Chapter.4
Chemical kinetics
Class-XII
Subject-Chemistry

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

i. $3NO(g) \rightarrow N_2O(g)$ Rate = $k[NO]^2$

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

iii. $CH_3CHO(g) \rightarrow CH_4(g) + CO(g)$ Rate = $k[CH_3CHO]^{3/2}$

iv. $C_2H_5Cl(g) \rightarrow C_2H_4(g) + HCl(g)$ Rate = $k[C_2H_5Cl]$

Answer 4.1

i. Rate = $k[NO]^2$

Hence, order of the reaction = 2

Unit of $k = \dfrac{Rate}{[NO]^2}$

$= \dfrac{mol/l\ \sec}{(mol/l)^2}$

$= l/mol\ \sec$

ii. Rate = $k[H_2O_2][I^-]$

Hence, order of the reaction = 2

Unit of $k = \dfrac{Rate}{[H_2O_2][I^-]}$

$= \dfrac{mol/l\ \sec}{(mol/l)^2}$

$= l/mol\ \sec$

iii. Rate = $k[CH_3CHO]^{3/2}$

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

Unit of $k = \frac{Rate}{[CH_3CHO]^{3/2}}$

$= \frac{mol/l \text{ sec}}{(mol/l)^{3/2}}$

$= l^{1/2}/mol^{1/2} \text{ sec}$

iv. Rate = $k\,[C_2H_5Cl]$

Hence, order of the reaction = 1

Unit of $k = \frac{Rate}{[C_2H_5Cl]}$

$= \frac{mol/l \text{ sec}}{(mol/l)}$

$= \text{sec}^{-1}$

4.2 For the reaction:

$2A + B \rightarrow A_2B$

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

Answer 4.2

The initial rate of the reaction is

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

$= (2.0\times10^{-6})\,(0.1)\,(0.2)^2$

$= 8.0 \times 10^{-9}$ mol^{-2} L^2 s^{-1}

Now,

Concentration of A reacted = (0.1 − 0.06) = 0.04 mol L^{-1}

Concentration of B reacted $= \frac{1}{2} \times 0.04 = 0.02$ mol L^{-1}

Concentration of B available, [B] = (0.2 − 0.02) = 0.18 mol L^{-1}

Now, rate of the reaction becomes,

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

$$= (2.0\times10^{-6})\ (0.06)\ (0.18)^2$$

$$= 3.89 \text{ mol } L^{-1} s^{-1}$$

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

Answer 4.3

The decomposition of NH_3 can be represented by,

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

Hence, rate of reaction will be,

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

We know that, reaction order = zero

Thus,

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

$$= 2.5\times10^{-4}\ mol/l\ \sec$$

Now,

Rate of formation of N_2 is

$$\frac{d[N_2]}{dt} = 2.5 \times 10^{-4}\ mol/l\ \sec$$

Rate of formation of H_2 is

$$\frac{d[H_2]}{dt} = 3 \times 2.5 \times 10^{-4}\ mol/l\ \sec$$

$$= 7.5 \times 10^{-4}\ mol/l\ \sec$$

4.4 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.,

$$Rate = k\left(p_{CH_3OCH_3}\right)^{3/2}$$

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

Answer 4.4

$$Rate = k\left(p_{CH_3OCH_3}\right)^{3/2}$$

$$k = \frac{Rate}{\left(p_{CH_3OCH_3}\right)^{3/2}}$$

Unit of rate = bar min^{-1}

Hence, dimensions of rate constants, $k = \frac{bar/\min}{bar^{3/2}}$

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

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

Answer 4.5

The factors that affect the rate of a reaction:

- Concentration of Reactants & pressure in case of gases
- Presence of a catalyst
- Temperature

4.6 A reaction is second order with respect to a reactant. How is the rate of reaction affected if the concentration of the reactant is?

i. doubled
ii. Reduced to half?

Answer 4.6

Let the concentration of the reactant [A] = a

Rate of reaction,

R = $k[A]^2$

$= ka^2$

i. [A] = $2a$,

Rate of the reaction will be,

$$R' = k(2a)^2$$
$$= 4ka^2$$
$$= 4R$$

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

ii. $[A] = \frac{a}{2}$

Then the rate of the reaction will be,

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

Hence, the rate of the reaction will reduce to one-fourth.

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

Answer 4.7

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

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

Where, k = rate constant

A = the Arrhenius factor or the frequency factor

R = gas constant

T = temperature

E_a = energy of activation for the reaction

For a chemical reaction, the rate constant is nearly doubled with a rise in temperature by 10°.

