



Class XII : Chemistry Chapter 3 : Chemical Kinetics

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Q1:

For the reaction $R \to P$, 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.

Answer:

Average rate of reaction
$$= -\frac{\Delta[R]}{\Delta t}$$
$$= -\frac{[R]_2 - [R]_1}{t_2 - t_1}$$

$$=-\frac{0.02-0.03}{25}$$
 M min⁻¹

$$=-\frac{-0.01}{25}$$
 M min⁻¹

$$= 4 \times 10^{-4} \text{ M min}^{-1}$$

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

$$= 6.67 \times 10_{-6} M s_{-1}$$

Q2:

In a reaction, 2A \rightarrow Products, the concentration of A decreases from 0.5 mol L-1to 0.4 mol L-1in 10 minutes. Calculate the rate during this interval?

Answer:

$$\text{Average rate} = -\frac{1}{2} \frac{\Delta \big[\mathbf{A} \big]}{\Delta t}$$





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

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

$$=-\frac{1}{2}\frac{-0.1}{10}$$

= 0.005 mol L-1 min-1

= 5 ×10₋₃M min₋₁

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Q3:

For a reaction, A + B $\tilde{A} \notin \hat{a} \in Product$; the rate law is given by, $r = k \left[A \right]^{1/2} \left[B \right]^2$. What is the order of the reaction?

Answer:

The order of the reaction = $\frac{1}{2} + 2$

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

Q4:

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?

Answer:

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

Therefore, the rate equation for this reaction will be:

Rate = $k[X]^2$ (1)

Let $[X] = a \mod L^{-1}$, then equation (1) can be written as:

Rate₁ = $k \cdot (a)^2$

= ka2

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

Now, the rate equation will be:

Rate = k (3a)

 $= 9(ka^2)$

Hence, the rate of formation will increase by 9 times.





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Q5:

A first order reaction has a rate constant 1.15 103s1. How long will 5 g of this reactant take to reduce to 3 g?

Answer:

From the question, we can write down the following information:

Initial amount = 5 g

Final concentration = 3

g

Rate constant = 1.15 10⁻³s⁻¹

We know that for a 1storder reaction,

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

$$=\frac{2.303}{1.15\times10^{-3}}\log\frac{5}{3}$$

$$=\frac{2.303}{1.15\times10^{-3}}\times0.2219$$

Q6:

Time required to decompose SO₂Cl₂to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Answer:

We know that for a 1storder reaction,

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

It is given that t_{1/2}= 60 min

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

$$=\frac{0.693}{60}$$

Or
$$k = 1.925 \times 10^{-4} \,\mathrm{s}^{-1}$$





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Q7:

What will be the effect of temperature on rate constant?

Answer:

The rate constant of a reaction is nearly doubled with a 10°rise in temperature. However, the exact dependence of the rate of a chemical reaction on temperature is given by Arrhenius equation,

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

Where,

A is the Arrhenius factor or the frequency factor

Tis the temperature

Ris the gas constant E₃is the activation energy

Q8:

The rate of the chemical reaction doubles for an increase of 10 K in absolute temperature from 298 K. Calculate E_a .

Answer:

It is given that $T_1 = 298 \text{ K}$

$$\therefore T_2 = (298 + 10) \text{ K}$$

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

Therefore, let us take the value of $k_1 = k$ and that of $k_2 = 2k$

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

Now, substituting these values in the equation:





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

We get:

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

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

$$\Rightarrow E_{\rm u} = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2}{10}$$

= 52897.78 J mol-1

= 52.9 kJ mol-1

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

Q9:

The activation energy for the reaction

$$\mathbf{2HI}_{(g)} \to \mathbf{H_2} + \mathbf{I}_{2(g)}$$

is 209.5 kJ mol⁻¹ at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Answer:

In the given case:

 $E_a = 209.5 \text{ kJ mol}^{-1} = 209500 \text{ J mol}^{-1}$

T = 581 K

R = 8.314 JK⁻¹ mol⁻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 In $x=-E$

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Q1:

