Chemical Kinetics

NCERT FOCUS

ANSWERS

Topic 1

1. (i) Order = 2, Dimensions of $k = \frac{\text{Rate}}{[\text{NO}]^2} = \frac{\text{mol } \text{L}^{-1} \text{ s}^{-1}}{(\text{mol } \text{L}^{-1})^2} = \text{L } \text{mol}^{-1} \text{ s}^{-1}$ (ii) Order = 2, Dimensions of $k = \text{L } \text{mol}^{-1} \text{ s}^{-1}$ (iii) Order = $\frac{3}{2}$, Dimensions of $k = \frac{\text{Rate}}{[\text{CH}_3\text{CHO}]^{3/2}} = \frac{\text{mol } \text{L}^{-1} \text{ s}^{-1}}{(\text{mol } \text{L}^{-1})^{3/2}}$ $= \text{L}^{1/2} \text{ mol}^{-1/2} \text{ s}^{-1}$ (iv) Order = 1, Dimensions of $k = \frac{\text{Rate}}{[\text{C}_2\text{H}_5\text{CI}]} = \frac{\text{mol } \text{L}^{-1} \text{ s}^{-1}}{\text{mol } \text{L}^{-1}} = \text{s}^{-1}$ 2. Initial rate = $k[A][B]^2$ $= (2.0 \times 10^{-6}) \times (0.1) \times (0.2)^2 = 8 \times 10^{-9} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$ When [A] is reduced from 0.10 mol L^{-1} to 0.06 mol L^{-1} , *i.e.* 0.04 mol L^{-1} of 4 has reacted. Then according to equation

0.04 mol L⁻¹ of A has reacted. Then according to equation, amount of B reacted is half of A.

$$[B] = \frac{1}{2} \times 0.04 \text{ mor } L^{-1} = 0.02 \text{ mor } L^{-1}$$

Hence, [B] left = 0.2 - 0.02 = 0.18 mol L⁻¹
Now, again rate = k[A][B]²
 \therefore Pate = (2.0 × 10⁻⁶) × (0.06) × (0.18)²

- $\therefore \text{ Rate} = (2.0 \times 10^{-6}) \times (0.06) \times (0.18)^{4}$ $= 3.89 \times 10^{-9} \text{ mol } \text{L}^{-1} \text{ s}^{-1}$
- **3.** For the reaction, $2NH_3 \rightarrow N_2 + 3H_2$

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

For zero order reaction,

Rate = k

From equation (1) and (2)

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

 $\therefore \text{ Rate of production of } N_2 = \frac{d[N_2]}{dt} = k$ $k = 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$ Rate of production of $H_2 = \frac{d[H_2]}{dt} = 3k$ $= 3 \times 2.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1} = 7.5 \times 10^{-4} \text{ mol } L^{-1} \text{ s}^{-1}$ 4. In terms of pressure,

Units of
$$k = \frac{\text{Rate}}{(p_{\text{CH}_3\text{OCH}_3})^{3/2}} = \frac{\text{bar min}^{-1}}{\text{bar}^{3/2}} = \text{bar}^{-1/2} \text{min}^{-1}$$

5. Following are the factors on which rate of reaction depends :

(i) Nature of the reactant : Rate of reaction depends on nature of reactant.

Example : Reactions of ionic compounds are faster than that of covalent compounds.

(ii) State of reactants : Solid reactions are slow, reactions of liquids are fast whereas that of gases are very fast.

(iii) Temperature : Rate of reaction largely depends on temperature. It has been observed that every 10°C rise in temperature increases rate of reaction by 2-3 times.

 $\frac{l_{t+10}}{L} = 2-3$. This ratio is called temperature coefficient.

There are two reasons for increasing rate of reaction with increasing temperature.

(a) Increase in temperature increases average kinetic energy of reactant molecules. Hence, rate of collision increases.

(b) With increase in temperature number of molecules having threshold energy also increases *i.e.*, number of active molecules increases. As a result, number of effective collisions increases. Hence, rate of reaction increases.

(iv) Concentration : Rate of reaction also depends on concentration of reactants.

Rate = $k \times C^n$, where n = order of reaction, C = concentration of reactant.