4.8 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 intervals 30 to 60 seconds.**

ii. **Calculate the pseudo first order rate constant for the hydrolysis of ester.**

Answer 4.8

i. time intervals = 30 to 60 seconds

Average rate of reaction $= \frac{d[ester]}{t}$

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

$$= \frac{0.14}{30}$$

$$= 4.67 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$$

ii. For a pseudo first order reaction,

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

$t = 30$ s

$$k_1 = \frac{2.303}{30} \log \frac{0.55}{0.31}$$

$= 1.911 \times 10^{-2}\ s^{-1}$

$t = 60$ s,

$$k_2 = \frac{2.303}{60}\log\frac{0.55}{0.17}$$

$= 1.957 \times 10^{-2}\ s^{-1}$

$t = 90$ s,

$$k_3 = \frac{2.303}{90}\log\frac{0.55}{0.085}$$

$= 2.075 \times 10^{-2}\ s^{-1}$

Now,

Average rate constant, $k = \dfrac{k_1 + k_2 + k_3}{3}$

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

$= 1.98\times10^{-2}\ \sec^{-1}$

4.9 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 4.9

i. The differential rate equation is,

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

ii. If the concentration of B is increased three times, then rate equation becomes as

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

Hence, the rate of reaction will increase 9 times.

iii. When the concentrations of both A and B are doubled, then rate equation becomes as

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

Hence, the rate of reaction will increase 8 times.

4.10 In a reaction between A and B, the initial rate of reaction (r_0) 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
r_0/ mol L^{-1} s^{-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 4.10

Let the order of the reaction with respect to A is *x* and with respect to B be *y*.

Hence, rate of reaction will be

$r_0 = k[A]^x[B]^y$

$5.07 \times 10^{-5} = k[0.20]^x[0.30]^y$ ....(1)

$5.07 \times 10^{-5} = k[0.20]^x[0.10]^y$ ....(2)

$1.43 \times 10^{-4} = k[0.40]^x[0.05]^y$ ....(3)

Dividing equation (1) by (3),

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

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

$[3]^y = 1$

$y = 0$

Dividing equation (3) by (2),

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

$y = 0$

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

$2.821 = [2]^x$

Taking log both sides

$x \log 2 = \log 2.821$

$x = 1.496$

$x \approx 1.5$

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

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

$2A + B \rightarrow C + D$

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 4.11

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

Hence, rate of reaction will be

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

Now,

As per the question,

$$6\times10^{-3} = k[0.1]^x[0.1]^y \text{......................}(1)$$
$$7.2\times10^{-2} = k[0.3]^x[0.2]^y \text{...................}(2)$$
$$2.88\times10^{-1} = k[0.3]^x[0.4]^y \text{.................}(3)$$
$$2.4\times10^{-2} = k[0.4]^x[0.1]^y \text{...................}(4)$$

Dividing equation (1) by (4),

$$\frac{6\times10^{-3}}{2.4\times10^{-2}} = \frac{k[0.1]^x[0.1]^y}{k[0.4]^x[0.1]^y}$$

$$\frac{1}{4}=\frac{[0.1]^x}{[0.4]^x}$$

$$(4)^x = 4$$

$$x = 1$$

Dividing equation (2) by (3),

$$\frac{7.2\times10^{-2}}{2.88\times10^{-1}}=\frac{k[0.3]^x[0.2]^y}{k[0.3]^x[0.4]^y}$$