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

(i) 3 NO(g) â†' N₂O(g) Rate = k[NO]²





(ii)
$$H_2O_2$$
 (aq) + 3 I^* (aq) + 2 $H^*\tilde{A}\phi\hat{a}\in '2$ H_2O (I) + I_3^- Rate = $k[H_2O_2][I^*]$

(iv)
$$C_2H_5CI(g) \tilde{A} \notin \hat{a} \in C_2H_4(g) + HCI(g)$$
 Rate = $k [C_2H_5CI]$

Answer:

(i) Given rate = $k [NO]^2$

Therefore, order of the reaction = 2

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

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

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

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

(ii) Given rate =
$$k [H_2O_2][I^-]$$

Therefore, order of the reaction = 2

$$=\frac{mol\ L^{-1}\ s^{-1}}{\left(mol\ L^{-1}\right)\!\left(mol\ L^{-1}\right)}$$

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

(iii) Given rate =
$$k [CH_3CHO]^{3/2}$$

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

Dimension of
$$k = \frac{\text{Rate}}{\left[\text{CH}_3\text{CHO}\right]^{\frac{3}{2}}}$$

$$= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\left(\text{mol } L^{-1}\right)^{\frac{3}{2}}}$$

$$= \frac{\text{mol } L^{-1} \text{ s}^{-1}}{\text{mol}^{\frac{3}{2}} L^{\frac{-3}{2}}}$$

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





(iv) Given rate = $k [C_2H_5Cl]$

Therefore, order of the reaction = 1

Dimension of
$$k = \frac{\text{Rate}}{\left[\text{C}_2\text{H}_5\text{Cl}\right]}$$

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

Q2:

For the reaction:

$$2A + B \rightarrow A_2B$$

the rate = $k[A][B]^2$ with $k= 2.0 \times 10^4$ mol 2 L 2 S 4 . Calculate the initial rate of the reaction when [A] = 0.1 mol L 4 , [B] = 0.2 mol L 4 . Calculate the rate of reaction after [A] is reduced to 0.06 mol L 4 .

Answer:

The initial rate of the reactionis

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

= $(2.0 \times 10_{-6} \text{mol}_{-2} \text{L}_2 \text{s}_{-1}) (0.1 \text{ mol} \text{L}_{-1}) (0.2 \text{ mol} \text{L}_{-1})_2$

 $= 8.0 \times 10_{-9} \text{mol}_{-2} \text{L}_2 \text{s}_{-1}$

When [A] is reduced from 0.1 mol L-1 to 0.06 mol-1, the concentration of A reacted = (0.1 - 0.06) mol L-1 = 0.04 mol L-1

 $= \frac{1}{2} \times 0.04 \text{ mol L}^{-1}$ Therefore, concentration of B reacted = 0.02 mol L⁻¹

Then, concentration of B available, [B] = (0.2 - 0.02) mol L⁻¹

 $= 0.18 \text{ mol } L^{-1}$

After [A] is reduced to 0.06 mol L-1, the rate of the reaction is given by,

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

= $(2.0 \times 10^{-6} \text{mol}^{-2} \text{L}^2 \text{s}^{-1}) (0.06 \text{ mol} \text{L}^{-1}) (0.18 \text{ mol} \text{L}^{-1})^2$

 $= 3.89 \text{ mol } L_{-1}s_{-1}$

Q3:

The decomposition of NH₃on platinum surface is zero order reaction. What are the rates of production of N₂and H₂if $k = 2.5 \times 10^{4}$ mol⁻¹L s⁻¹?

Answer:

The decomposition of NH₃on platinum surface is represented by the following equation.

$$2 \text{ NH}_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3 \text{ H}_{2(g)}$$





Therefore,

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

However, it is given that the reaction is of zero order. Therefore,

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

Therefore, the rate of production of N_2 is

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

And, the rate of production of H2is

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

7.5 × 10-4mol L-1S-1

Q4:

The decomposition of dimethyl ether leads to the formation of CH₄, H₂and CO and the reaction rate is given by Rate = $k \left[\text{CH}_3\text{OCH}_3 \right]^{3/2}$