(v) Presence of catalyst : Rate of reaction also depends on presence of catalyst. Catalyst increases rate of reaction by any of the following ways :

(a) Increasing surface area of reaction.

(b) Adsorbing the reactants on its surface and thus increasing chances of collision.

- (c) By forming unstable intermediate with the substrate.
- (d) By providing alternate path of lower activation energy.

6. Rate =
$$k[A]^2$$

...(2)

(i) If [A] = 2R, rate $= k(2R)^2 = 4kR^2$ *i.e.*, rate of reaction increases 4 times when concentration is doubled.

(ii) If
$$[A] = \frac{1}{2}R$$
, rate $= k\left(\frac{R}{2}\right)^2 = \frac{1}{4}kR^2$ *i.e.*, rate becomes $\frac{1}{4}$ when concentration is reduced to $\frac{1}{2}$.

Units of rate = bar min^{-1}

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7. (i) Reaction is first order in A and second order in B, hence, differential rate equation is $\frac{dx}{dt} = k[A][B]^2$

(ii) Let rate = kab^2

If [B] is tripled, Rate = $ka (3b)^2 = 9kab^2$

i.e., Rate increases 9 times.

(iii) If both [A] and [B] are doubled,

Rate = $k(2a)(2b)^2 = 8kab^2$

i.e. Rate of reaction increases 8 times.

8. Suppose oder with respect to *A* is '*X*' and with respect to *B* is '*Y*'. Then the rate of law will be

$$r_{0} = \frac{dx}{dt} = k[A]^{x}[B]^{y}$$
5.07 × 10⁻⁵ = k(0.2)^x (0.3)^y ...(i)
5.07 × 10⁻⁵ = k(0.2)^x (0.10)^y ...(ii)
Dividing (i) by (ii), we get
1 = 3^y \Rightarrow 3⁰ = 3^y \Rightarrow y = 0
5.07 × 10⁻⁵ = k(0.2)^x (0.1)⁰ ...(iii)
1.43 × 10⁻⁴ = k(0.4)^x (0.05)⁰ ...(iv)
Dividing (iv) by (iii), we get 2.8 = 2^x

 $\log 2.8 = x \log 2$

or
$$x = \frac{\log 2.8}{\log 2.0} = \frac{0.4472}{0.3010} = 1.48 \approx 1.5$$

The order of reaction is 1.5 with respect to 'A' and zero with respect to 'B'.

9. Suppose order with respect to A is m and with respect to B is n. Then the rate law will be Rate = $k[A]^m[B]^n$

Substituting the value of experiments I to IV, we get

Expt. I : Rate = $6.0 \times 10^{-3} = k (0.1)^m (0.1)^n$	(i)
Expt. II : Rate = $7.2 \times 10^{-2} = k (0.3)^m (0.2)^n$	(ii)
Expt. III : Rate = $2.88 \times 10^{-1} = k (0.3)^m (0.4)^n$	(iii)
Expt. IV : Rate = $2.4 \times 10^{-2} = k (0.4)^m (0.1)^n$	(iv)
Comparing equation (i) and equation (iv)	

$$\therefore \quad \frac{(\text{Rate})_{\text{I}}}{(\text{Rate})_{\text{IV}}} = \frac{6.0 \times 10^{-3}}{2.4 \times 10^{-2}} = \frac{k(0.1)^m (0.1)^n}{k(0.4)^m (0.1)^n}$$

or,
$$\frac{1}{4} = \frac{(0.1)^m}{(0.4)^m} = \left(\frac{1}{4}\right)^m$$
 \therefore $m = 1$

Comparing equation (ii) and equation (iii)

$$\frac{(\text{Rate})_{||}}{(\text{Rate})_{|||}} = \frac{7.2 \times 10^{-2}}{2.88 \times 10^{-1}} = \frac{k(0.3)^m (0.2)^n}{k(0.3)^m (0.4)^n}$$

or, $\left(\frac{1}{2}\right)^2 = \frac{(0.2)^n}{(0.4)^n} = \left(\frac{1}{2}\right)^n \therefore n = 2$

 \therefore Rate law expression is : Rate = $k[A][B]^2$.

