3} \text{ s}$$

So, the rate of the reaction is  $3.46 \times 10^{-3}$  s

### (ii) 2 min<sup>-1</sup>

**Ans:** Half-life of the reaction can be related with the rate constant of the reaction as:

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

Putting the value of time, we get:

$$k = \frac{0.693}{2} = 0.346 \text{ min}$$

So, the rate of the reaction is 0.346 min.

## (iii) 4 years<sup>-1</sup>

**Ans:** Half-life of the reaction can be related with the rate constant of the reaction as:

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

Putting the value of time, we get:

$$k = \frac{0.693}{4} = 0.173$$
 years

So, the rate of the reaction is 0.173 years.

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

**Ans:** The given reaction in the above question is radioactive decay and the radioactive decay follows the first order kinetics. Therefore, the decay constant:

$$\lambda=\frac{0.693}{t_{_{1/2}}}$$

We are given the half-life time as 5730 years.

$$\lambda = \frac{0.693}{5730} \text{ years}^{-1}$$

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To find the age of the sample, we can write:

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

80% of the wood is found so, the initial amount can be taken as 100 and the final amount as 80. Putting the values, we get:

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

t = 1845 years

Therefore, the age of the sample is 1845 years.

# 15. The experiment data for decomposition of $N_2O_5$

$$[2N_2O_5 \rightarrow 4NO_2 + O_2]$$

In gas phase at 318 K are given below:

t/s	0	<b>400</b>	800	1200	1600	2000	2400	1800	<b>3</b> 200
$10^{-2} \times [N_2O_5]/mol L^{-1}$	<b>1.63</b>	1.36	1.14	<b>0.9</b> 3	0.78	0.64	0.53	0.43	<mark>0</mark> .35

(i) Plot  $[N_2O_5]$  against t

**Ans:** The graph is given below:



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## (ii) Find the half-life period for the reaction

Ans: Time corresponding to the concentration,  $\frac{1.630 \times 10^{-2}}{2} \mod L^{-1} = 0.815 \times 10^{-2} \mod L^{-1}$  is the half-life. From the graph, the half-life obtained is 1440 s.

# (iii) Draw the graph between $log[N_2O_5]$ and t

Ans:

T(s)	$10^{-2} \times [N_2O_5]/mol L^{-1}$	log[N <sub>2</sub> O <sub>5</sub> ]
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	0.53	-2.28
2800	0.43	-2.37
3200	0.35	-2.46



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### (iv) What is the rate law?

**Ans:** The rate law of the reaction will be: Rate =  $k[N_2O_5]$ 

### (v) Calculate the rate constant.

Ans: From the plot  $[N_2O_5]$  v/s t, is given by:

 $= -\frac{k}{2.303}$ Therefore, we obtain:  $= -\frac{k}{2.303} = \frac{0.67}{3200}$ 

 $=4.82 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ 

### (vi) Calculate the half-life period from k and compare it will (ii)

Ans: Half-life is given by:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4}} s$$

#### = 1438 seconds.

The value of half-life calculated from the k is very close to that obtained from the graph.

# 16. The rate constant for a first order reaction is 60 s<sup>-1</sup>. How much time will it take to reduce the initial concentration of the reactant to its 1/16<sup>th</sup> value?

**Ans:** As we know that:

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

The initial value of the reactant has become 1/16<sup>th</sup>. Now, putting the values, we get:

$$t = \frac{2.303}{60} \log \frac{16}{1}$$
$$t = \frac{2.303}{60} \log 16 = 4.62 \times 10^{-2} \text{ s}$$

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Therefore, the time required will be  $4.62 \times 10^{-2}$  s.

17. During nuclear explosion, one of the products is <sup>90</sup>Sr with a half-life of 28.1 years. If 1  $\mu$ g of <sup>90</sup>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.

**Ans:** As radioactive disintegration follows first order kinetics.

Decay constant of <sup>90</sup>Sr (k) =  $\frac{0.693}{t_{1/2}} = \frac{0.693}{28.1} = 2.466 \times 10^{-2}$  y<sup>-1</sup>

μg

To calculate the amount left after 10 years.

a = 1 µg  
t = 10 years  
k=2.466 × 10<sup>-2</sup> y<sup>-1</sup>  
(a-x) = ?  
k = 
$$\frac{2.303}{t} \log \frac{a}{a-x}$$
  
2.466 × 10<sup>-2</sup> =  $\frac{2.303}{10} \log \frac{1}{a-x}$   
log(a-x) = -0.1071  
(a-x) = Antilog -0.1071 = 0.7814

To calculate the amount left after 60 years.