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 =
$$k \left(p_{\text{CH}_3\text{OCH}_3} \right)^{\frac{3}{2}}$$

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

Answer:

If pressure is measured in bar and time in minutes, then

Unit of rate = bar min-1

Rate =
$$k \left(p_{\text{CH}_3\text{OCH}_3} \right)^{\frac{3}{2}}$$

$$\Rightarrow k = \frac{\text{Rate}}{\left(p_{\text{CH,OCH,}}\right)^{\frac{3}{2}}}$$

$$(k) = \frac{\text{bar min}^{-1}}{\text{bar}^{\frac{3}{2}}}$$

Therefore, unit of rate constants

$$= bar^{-1/2} min^{-1}$$





Q5:

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

Answer:

The factors that affect the rate of a reaction areas follows.

- (i) Concentration of reactants (pressure in case of gases)
- (ii) Temperature
- (iii) Presence of a catalyst

Q6:

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?

Answer:

Letthe concentration of the reactant be [A] = a

Rate of reaction, $R = k [A]^2$

= ka2

(i) If the concentration of the reactant is doubled, i.e. [A] = 2a, then the rate of the reaction would be

$$R' = k (2a)^2$$

 $= 4ka^2$

=4R

Therefore, the rate of the reaction would increase by 4 times.

(ii) If the concentration of the reactant is reduced to half, i.e. $[A] = \frac{1}{2}a$, then the rate of the reaction would be

$$R' = k(\frac{1}{2}\alpha)^2$$
$$= \frac{1}{4}k\alpha^2$$
$$= \frac{1}{4}R$$

Therefore, the rate of the reaction would be reduced to $\frac{1}{4}^{th}$.





Q7:

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

Answer:

The rate constant is nearly doubled with a rise in temperature by 10° for a chemical reaction.

The temperature effect on the rate constant can be represented quantitatively by Arrhenius equation,

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

where, kis the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

Tis the temperature, and

E₃is the energy of activation for the reaction

Q8:

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

t/s	0	30	60	90
[Ester]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.

Answer:

(i) Average rate of reaction between the time interval, 30 to 60 seconds,
$$=\frac{d[Ester]}{dt}$$

$$= \frac{0.31 - 0.17}{60 - 30}$$
$$= \frac{0.14}{30}$$

= 4.67 × 10₋₃mol L₋₁s₋₁

(ii) For a pseudo first order reaction,





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

Fo
$$k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$$
 r $t=30$ s,

For
$$t = 60 \text{ s}$$
, $k_2 = \frac{2.303}{60} \log \frac{0.55}{0.17}$

$$= 1.957 \times 10_{-2}s_{-1}$$

For
$$t$$
= 90 s, $k_3 = \frac{2.303}{90} \log \frac{0.55}{0.085}$

$$= 2.075 \times 10_{-2}$$
s₋₁

Then, average rate constant,
$$k = \frac{k_1 + k_2 + k_3}{3}$$

$$=\frac{\left(1.911\times10^{-2}\right)+\left(1.957\times10^{-2}\right)+\left(2.075\times10^{-2}\right)}{3}$$

$$=1.98\times10^{-2} \text{ s}^{-1}$$

Q9:

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

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

Answer:

(i) The differential rate equation will be

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

(ii) If the concentration of B is increased three times, then

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

Therefore, the rate of reaction will increase 9 times.

(iii) When the concentrations of both A and B are doubled,





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

Therefore, the rate of reaction will increase 8 times.

Q10:

In a reaction between A and B, the initial rate of reaction (r₀) was measured for different initial concentrations of A and B as given below:

A/ mol L-1	0.20	0.20	0.40
B/ mol L-1	0.30	0.10	0.05
/ mol r L-1	5.07 × 10-5	5.07 × 10-5	1.43 × 10-4

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

Answer:

Let the order of the reaction with respect to A be xand with respect to B be y.