$$\frac{1}{4}=\frac{[0.2]^y}{[0.4]^y}$$

$$[2]^y = 4$$

$$y = 2$$

Hence, the rate law is

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

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

From experiment I,

$$k = \frac{6\times10^{-3}}{0.1\times0.1}$$

$$= 6\ L^2 / mol^2 \min$$

From experiment II,

$$k = \frac{7.2\times10^{-2}}{0.3\times0.2}$$

$$= 6\ L^2 / mol^2 \min$$

From experiment III,

$$k = \frac{2.88 \times 10^{-1}}{0.3 \times 0.4}$$

$$= 6\ L^2 / mol^2 \min$$

From experiment IV,

$$k = \frac{2.4 \times 10^{-2}}{0.1 \times 0.4}$$

$$= 6\ L^2 / mol^2 \min$$

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

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

Experiment	A/ mol L^{-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 4.12

As per the question, rate of the reaction will be,

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

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

From experiment 1,

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

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

From experiment 2,

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

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

From experiment 3,

Rate = 0.2 × 0.4

= 0.08 mol L^{-1} min^{-1}

From experiment 4,

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

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

4.13 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 $years^{-1}$

i. Half life of a first order reaction, $t_{1/2} = \frac{0.693}{k}$

$= \frac{0.693}{200}$

= 3.47 s

ii. Half life, $t_{1/2} = \frac{0.693}{k}$

$= \frac{0.693}{2}$

= 0.35 min

iii. Half life, $t_{1/2} = \frac{0.693}{k}$

$$= \frac{0.693}{4}$$

$= 0.173$ years

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

Answer 4.14

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

$$= \frac{0.693}{5730} yr^{-1}$$

Using relation,

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

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

$= 1845$ years

Thus, the age of the sample is 1845 years.

4.15 The experimental data for decomposition of N_2O_5

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

In gas phase at 318K are given below:

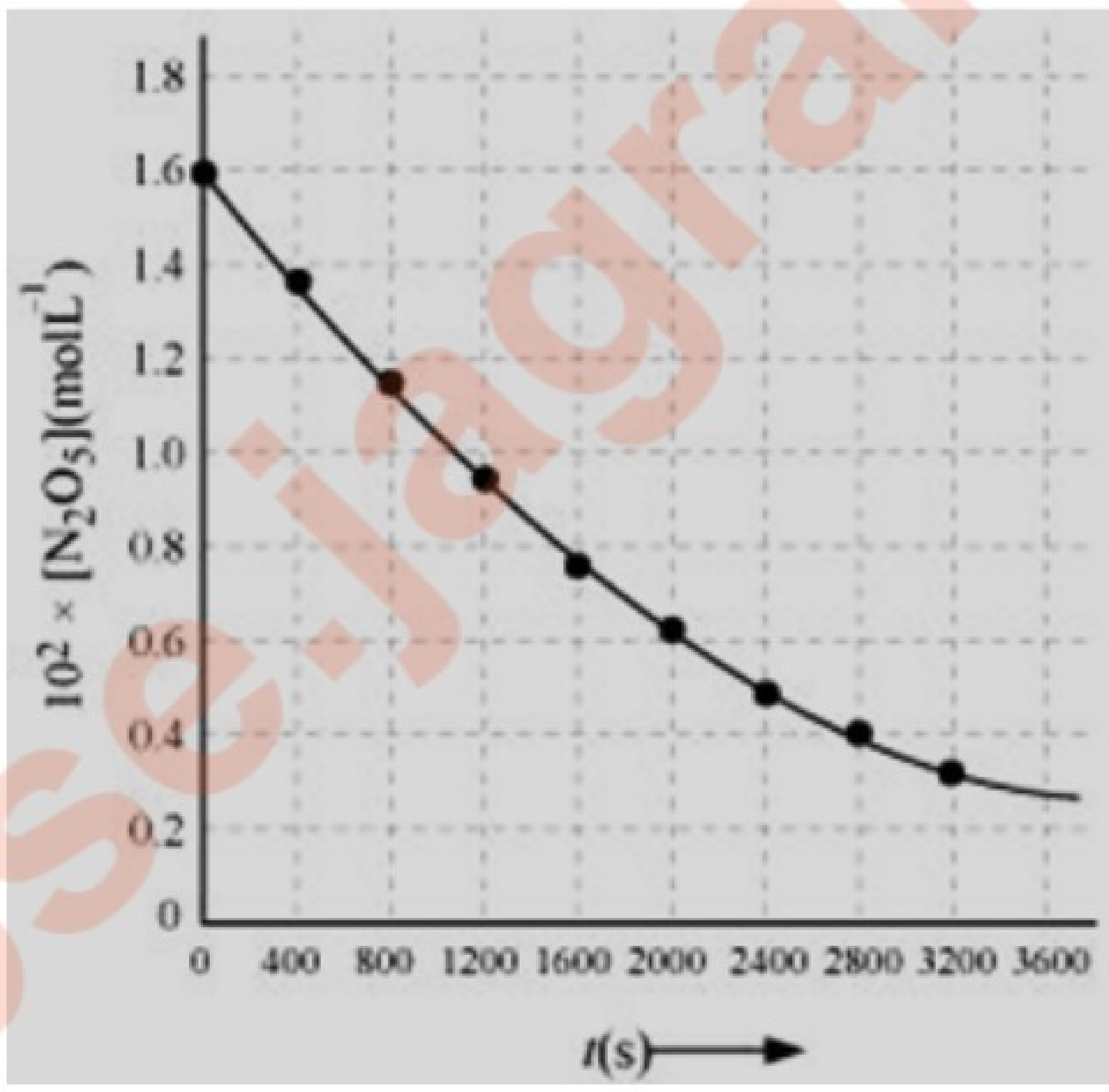
t(s)	0	400	800	1200	1600	2000	2400	2800	3200