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$
  
2.466 × 10<sup>-2</sup> =  $\frac{2.303}{60} \log \frac{1}{a-x}$   
log(a-x) = -0.6425  
(a-x) = Antilog -0.6425 = 0.2278 µg

# **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.

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Ans: For first order reaction, we can write:

$$t = \frac{2.303}{k} \log \frac{a}{a-x}$$

99% completion means that x = 99% of a = 0.99 a So, we can write:

$$t_{99\%} = \frac{2.303}{k} \log \frac{a}{a - 0.99a}$$
$$t_{99\%} = \frac{2.303}{k} \log 10^{2}$$
$$t_{99\%} = 2 \times \frac{2.303}{k}$$

90% completion means that x = 90% of a = 0.90 a

$$t_{99\%} = \frac{2.303}{k} \log \frac{a}{a - 0.90a}$$
$$t_{99\%} = \frac{2.303}{k} \log 10$$
$$t_{99\%} = \frac{2.303}{k}$$

Now, we can take the ratio as given below:

$$\frac{t_{99\%}}{t_{90\%}} = \frac{\left(\frac{2 \times 2.303}{k}\right)}{\left(\frac{2.303}{k}\right)}$$

 $t_{99\%} = 2 \times t_{90\%}$ 

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

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

Ans: 30% decomposition means that x = 30% of a = 0.30 a Since, the reaction is of 1<sup>st</sup> order, we can write:

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

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Time is given as 40 min. So, putting the values, we get:

$$k = \frac{2.303}{40} \log \frac{a}{a - 0.30a}$$

$$k = \frac{2.303}{40} \log \frac{10}{7} \min^{-1}$$

$$k = \frac{2.303}{40} \times 0.1549 \min^{-1} = 8.918 \times 10^{-3} \min^{-1}$$

Now, we can calculate the half-life period as we have the rate constant value. We can write:

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3}} = 7.77 \text{ min}$$

So, the half-life is 7.77 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.

**Ans:** The decomposition of azoisopropane to hexane and nitrogen at 54.3 k is represent by the following equation.

$$(CH_{3})_{2}CHN=NCH(CH_{3})_{2} \longrightarrow N_{2} + C_{6}H_{14}$$
At t = 0 P<sub>0</sub> 0 0  
At t = t P<sub>0</sub> - P p p  
Total pressure after time t, we will be:  
P<sub>t</sub> = (P<sub>0</sub>-p) + p + p  
P<sub>t</sub>=P<sub>0</sub>+p  
p=P<sub>t</sub> - P<sub>0</sub>  
Now, we can substitute the value of p for the pressure of reactant at time t

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 $=P_{o}-p$  $=P_{0}-(P_{1}-P_{0})$  $= 2P_{0} - P_{1}$ Now, we can apply the rate constant formula of 1<sup>st</sup> order reaction.  $k = \frac{2.303}{t} \log \frac{P}{2P_{c} - P_{c}}$ When t = 360 s, Putting the values, we get:  $k = \frac{2.303}{360} \log \frac{35.0}{2 \times 35 - 54} = 2.175 \times 10^{-3} \text{ s}^{-1}$ When t = 720 s, Putting the values, we get:  $k = \frac{2.303}{720} \log \frac{35.0}{2 \times 35 - 63} = 2.235 \times 10^{-3} \text{ s}^{-1}$ Now, we can find the average value:  $k = \frac{(2.175 \times 10^{-3}) + (2.235 \times 10^{-3})}{2} s^{-1}$ 

 $k = 2.20 \times 10^{-3} s^{-1}$ 

21. The following data were obtained during the first order thermal decomposition of SO<sub>2</sub>Cl<sub>2</sub> at a constant volume.