Therefore,

$$\mathbf{r}_0 = k \left[\mathbf{A} \right]^x \left[\mathbf{B} \right]^y$$

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

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

$$1.43 \times 10^{-4} = k [0.40]^x [0.05]^y$$
 (iii)

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

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

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

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

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





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

$$\Rightarrow \frac{1.43 \times 10^{-4}}{5.07 \times 10^{-5}} = \frac{[0.40]^x}{[0.20]^x} \qquad \begin{bmatrix} \text{Since } y = 0, \\ [0.05]^y = [0.30]^y = 1 \end{bmatrix}$$

$$\Rightarrow$$
 2.821 = 2^x

$$\Rightarrow \log 2.821 = x \log 2$$
 (Taking log on both sides)

$$\Rightarrow x = \frac{\log 2.821}{\log 2}$$

= 1.496

∜Saral

= 1.5 (approximately)

Hence, the order of the reaction with respect to A is 1.5 and with respect to B is zero.

Q11:

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

2A + B â†' C + D

Experiment	A/ mol L-1	B/ mol L-1	Initial rate of formation of D/mol L-1 min-1
I	0.1	0.1	6.0 × 10-3
II	0.3	0.2	7.2×10^{-2}
III	0.3	0.4	2.88 × 10-1
IV	0.4	0.1	2.40 × 10-2

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

Answer:

Let the order of the reaction with respect to A be xand with respect to B be y.

Therefore, rate of the reaction is given by,

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

According to the question,





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

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

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

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

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

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

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

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

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

$$\Rightarrow x = 1$$

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

Therefore, the rate law is

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

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

From experiment I, we obtain

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

= 6.0 L₂mol₋₂min₋₁

From experiment II, weobtain





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

 $= 6.0 L_2 mol_{-2} min_{-1}$

From experiment III, we obtain

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

= 6.0 L₂mol₋₂min₋₁

From experiment IV, we obtain

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

 $= 6.0 L_2 mol_{-2} min_{-1}$

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

Q12:

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-1	B/ mol L-1	Initial rate/mol L-1 min-1
I	0.1	0.1	2.0 × 10-2
II		0.2	4.0 × 10-2
III	0.4	0.4	
IV		0.2	2.0 × 10-2

Answer:

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,

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

 \Rightarrow Rate = k [A]

From experiment I, we obtain

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

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

From experiment II, we obtain

4.0 x 10⁻²mol L⁻¹min⁻¹= 0.2 min⁻¹[A]





$$\Rightarrow$$
 [A] = 0.2 mol L⁻¹

From experiment III, we obtain

Rate = 0.2 min⁻¹ x 0.4 mol L⁻¹

= 0.08 mol L-1min-1

From experiment IV, we obtain

2.0 x 10⁻²mol L⁻¹min⁻¹= 0.2 min⁻¹[A]

 \Rightarrow [A] = 0.1 mol L⁻¹

Q13:

Calculate the half-life of a first order reaction from their rate constants given below: (i)

200 s-1 (ii) 2 min-1 (iii) 4 years-1

Answer:

(i) Half life,
$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$=\frac{0.693}{200 \text{ s}^{-1}}$$

(ii) Half life,
$$t_{1/2} = \frac{0.692}{k}$$

$$=\frac{0.693}{2 \, \text{min}^{-1}}$$

(iii) Half life,
$$t_{\frac{1}{2}} = \frac{0.693}{k}$$

$$=\frac{0.093}{4 \text{ years}^-}$$

= 0.173 years (approximately)

Q14:

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

Answer:





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

$$=\frac{0.693}{5730}$$
 years⁻¹

It is known that,

$$t = \frac{2.303}{k} \log \frac{[R]_0}{[R]}$$
$$= \frac{2.303}{0.693} \log \frac{100}{80}$$
$$= \frac{5730}{100} \log \frac{100}{80}$$

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

Q15:

The experimental data for decomposition of N₂O₅

$$\left[2N_2O_5 \longrightarrow 4NO_2 + O_2\right]$$

in gas phase at 318K are given below:

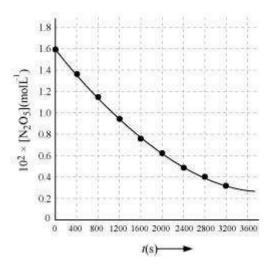
t(s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5] \text{mol } L^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

- (i) Plot [N₂O₅] against t.
- (ii) Find the half-life period for the reaction.
- (iii) Draw a graph between log [N₂O₅] and t.
- (iv) What is the rate law?
- (v) Calculate the rate constant
- (vi) Calculate the half-life period from k and sompare it will (ii).