The rate constant can be calculated from the given data of any experiment using expression :

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

From Expt. I,
$$k = \frac{6.0 \times 10^{-3}}{0.1 \times (0.1)^2} = 6.0$$

 \therefore Rate constant $k = 6.0 \text{ mol}^{-2} \text{ L}^2 \text{ min}^{-1}$
Unit of k , $k = \frac{\text{Rate}}{[A][B]^2} = \frac{\text{mol} \text{ L}^{-1} \text{ min}^{-1}}{(\text{mol} \text{ L}^{-1})(\text{mol} \text{ L}^{-1})^2}$
 $= \text{mol}^{-2} \text{ L}^2 \text{ min}^{-1}$
10. The reaction is first order with respect to A and zero order with respect to B ,
Hence the rate expression will be $= k[A]^1 [B]^0 = k[A]$
From expt. I : $2.0 \times 10^{-2} = k(0.1)$
or, $k = 0.2 \text{ min}^{-1}$
From expt. II : $4.0 \times 10^{-2} = (0.2) \times [A]$
 $\Rightarrow [A] = 0.2 \text{ mol} \text{ L}^{-1}$
From expt. III : Rate $= (0.2)(0.4)$
 $= 0.08 \text{ mol} \text{ L}^{-1} \text{ min}^{-1} = 8 \times 10^{-2} \text{ mol} \text{ L}^{-1} \text{ min}^{-1}$
From expt. IV : $2.0 \times 10^{-2} = (0.2) \times [A]$

Topic 2

Rate =
$$-\frac{C_2 - C_1}{t_2 - t_1} = -\frac{0.17 - 0.31}{60 - 30} = \frac{0.14}{30} \text{ mol } L^{-1} \text{ s}^{-1}$$

= 4.67 × 10⁻³ mol L⁻¹ s⁻¹

2. Half-life period of a first order reaction is given by $t_{1/2} = \frac{0.693}{k}$, hence

(i) $t_{1/2} = \frac{0.693}{200} = 3.46 \times 10^{-3} \text{ s}$

(ii)
$$t_{1/2} = \frac{0.693}{2} = 0.346 \text{ min}$$

(iii)
$$t_{1/2} = \frac{0.693}{4} = 0.173$$
 year

3. Radioactive decay follows first order kinetics. Therefore,

Decay constant (
$$\lambda$$
) = $\frac{0.693}{t_{1/2}} = \frac{0.693}{5730} \text{ yr}^{-1}$
Given, $[R]_0 = 100 \therefore [R] = 80$

Given,
$$[R]_0 = 100$$
 : $[R] =$

and
$$t = \frac{2.303}{\lambda} \log \frac{[R]_0}{[R]} = \frac{2.303}{\left(\frac{0.693}{5730}\right)} \log \left(\frac{100}{80}\right)$$

$$=\frac{2.303\times5730}{0.693}\times0.0969 \text{ yr} = 1845 \text{ years}$$

$$t/s$$
 $[N_2O_5] \times 10^{-2}$ /mol L⁻¹ $log[N_2O_5]$ 01.63-1.794001.36-1.878001.14-1.94

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	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		

(i) Plot of $[N_2O_5]$ vs time



- (ii) Initial conc. of N₂O₅ = 1.63×10^{-2} M Half of this concentration = 0.815×10^{-2} M Time corresponding to this concentration = 1440 s. Hence, $t_{1/2}$ = 1440 s
- (iii) Plot of log $[N_2O_5]$ vs time



(iv) As plot of log $[N_2O_5]$ vs time is a straight line, it is a reaction of first order, *i.e.* rate law is,

$$Rate = k[N_2O_5]$$

(v) For first order reaction,

$$\log R = -\frac{k}{2.303}t + \log R_0$$

Therefore slope of the graph drawn between log R and t will

be
$$\frac{-1}{2.303}$$

$$\therefore \text{ Slope of the line} = -\frac{k}{2.303} = \frac{y_2 - y_1}{t_2 - t_1}$$

or, Slope = $\frac{-2.46 - (-1.79)}{3200 - 0} = -\frac{0.67}{3200}$
or, $\frac{k}{2.303} = \frac{0.67}{3200}$
or, $k = \frac{0.67}{3200} \times 2.303 = 4.82 \times 10^{-4} \text{ s}^{-1}$

(vi)
$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{4.82 \times 10^{-4}} = 1438 \text{ s}$$

The value of $t_{1/2}$ calculated from the value of k is very close to that obtained from graph.