$10^2 \times [N_2O_5]$ m	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

i. **Plot [N_2O_5] against *t*.**
ii. **Find the half-life period for the reaction.**
iii. **Draw a graph between log [N_2O_5] and *t*.**
iv. **What is the rate law?**
v. **Calculate the rate constant.**
vi. **Calculate the half-life period from *k* and compare it with b.**

Answer 4.15

i.



ii. The concentration = $\dfrac{1.63 \times 100}{2} = 81.5\ mol/l$ is corresponds to the half-life.

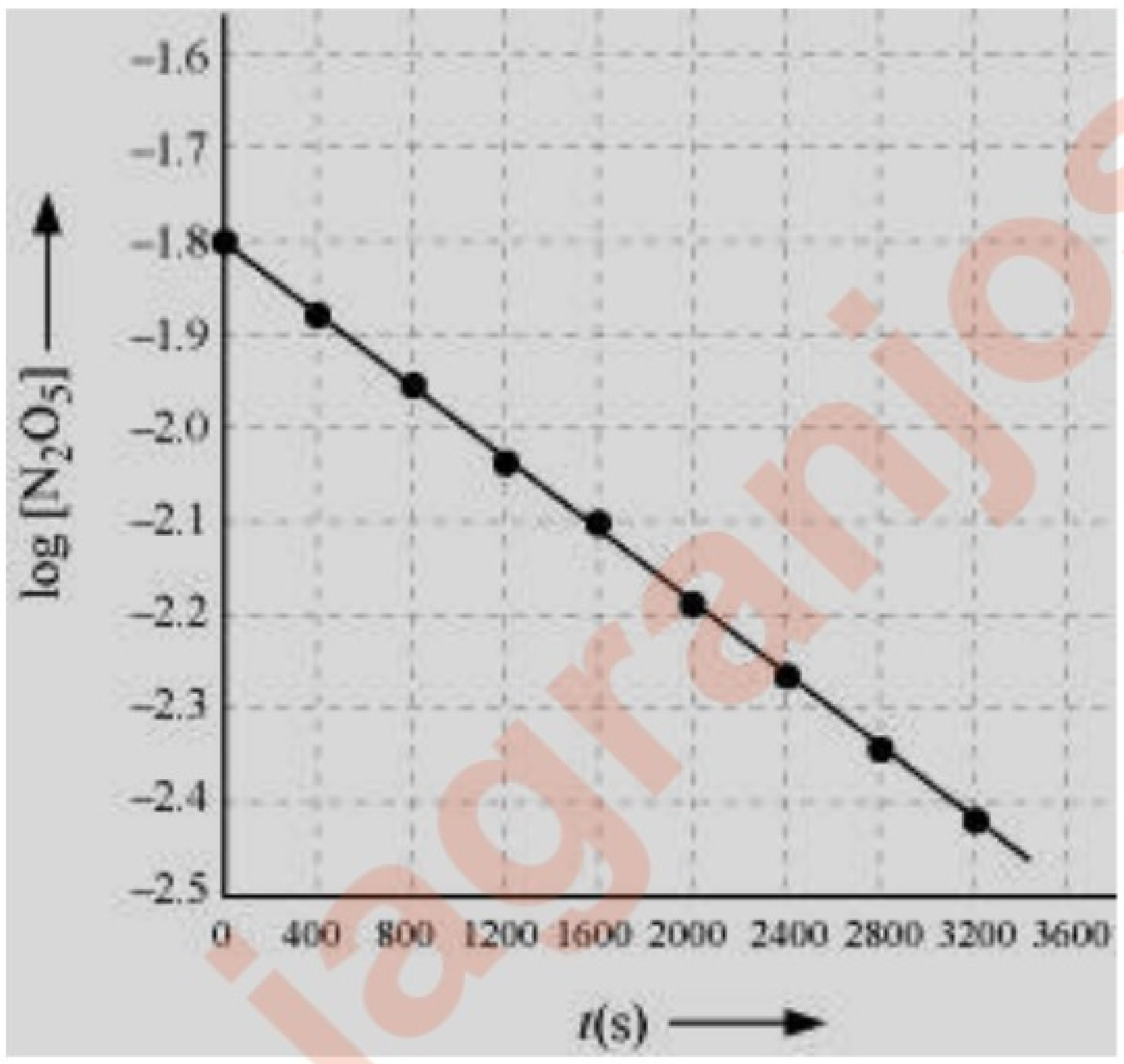
iii.

t(s)	$10^2 \times [N_2O_5]\ mol/l$	$\log[N_2O_5]$
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.

v.



vi. The plot, $\log\left[N_2O_5\right]$ v/s *t*, is a straight line. Therefore, The given reaction is of the first order.