Answer:







$$\frac{1.630 \times 10^2}{2} \text{ mol L}^{-1} = 81.5 \text{ mol L}^{-1}, \text{ (ii)}$$

(ii) Time corresponding to

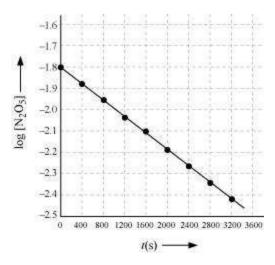
the concentration, is the half life. From the graph, the half life is obtained as 1450 s.

(iii)

t(s)	$10^2 \times [N_2O_5]/ \text{mol L}^{-1}$	$log[N_2O_5]$
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	0.53	- 2.28
2800	0.43	- 2.37
3200	0.35	- 2.46







(iv) The given reaction is of the first order as the plot, $log[N_2O_5]$ v/s t, is a straight line. Therefore, the rate law of the reaction is

Rate =
$$k[N_2O_5]$$

(v) From the plot, $\log \left[N_2 O_5 \right]$ v/s t, we obtain

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

Again, slope of the line of the plot $\log \left[N_2 O_5 \right]$ v/s t is given by

$$-\frac{k}{2.303}$$

Therefore, we obtain,

$$-\frac{k}{2.303} = -\frac{0.67}{3200}$$

Q16:

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

Answer:

It is known that,





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

$$= \frac{2.303}{60 \text{ s}^{-1}} \log \frac{1}{\frac{1}{16}}$$

$$= \frac{2.303}{60 \text{ s}^{-1}} \log 16$$

$$= 4.6 \times 10^{-2} \text{ s (approximately)}$$

Hence, the required time is 4.6×10^{-2} s.

Q17:

During nuclear explosion, one of the products is ⁹⁰Sr with half-life of 28.1 years. If 1μg of ⁹⁰Sr 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.

Answer:

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

Here,

It is known that,

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

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

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

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

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

$$= \text{antilog} (\overline{1.8929})$$

 $= 0.7814 \mu g$

Therefore, 0.7814 $\tilde{A}\check{Z}\hat{A}^{1/4}g$ of ${}^{90}Sr$ will remain after 10 years.

Again,





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

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

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

$$\Rightarrow [R] = \text{antilog} (-0.6425)$$
$$= \text{antilog} (\overline{1.3575})$$

$$= 0.2278 \mu g$$

Therefore, 0.2278 μg of 90Sr will remain after 60 years.

Q18:

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

Answer:

For a first order reaction, the time required for 99% completionis

$$t_1 = \frac{2.303}{k} \log \frac{100}{100 - 99}$$
$$= \frac{2.303}{k} \log 100$$
$$= 2 \times \frac{2.303}{k}$$

For a first order reaction, the time required for 90% completion is

$$t_2 = \frac{2.303}{k} \log \frac{100}{100 - 90}$$
$$= \frac{2.303}{k} \log 10$$
$$= \frac{2.303}{k}$$

Therefore, $t_1 = 2t_2$

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.





Q19:

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

Answer:

For a first order reaction,

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

$$k = \frac{2.303}{40 \text{ min}} \log \frac{100}{100 - 30}$$
$$= \frac{2.303}{40 \text{ min}} \log \frac{10}{7}$$
$$= 8.918 \times 10^{-3} \text{ min}^{-1}$$

Therefore, $t_{1/2}$ of the decomposition reaction is

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

= 77.7 min (approximately)

Q20:

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.