5. Given,
$$k = 60 \text{ s}^{-1}$$
, $[R] = \frac{[R]_0}{16}$, $t = ?$
Using formula, $t = \frac{2.303}{k} \log \frac{[R]_0}{[R]} = \frac{2.303}{60} \log 16$
 $= 4.62 \times 10^{-2} \text{ s}$

Alternatively,

In general, amount of the substance left after *n* half lives,

$$[R] = \frac{[R]_0}{2^n} = \frac{[R]_0}{16}$$

 $\therefore \quad n = 4 \text{ and } t = n \times t_{1/2}$
 $t = n \times \frac{0.693}{k} = 4 \times \frac{0.693}{60} = 0.0462 \text{ s}$

6. As radioactive disintegration follows first order kinetics. Hence

Decay constant of ⁹⁰Sr, $(\lambda) = \frac{0.693}{t_{1/2}} = \frac{0.693}{28.1}$ = 2.466×10⁻² yr⁻¹

To calculate the amount left after 10 years Given, $[R]_0 = 1 \ \mu g$, $t = 10 \ years$, $k = 2.466 \times 10^{-2} \ yr^{-1}$, [R] = ?Using formula, $\lambda = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$ or $2.466 \times 10^{-2} = \frac{2.303}{10} \log \frac{1}{[R]}$ $\frac{2.466 \times 10^{-2} \times 10}{2.303} = -\log[R]$ or, $\log [R] = -0.1071$ or, $[R] = \text{Antilog} (-0.1071) = 0.7814 \ \mu g$ To calculate the amount left after 60 years, t = 60 years, $[R]_0 = 1 \ \mu g$, [R] = ?or, $2.466 \times 10^{-2} = \frac{2.303}{60} \log \frac{1}{[R]}$ 4

 $\log [R] = -0.6425$ or, or, $[R] = \text{Antilog}(-0.6425) = 0.2278 \,\mu\text{g}$ **7.** 99% completion means that x = 99% of $[R]_0$ or, $[R] = [R]_0 - 0.99[R]_0 = 0.01[R]_0$ For first order reaction, $t = \frac{2.303}{k} \log \frac{[R]_0}{[P]}$ $\therefore \quad t_{99\%} = \frac{2.303}{k} \log \frac{[R]_0}{0.01[R]_0} = \frac{2.303}{k} \log 10^2 = 2 \times \frac{2.303}{k}$ 90% completion means that $[R] = [R]_0 - 0.90[R]_0$ $= 0.1[R]_{0}$ $\therefore t_{90\%} = \frac{2.303}{k} \log \frac{[R]_0}{0.1[R]_0} = \frac{2.303}{k} \log 10 = \frac{2.303}{k}$ $\therefore \frac{t_{99\%}}{t_{90\%}} = \left(\frac{2 \times 2.303}{k}\right) / \left(\frac{2.303}{k}\right) = 2$ or, $t_{99\%} = 2 \times t_{90\%}$ **8.** 30% decomposition means that x = 30% of $[R]_0$ or, $[R] = [R]_0 - 0.3[R]_0 = 0.7[R]_0$ For reaction of 1st order, $k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{40} \log \frac{[R]_0}{0.70[R]_0}$ $=\frac{2.303}{40}\log\frac{10}{7}$ min⁻¹ $=\frac{2.303}{40}\times 0.1549 \text{ min}^{-1}=8.918\times 10^{-3} \text{ min}^{-1}$ For a 1st order reaction, $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{8.918 \times 10^{-3} \text{ min}^{-1}} = 77.7 \text{ min}$ $(CH_3)_2 CHN = NCH(CH_3)_{2(g)} \longrightarrow N_{2(g)} + C_6 H_{14(g)}$ 9. Azoisopropane Initial pressure P_0 Pressure $P_0 - p$ Hexane р after time t Total pressure after time $t(P_t)$ $= (P_0 - p) + p + p = P_0 + p \text{ or } p = P_t - P_0$ $[R]_0 \propto P_0$ and $[R] \propto P_0 - p$ On substituting the value of p $[R] \propto P_0 - (P_t - P_0), i.e. [R] \propto 2P_0 - P_t$ As decomposition of azoisopropane is a first order reaction $\therefore \quad k = \frac{2.303}{t} \log \frac{[R]_0}{[R]} = \frac{2.303}{t} \log \left(\frac{P_0}{2P_0 - P_t} \right)$ When t = 360 sec, $\frac{2.303}{2.303}\log\left(\frac{35.0}{16}\right) = \frac{2.303}{260}\log\frac{35.0}{16}$