<b>– –</b> (g) <b>–</b> (g) <b>–</b> (g)		
Experiment	Time/ s	Total pressure/ atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm. Ans: The given reaction shows the thermal decomposition of SO<sub>2</sub>Cl<sub>2</sub> at constant volume.

$$\mathrm{SO}_{2}\mathrm{CI}_{2_{\mathrm{(g)}}} \rightarrow \mathrm{SO}_{2_{\mathrm{(g)}}} + \mathrm{CI}_{2_{\mathrm{(g)}}}$$



SO<sub>2</sub>  $Cl_2$ +SO<sub>2</sub>Cl<sub>2</sub> 0 0 At  $t = 0 P_0$ At  $t = t P_o - P$ р р Total pressure after time t, we will be:  $\mathbf{P}_{t} = (\mathbf{P}_{o} - \mathbf{p}) + \mathbf{p} + \mathbf{p}$  $P_{t}=P_{o}+p$  $p=P_t - P_o$ Now, we can substitute the value of p for the pressure of reactant at time t  $=P_{0}-p$  $=P_{0}-(P_{1}-P_{0})$  $= 2P_{0} - P_{t}$ Now, we can apply the rate constant formula of 1<sup>st</sup> order reaction.  $k = \frac{2.303}{t} \log \frac{P}{2P_0 - P_1}$ When the t = 100 s $k = \frac{2.303}{100} \log \frac{0.5}{2 \times 0.5 - 0.6}$  $k = 2.231 \times 10^{-3} s^{-1}$ When  $P_{t} = 0.65$  atm Therefore, pressure of SO<sub>2</sub>Cl<sub>2</sub> at time t total pressure is 0.65 atm, is  $P_{SO_2Cl_2} = 2P_o - P_t$  $= 2 \times 0.50 - 0.65$ = 0.35 atm Therefore, the rate of equation, when total pressure is 0.65 atm, is given by: Rate =  $k(P_{SO_{2}Cl_{2}})$ Rate =  $(2.33 \times 10^{-3})(0.354) = 7.8 \times 10^{-4}$  atm s<sup>-1</sup>

### 22. The rate constant for the decomposition of $N_2O_5$ at various temperature is

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### given below:

T/°c	0	20	40	60	80
$10^5 \times \text{k/s}$	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° and 50°C.

**Ans:** As the data is given we can write:

T/°c	0	20	40	60	80
T/K	273	293	313	333	353
$\frac{1}{T}/k^{-1}$	$3.66 \times 10^{-3}$	$3.41 \times 10^{-3}$	$3.19 \times 10^{-3}$	$3.0 \times 10^{-3}$	$2.83 \times 10^{-3}$
$10^5 \times \text{k/s}$	0.0787	4.075	25.7	178	2140
ln K	-7.147	- <mark>4.075</mark>	-1.359	-0.577	3.063

The graph is draw below:



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

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According to the Arrhenius equation,

Slope =  $-\frac{E_a}{R}$  $= E_a = -slope \times R$ = (-12.301)(8.314)=102.27 KJ mol<sup>-1</sup> Again,  $\ln k = \ln A - \frac{E_a}{RT}$  $\ln A = \ln k + \frac{E_a}{RT}$ As T = 273 K and ln k = -7.147 Applying this in the formula, we get:  $\ln A = -7.147 - \frac{102.27 \times 10^3}{8.314 \times 273} = 37.911$ So, A=2.91  $\times 10^{6}$ When T = 30 + 273 K = 303 K $\frac{1}{T} = 0.0033 \text{K} = 3.3 \times 10^{-3} \text{K}$ Now, at  $\frac{1}{T} = 0.0033 \text{K} = 3.3 \times 10^{-3} \text{K}$  $\ln k = -2.8$ Therefore,  $k = 6.08 \times 10^{-2} \text{ s}^{-1}$ When T = 50 + 273 K = 323 K $\frac{1}{T} = 0.0031 \text{K} = 3.1 \times 10^{-3} \text{K}$ Now, at  $\frac{1}{T} = 0.0031 \text{K} = 3.1 \times 10^{-3} \text{K}$  $\ln k = -0.5$ Therefore,  $k = 0.607 \text{ s}^{-1}$ 

## 23. The rate constant for the decomposition of hydrocarbons is $2.418 \times 10^{-5}$ s<sup>-1</sup>

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at 546 K. If the energy of activation is 179.9 kJ /mol, what will be the value of the pre-exponential factor?