Answer:

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

$$(CH_3)_2 CHN=NCH(CH_3)_{2(g)} \longrightarrow N_{2(g)} + C_6H_{14(g)}$$
At $t=0$ P_0 0 0
At $t=t$ P_0-p p





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

$$\Rightarrow P_t = P_0 + p$$

$$\Rightarrow p = P_t - P_0$$

Therefore, $P_0 - p = P_0 - (P_1 - P_0)$

$$= 2P_0 - P_t$$

For a first order reaction,

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

$$k = \frac{2.303}{360 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 54.0}$$
_{t = 360 s,}

When

 $= 2.175 \times 10_{-3} s_{-1}$

When
$$t = 720 \text{ s}$$
 $k = \frac{2.303}{720 \text{ s}} \log \frac{35.0}{2 \times 35.0 - 63.0}$

 $= 2.235 \times 10_{-3} \, s_{-1}$

Hence, the average value of rate constant is

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

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

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

Q21:

The following data were obtained during the first order thermal decomposition of SO₂Cl₂at a constant volume.

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

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

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

Answer:

The thermal decomposition of SO₂Cl₂at a constant volume is represented by the following equation.





$$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$$
At $t = 0$ P_0 0 0
At $t = t$ $P_0 - p$ p p

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

$$\Rightarrow P_{t} = P_{0} + p$$

$$\Rightarrow p = P_{t} - P_{0}$$

Ther
$$\mathbf{P}_{o} - p = \mathbf{P}_{o} - (\mathbf{P}_{t} - \mathbf{P}_{o})_{\text{efore}},$$

$$= 2 P_0 - P_t$$

For a first order reaction,

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

W
$$k = \frac{2.303}{100 \text{ s}} \log \frac{0.5}{2 \times 0.5 - 0.6}$$
 hen $t = 100 \text{ s}$,

When P_t = 0.65 atm,

$$P_0$$
+ p = 0.65 \Rightarrow

$$= 0.65 - 0.5$$

Therefore, when the total pressure is 0.65 atm, pressure of SOCl₂is

$$p_{SOCl_2} = P_0 - p$$

$$= 0.5 - 0.15$$

Therefore, the rate of equation, when total pressure is 0.65 atm, is given by,

Rate =
$$k(^{p_{SOCl_2}})$$

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

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

Q22:

The rate constant for the decomposition of N₂O₅ at various temperatures is given below:





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

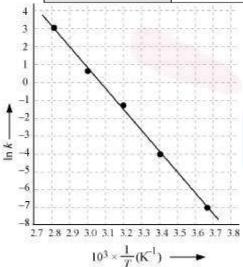
Draw a graph between $\ln k$ and 1/T and calculate the values of A and E_a .

Predict the rate constant at 30 ° and 50 °C.

Answer:

From the given data, we obtain

T/°C	0	20	40	60	80
T/K	273	293	313	333	353
$\frac{1}{T}/\mathrm{K}^{-1}$	3.66×10-3	3.41×10-3	3.19×10·3	3.0×10-3	2.83 ×10-3
$10^5 \times k/\mathrm{s}^{-1}$	0.0787	1.70	25.7	178	2140
ln k	- 7.147	- 4. <mark>075</mark>	- 1.359	- 0.577	3.063



Slope of the line,

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

According to Arrhenius equation,





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

 $\Rightarrow E_a = -Slope \times R$
= $-(-12.301 \text{K}) \times (8.314 \text{ J K}^{-1} \text{mol}^{-1})$
= $102.27 \text{ kJ mol}^{-1}$

Again,

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

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

When
$$T = 273 \,\text{K}$$
, $\ln k = -7.147$

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

= 37.911

Therefore,
$$A = 2.91 \times 10^6$$

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

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

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

$$\ln k = -2.8$$

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

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

Q23:

The rate constant for the decomposition of hydrocarbons is 2.418 x 10-5 s-1at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

Answer:

$$k = 2.418 \times 10_{-5} s_{-1}$$





 E_a = 179.9 kJ mol⁻¹= 179.9 × 10³J mol⁻¹

According to the Arrhenius equation,

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

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

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

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

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

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

= 12.5917

Therefore, A = antilog (12.5917)

= $3.9 \times 10^{12} s^{-1}$ (approximately)

Q24:

Consider a certain reaction A \rightarrow 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 mol L⁻¹.