$$k = \frac{2.303}{360} \log\left(\frac{35.0}{2 \times 35.0 - 54.0}\right) = \frac{2.303}{360} \log\frac{35}{10}$$
$$= 2.175 \times 10^{-3} \text{ s}^{-1}$$
When $t = 720 \text{ sec}$,

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$$k = \frac{2.303}{720} \log \frac{35.0}{2 \times 35.0 - 63} = \frac{2.303}{720} \log 5$$

= 2.235 × 10⁻³ s⁻¹
 \therefore Average value of $k = \frac{2.175 + 2.235}{2} \times 10^{-3} s^{-1}$
= 2.20 × 10⁻³ s⁻¹
10. SO₂Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}
Let initial pressure $P_0 = 0$ 0 0
Pressure at time $t P_0 - p = p$ p
Let initial pressure $P_0 \propto R_0$
Pressure at time $t P_1 = P_0 - p + p + p = P_0 + p$
 \therefore Pressure of reactant at time t
= $P_0 - p = 2P_0 - P_1 \propto R$
Using formula, $k = \frac{2.303}{t} \log \left(\frac{P_0}{2P_0 - P_t} \right)$
When $t = 100$ s,
 $k = \frac{2.303}{100} \log \left(\frac{0.5}{2 \times 0.5 - 0.6} \right) = \frac{2.303}{100} \log(1.25)$
= $\frac{2.303}{100} (0.0969) = 2.2316 \times 10^{-3} s^{-1}$
When $P_t = 0.65$ atm,
 \therefore Pressure of SO₂Cl₂ at time $t (P_{SO_2Cl_2})$,
 $R = 2P_0 - p_t = 2 \times 0.50 - 0.65$ atm = 0.35 atm
Rate at that time $k \times p_{SO_2Cl_2} = (2.2316 \times 10^{-3}) \times (0.35)$
 $= 7.8 \times 10^{-4}$ atm s⁻¹
11. The units of k shows that the reaction is of first order.
Hence, $k = \frac{2.303}{100} \log \frac{|R|_0}{|R|}$
or, $2.0 \times 10^{-2} = \frac{2.303}{100} \log \frac{1.0}{|R|}$
or, $\log [R] = -0.8684$
 $\therefore [R] = Antilog (-0.8684) = 0.1354$ mol L⁻¹
12. Sucrose decomposes according to first order rate law,
Hence,
 $k = \frac{2.303}{l} \log \frac{|R|_0}{|R|}$, $t_{1/2} = 3$ hrs, $t = 8$ hrs, $\frac{|R|}{|R|_0} = ?$
 $t_{1/2} = 3.0$ hrs, $\therefore k = \frac{0.693}{l_{1/2}} = \frac{0.693}{3} = 0.231$ hr⁻¹
Hence, $0.231 = \frac{2.303}{8} \log \frac{|R|_0}{|R|}$
or, $\log \frac{|R|_0}{|R|} = 0.8024$
or, $\frac{|R|_0}{|R|} =$ Antilog (0.8024) = 6.345
or, $\frac{|R|}{|R|} =$ Antilog (0.8024) = 6.345
or, $\frac{|R|}{|R|} =$ Antilog (0.8024) = 6.345
or, $\frac{|R|}{|R|} = \frac{1}{6.345} = 0.158$