Ans: We are given some values as:

 $K = 2.418 \times 10^{-5} \text{ s}^{-1}$  T = 546 K  $E_{a} = 179.9 \text{ kJ mol}^{-1} = 179.9 \times 10^{3} \text{ J mol}^{-1}$ We the Arrhenius equation is:  $k = A e^{-E_{a}/RT}$ In the log form, this can be written as:  $\ln k = \ln A - \frac{E_{a}}{RT}$   $\log k = \log A - \frac{E_{a}}{2.303 \text{ RT}}$   $\log k = \log (2.418 \times 10^{-5}) - \frac{179.9 \times 10^{3}}{2.303 \times 8.314 \times 546}$  = (0.3835 - 5) + 17.2082 = 12.5917Therefore, A = antilog (12.5917)  $A = 3.912 \times 10^{12} \text{ s}^{-1}$ 

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

Ans: We are given some values, that are given below:

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

t = 100 s

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

As we can see that the units of k is given in s<sup>-1</sup>, this means that the reaction is a first order reaction.

Therefore, we can write:

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

Putting the values, we get:

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$$2.0 \times 10^{-2} = \frac{2.303}{100} \log \frac{1.0}{[A]}$$
$$2.0 \times 10^{-2} = \frac{2.303}{100} (-\log[A])$$
$$(-\log[A]) = \frac{2.0 \times 10^{-2} \times 100}{2.303}$$
$$[A] = \operatorname{antilog} \left( \frac{2.0 \times 10^{-2} \times 100}{2.303} \right)$$

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

Therefore, the remaining amount of A is  $0.135 \text{ mol } L^{-1}$ .

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

**Ans:** The given reaction is a first order reaction. So, we can write:

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

We are given a half-life of 3 hours. Therefore, we can write:

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

So, putting the values in this, we get:

$$k = \frac{0.693}{3} = 0.231 \text{ h}^{-1}$$

Now, we can put this value of rate constant in the first order reaction formula.

$$0.231 = \frac{2.303}{8} \log \frac{[R]_0}{[R]}$$
$$\log \frac{[R]_0}{[R]} = \frac{0.231 \times 8}{2.303}$$
$$\log \frac{[R]_0}{[R]} = 0.8024$$

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 $\frac{[\mathbf{R}]_0}{[\mathbf{R}]} = \text{antilog (0.8024)}$  $\frac{[\mathbf{R}]_0}{[\mathbf{R}]} = 6.3445$ Or we can write: $\frac{[\mathbf{R}]}{[\mathbf{R}]_0} = 0.158$ 

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

# 26. The decomposition of hydrocarbon follows the equation $\mathbf{k} = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-280000 \text{ K/T}}$ . Calculate $E_a$ .

Ans: According to the Arrhenius equation,

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

We are given the equation as:

 $k = (4.5 \times 10^{11} \text{ s}^{-1})e^{-280000 \text{ K/T}}$ 

Therefore, the formula can be written as:

 $-\frac{E_a}{RT} = -\frac{28000 \text{ K}}{T}$ This can be written as:  $E_a = 28000 \times \text{R}$   $E_a = 28000 \times 8.314 = 232.79 \text{ kJ mol}^{-1}$ 

Therefore, the value of  $E_a$  is 232.79 kJ mol<sup>-1</sup>

# 27. The rate constant for the first order decomposition of $H_2O_2$ 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?

Ans: According to the Arrhenius equation,

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

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This can be written as:

 $\ln k = \ln A - \frac{E_a}{RT}$ In the log form it can be written as:  $\log k = \log A - \frac{E_a}{2.303 \text{ RT}}$ We are given:  $\log k = 14.34 - 1.25 \times 10^4 \text{ K/T}$ Comparing these two, we get:  $\frac{E_a}{2.303 \text{ RT}} = \frac{1.25 \times 10^4 \text{ K}}{\text{T}}$   $E_a = 2.303 \text{ R} \times 1.25 \times 10^4 \text{ K}$   $E_a = 2.303 \times 8.314 \times 1.25 \times 10^4 \text{ K}$   $E_a = 239.34 \text{ kJ mol}^{-1}$ We are given half-life time as 256 minutes.  $k = \frac{0.693}{t_{1/2}}$   $k = \frac{0.693}{t_{1/2}} = 4.51 \times 10^{-5} \text{ s}^{-1}$ 

Now, we have the value of rate constant, we can put in the equation:

$$log(4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^{4}}{T}$$
$$T = 669 \text{ K}$$

28. The decomposition of A into product has value of k as  $4.5 \times 10^3$  s<sup>-1</sup> at 10°C and energy of activation 60 kJ mol<sup>-1</sup>. At what temperature would k be  $1.5 \times 10^4$  s<sup>-1</sup>?