Answer:

$$k = 2.0 \times 10_{-2} s_{-1}$$

T = 100 s

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

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

Therefore,

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

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

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

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

= 0.135 mol L-1(approximately)

Hence, the remaining concentration of A is 0.135 mol L-1.





Q25:

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 sample of sucrose remains after 8 hours?

Answer:

For a first order reaction,

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

It is given that, $t_{1/2}$ = 3.00 hours

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

Therefore.

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

= 0.231 h⁻¹

Then, 0.231 h-1 =
$$\frac{2.303}{8 \text{ h}} log \frac{\left[R\right]_0}{\left[R\right]}$$

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

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

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

$$\Rightarrow \frac{[R]}{[R]_0} = 0.1576 \text{ (approx)}$$
$$= 0.158$$

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

Q26:

The decomposition of hydrocarbon follows the equation

$$k = (4.5 \times 10_{11} \text{ s}_{-1}) \text{ e}_{-28000 \text{ K/T}}$$
 Calculate

 \boldsymbol{E}_{a} .





Answer:

The given equation is

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

Arrhenius equation is given by,

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

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

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

= 8.314 J K-1mol-1× 28000 K

= 232792 J mol⁻¹

= 232.792 kJ mol

Q27:

The rate constant for the first order decomposition of H₂O₂is given by the following equation:

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

Calculate E_afor this reaction and at what temperature will its half-period be 256 minutes?

Answer:

Arrhenius equation is given by,

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

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

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

$$\Rightarrow \log k = \log A - \frac{E_a}{2.303 \text{ R}T}$$
 (i)

The given equation is

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

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

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

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

= 1.25 × 10⁴K × 2.303 × 8.314 J K⁻¹mol⁻¹





= 239339.3 J mol-1 (approximately)

= 239.34 kJ mol-1

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

$$k = \frac{0.693}{t_{\frac{1}{2}}}$$
$$= \frac{0.693}{256}$$

 $= 2.707 \times 10^{-3} \text{min}^{-1}$

 $= 4.51 \times 10_{-5}$ 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 K

= 669 K (approximately)

Q28:

The decomposition of A into product has value of k as 4.5 x 10³ s⁻¹ at 10°C and energy of activation 60 kJ mol¹. At what temperature would k be 1.5 x 10⁴ s⁻¹?

Answer:

From Arrhenius equation, we obtain

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

Also, $k_1 = 4.5 \times 10^3 \text{ s}^{-1}$

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

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

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

Then.





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

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

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

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

$$\Rightarrow$$
 0.9528 $T_2 = 283$

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

= 297 K

= 24°C

Hence, k would be 1.5×10^4 s⁻¹ at 24°C.

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

Q29:

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 x 10¹⁰ s⁻¹, Calculate K at 318 K and E_n .

Answer:

For a first order reaction,

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

At 298 K,
$$t = \frac{2.303}{k} \log \frac{100}{90}$$

$$=\frac{0.1054}{k}$$

At 308 K,
$$t' = \frac{2.303}{k'} \log \frac{100}{75}$$

$$=\frac{2.2877}{1}$$

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

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

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

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

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

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

To calculate *k* at 318 K,

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

Again, from Arrhenius equation, we obtain

$$\log k = \log A - \frac{E_a}{2.303 \,\text{R T}}$$

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

$$= \left(0.6021 + 10\right) - 12.5876$$

$$= -1.9855$$

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

= 1.034×10⁻² s⁻¹

Q30:

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.

Answer:

From Arrhenius equation, we obtain





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

It is given that, $k_2 = 4k_1$

$$T_1 = 293 \,\mathrm{K}$$

$$T_2 = 313 \,\mathrm{K}$$

Therefore,
$$\log \frac{4k_1}{k_2} = \frac{E_a}{2.303 \times 8.314} \left(\frac{313 - 293}{293 \times 313} \right)$$

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

$$\Rightarrow E_o = \frac{0.6021 \times 2.303 \times 8.314 \times 293 \times 313}{20}$$
$$= 52863.33 \text{ J mol}^{-1}$$

= 52.86 kJ mol⁻¹

Hence, the required energy of activation is 52.86 kJmol⁻¹.