Topic 3

1. The values of rate constants for the decomposition of N_2O_5 at various temperatures are given below :

	<i>T</i> (°C)	<i>T</i> (K)	1/ <i>T</i>	<i>k</i> (s ⁻¹)	In <i>k</i> (= 2.303 log <i>k</i>)			
	0	273	3.6×10^{-3}	7.87 × 10 ⁻⁷	-14.06			
	20	293	3.4×10^{-3}	1.70 × 10 ⁻⁵	-10.98			
	40	313	3.19×10^{-3}	25.7×10^{-5}	-8.266			
	60	333	3.00×10^{-3}	178 × 10 ⁻⁵	-6.332			
	80	353	2.8×10^{-3}	2140×10^{-5}	-3.844			
	$ \begin{array}{c} -2 \\ -4 \\ -6 \\ -8 \\ -10 \\ -12 \\ -14 \\ -16 \\ -18 \\ -20 \\ 2.2 \ 2.4 \ 2.6 \ 2.8 \ 3.0 \ 3.2 \ 3.4 \ 3.6 \ 3.8 \ 4.0 \\ \hline -10 \\ -13 \\ -10 \\ -12 \\ -14 \\ -16 \\ -18 \\ -20 \\ -2.2 \ 2.4 \ 2.6 \ 2.8 \ 3.0 \ 3.2 \ 3.4 \ 3.6 \ 3.8 \ 4.0 \\ -10 \\$							
Graph between $\ln k$ and $1/T$								
	V2 -	– V₁	-10.98 - (-	14.08) 2	2			
$= \frac{y_2 - y_1}{x_2 - x_1} = \frac{-10.98 - (-14.08)}{3.4 - 3.6} \times 10^3 = -15.5 \times 10^3$								
$E_a = -\text{slope} \times R = -(-15.5 \times 10^3 \times 8.314)$ = 128.86 kJ K ⁻¹ mol ⁻¹								
Again ln $A = \ln k + \frac{E_a}{RT}$								
$= -14.06 + \frac{128.86 \times 10^3 \text{ JK}^{-1} \text{mol}^{-1}}{8.314 \times 273}$								
= -14.06 + 56.77 = 42.71								
or, $\log A = 18.53$								
	or, $A = antilog 18.53 = 0.3388 \times 10^{19}$							

or, $A = 3.388 \times 10^{18}$

Value of rate constant k at 303 K and 323 K can be obtained from graph.

First of all ln *k* is obtained corresponding to $\frac{1}{303 \text{ K}}$ and $\frac{1}{323 \text{ K}}$ and then *k* is calculated.

2. Here, $k = 2.418 \times 10^{-5} \text{ s}^{-1}$, $E_a = 179.9 \text{ kJ mol}^{-1}$, T = 546 K, A = ?According to Arrhenius equation,

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

 $= \log(2.418 \times 10^{-5}) + \frac{179.9}{2.303 \times 8.314 \times 10^{-3} \times 546}$ $= (-5 + 0.3834) + 17.2081 = 12.5924 \text{ s}^{-1}$ or, $A = \text{Antilog} (12.5924) \text{ s}^{-1} = 3.912 \times 10^{12} \text{ s}^{-1}$ **3.** Arrhenius equation, $k = Ae^{-E_a/RT}$ Given equation is $k = (4.5 \times 10^{11} \text{ s}^{-1})e^{-28000 \text{ K/T}}$ Comparing both th $-\frac{E_a}{RT} = -\frac{28000 \text{ K}}{T}$ Comparing both the equations, we get or, $E_a = 28000 \text{ K} \times R = 28000 \times 8.314$ $= 232.79 \text{ kJ mol}^{-1}$ **4.** According to Arrhenius equation, $k = Ae^{-E_a/RT}$ or, $\ln k = \ln A - \frac{E_a}{BT}$ or, $\log k = \log A - \frac{E_a}{2.303BT}$...(i) Given equation is $\log k = 14.34 - 1.25 \times 10^4 \text{ K/T}$...(ii) Comparing (i) with (ii), $\frac{E_a}{2.303RT} = \frac{1.25 \times 10^4 \text{ K}}{T}$ or, $E_a = 2.303R \times 1.25 \times 10^4 \text{ K}$ $= 2.303 \times (8.314) \times 1.25 \times 10^4 = 239.34$ kJ mol⁻¹ When $t_{1/2} = 256$ min, $k = \frac{0.693}{256 \times 60} = 4.51 \times 10^{-5} \text{ s}^{-1}$ Substituting this value in the given equation, $\log(4.51 \times 10^{-5}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{\tau}$ *i.e.*, $(-5 + 0.6542) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{7}$ or, $\frac{1.25 \times 10^4 \text{ K}}{T} = 18.6858 \text{ or}, T = 669 \text{ K}$ **5.** Given $k_1 = 4.5 \times 10^3 \text{ s}^{-1}$, $T_1 = 10 + 273 \text{ K} = 283 \text{ K}; k_2 = 1.5 \times 10^4 \text{ s}^{-1}, T_2 = ?,$ $E_{a} = 60 \text{ kJ mol}^{-1}$ Applying Arrhenius equation, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$ $\log \frac{1.5 \times 10^4}{4.5 \times 10^3} = \frac{60000}{2.303 \times 8.314} \left(\frac{T_2 - 283}{283T_2} \right)$ or, log 3.333 = 3133.63 $\left(\frac{T_2 - 283}{283T_2}\right)$