**Ans:** We are some information:

$$\begin{split} k_{_1} &= 4.5 \times 10^3 \\ T_{_1} &= 10 + 273 = 283 \ \mathrm{K} \end{split}$$



$$\log \frac{1.5 \times 10^{4}}{4.5 \times 10^{3}} = \frac{60}{2.303 \times 8.314} \left(\frac{T_{2}-283}{283T_{2}}\right)$$
  
$$\log 3.333 = 3133.63 \left(\frac{T_{2}-283}{283T_{2}}\right)$$
  
$$\frac{0.5228}{3133.63} = \left(\frac{T_{2}-283}{283T_{2}}\right)$$
  
$$0.0472T_{2} = T_{2} - 283$$
  
$$T_{2} = 297 \text{ K}$$
  
Or we can write:  
$$T_{2} = 24^{\circ}\text{C}$$

# 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 $4 \times 10^{10}$ s<sup>-1</sup>, Calculate k at 318 K and E<sub>a</sub>.

Ans: There are two cases in this question. As the reaction given is first order reaction, we can use:

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

For case 1:

$$k_{_{298K}} = \frac{2.303}{t_{_1}} \log \frac{a}{a - 0.10a}$$



$$k_{298K} = \frac{2.303}{t_1} \log \frac{10}{9}$$

$$k_{298K} = \frac{2.303}{t_1} \times 0.0458$$

$$t_1 = \frac{0.1055}{k_{298K}}$$
For case 2:  

$$k_{308K} = \frac{2.303}{t_2} \log \frac{a}{a - 0.25a}$$

$$k_{308K} = \frac{2.303}{t_2} \log \frac{4}{3}$$

$$k_{308K} = \frac{2.303}{t_2} \times 0.125$$

$$t_2 = \frac{0.2879}{k_{308K}}$$
But  $t_1 = t_2$ 
Hence,  

$$\frac{0.1055}{k_{298K}} = \frac{0.2879}{k_{308K}}$$
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Now, applying the Arrhenius equation,

$$\log \frac{k_{308K}}{k_{298K}} = \frac{E_{a}}{2.303R} \left(\frac{T_{2}-T_{1}}{T_{1}T_{2}}\right)$$
$$\log(2.7289) = \frac{E_{a}}{2.303 \times 8.314} \left(\frac{308-298}{298 \times 308}\right)$$
$$E_{a} = 76.623 \text{ kJ mol}^{-1}$$
Now, the calculation of k at 318 K

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$$\begin{split} \log k &= \log A - \frac{E_a}{2.303 \text{RT}} \\ \log k &= \log (4 \times 10^{10}) - \frac{7623}{2.303 \times 8.314 \times 318} \\ \log k &= 10.6021 - 12.5843 = -1.9822 \\ k &= \text{Antilog (-1.9822)} = \text{antilog } (\overline{2}.0178) = 1.042 \times 10^{-2} \text{ s}^{-1} \\ \text{Therefore, k is } 1.042 \times 10^{-2} \text{ s}^{-1}. \end{split}$$

# 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.

**Ans:** We are given that:

$$k_2 = 4 k_1$$

 $T_{1} = 293K$ 

$$T_2 = 313K$$

According the Arrhenius equation, we get:

$$\log \frac{k_{2}}{k_{1}} = \frac{E_{a}}{2.303R} \left( \frac{T_{2} - T_{1}}{T_{1}T_{2}} \right)$$

Putting the values, we get:

$$\log \frac{4k_{1}}{k_{1}} = \frac{E_{a}}{2.303 \times 8.314} \left(\frac{313-293}{293 \times 313}\right)$$
  

$$0.6021 = \frac{E_{a}}{2.303 \times 8.314} \left(\frac{313-293}{293 \times 313}\right)$$
  

$$E_{a} = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$$
  

$$E_{a} = 52863.00 \text{ J mol}^{-1}$$
  

$$E_{a} = 52.863 \text{ kJ mol}^{-1}$$

Therefore, the required activation energy is 52.863 kJ mol<sup>-1</sup>.