or,
$$\frac{0.5228}{3133.63} = \frac{T_2 - 283}{283T_2}$$

or, $0.0472T_2 = T_2 - 283$ or $0.9528T_2 = 283$

or,
$$T_2 = \frac{283}{0.9528} = 297 \text{ K} = 297 - 273 = 24^{\circ}\text{C}$$

6.
$$t = \frac{2.303}{k_1} \log \left(\frac{[R]_0}{\frac{90}{100} [R]_0} \right),$$

$$t = \frac{2.303}{k_2} \log \left(\frac{[R]_0}{\frac{75}{100} [R]_0} \right),$$

$$t = \frac{2.303}{k_1} \log \frac{10}{9}, t = \frac{2.303}{k_2} \log \frac{4}{3},$$

$$\frac{2.303}{k_1} \log \frac{10}{9} = \frac{2.303}{k_2} \log \frac{4}{3},$$

$$\Rightarrow \frac{k_2}{k_1} = \frac{\log \frac{4}{3}}{\log \frac{10}{9}} = \frac{\log 1.333}{\log 1.111} = \frac{0.1249}{0.0457} = 2.733,$$

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

$$\log 2.733 = \frac{E_a}{2.303 \times 8.314} \left(\frac{308 - 298}{298 \times 308} \right),$$

$$E_a = \frac{2.303 \times 8.314 \times 308 \times 298}{10} \times 0.4367 = 76.75 \text{ kJ mol}^{-1},$$

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

$$\log k = \log A - \frac{E_a}{2.303 \times 8.314 \times 318},$$

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$$= 10.6021 - \frac{76750}{6088.746}$$

= 10.6021 - 12.6051 = -2.003
 $k = \text{Antilog} (-2.003) = 9.93 \times 10^{-3}$
7. Given $r_2 = 4r_1$, $T_1 = 293$ K, $T_2 = 313$ K, $E_a = ?$
We know, $\frac{r_2}{r_1} = \frac{k_2}{k_1} = \frac{4}{1}$
Using Arrhenius equation,
 $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$
 $\log 4 = \frac{E_a}{2.303 \times 8.314} \left(\frac{1}{293} - \frac{1}{313}\right)$
or, $E_a = \log 4 \times \frac{2.303 \times 8.314 \times 293 \times 313}{20}$
or, $E_a = 52.864$ kJ/mol
8. The rate constant increases with increase in temperature
and becomes almost double for every 10° increase in
temperature. Swedish chemist, Arrhenius derived a quantitative

temperature. Swedish chemist, Arrhenius derived a quantitative relation between rate of reaction and temperature. According to Arrhenius, $k = Ae^{-\frac{E_a}{RT}}$ or, log $k = \log A - \frac{E_a}{2T}$

$$k = Ae^{-RT}$$
 or, $\log k = \log A - \frac{L_a}{RT}$
or, $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$

where k_1 = rate constant at temperature T_1 , k_2 = rate constant at temperature T_2 , E_a = energy of activation, R = universal gas constant.

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