The rate law of the reaction is

$$Rate = k\left[N_2O_5\right]$$

vii. From the plot, we have

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

Slope of the line of the plot is $= -\frac{k}{2.303}$

Thus,

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

$$k = 4.82 \times 10^{-4}\,\text{sec}^{-1}$$

viii. Half-life of the given reaction is,

$$t_{1/2} = \frac{0.639}{k}$$
$$= \frac{0.693}{4.82 \times 10^{-4}} s$$

$$= 1.438 \times 10^{3} s$$

$$= 1438\ s$$

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

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

Answer 4.16

For a first order reaction,

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

$$= \frac{2.303}{60} \log \frac{[R]_0}{[R]}$$

$$= \frac{2.303}{60} \log 16$$

$$= 4.6 \times 10^{-2}\ s$$

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

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

Answer 4.17

We have,

$$t_{1/2} = 28.1\ year$$

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

$$= \frac{0.693}{28.1}\ y^{-1}$$

For a first order reaction,

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

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

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

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

$$\log[R] = -0.1071$$

$$[R] = anti\log(-0.1071)$$
$$= 0.7814\ \mu g$$

Hence, 0.7814 μg of ^{90}Sr will remain after 10 years.

Again,

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

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

$$60 = \frac{2.303 \times 28.1}{0.693} \left(-\log[R]\right)$$

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

$$\log[R] = -0.6425$$

$$[R] = anti\log(-0.6425)$$
$$= 0.2278\ \mu g$$

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

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

Answer 4.18

For a first order reaction,

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

Time required for 99% completion is $= t_1$

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

Time required for 90% completion is $= t_2$

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

Hence,

$t_1 = 2t_2$

Thus, we can say that time require for 99% completion is twice the time required for the completion of 90% of the reaction.

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

Answer 4.19

For a first order reaction,

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

$$k = \frac{2.303}{40}\log\frac{100}{100-30}$$
$$= \frac{2.303}{40}\log\frac{10}{7}$$
$$= 8.918\times10^{-3}\ \text{min}^{-1}$$

Now, we can calculate $t_{1/2}$ of the decomposition reaction

$$t_{1/2} = \frac{0.693}{k}$$
$$= \frac{0.693}{8.918\times10^{-3}}\ \text{min}$$

$$= 77.7\ \text{min}$$

4.20 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.

Answer 4.20

$$(CH_3)_2CHN = NCH(CH_3)_2 \rightarrow N_{2(g)} + C_6H_{14(g)}$$

$At\ t = 0$	P_0	0	0
$At\ t = t$	$P_0 - p$	p	p

After time t,

Total pressure, $P_t = P_0 - p + p + p$

$$P_t = P_0 + p$$
$$p = P_t - P_0$$

$$P_0 - p = P_0 - [P_t - P_0]$$

$$= 2P_0 - P_t$$

For a first order reaction,

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

When $t = 360$ s,

$$k = \frac{2.303}{360}\log\frac{35}{2\times35-54}$$

$$= 2.175 \times 10^{-3}\ \text{s}^{-1}$$

When $t = 720$ s,

$$k = \frac{2.303}{720}\log\frac{35}{2\times35-63}$$

$$= 2.235 \times 10^{-3}\ \text{s}^{-1}$$

Hence, the average value of rate constant is

$$k = \frac{\left(2.175\times10^{-3}\right)+\left(2.235\times10^{-3}\right)}{2}$$

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

4.21 The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume.

$$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$$

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 4.21

The thermal decomposition of SO_2Cl_2 at a constant volume is represented by the following equation.

$$SO_2Cl_{2(g)} \rightarrow SO_{2(g)} + Cl_{2(g)}$$

$At\ t = 0$	P_0	0	0
$At\ t = t$	$P_0 - p$	p	p

After time t,

Total pressure, $P_t = P_0 - p + p + p$

$$P_t = P_0 + p$$
$$p = P_t - P_0$$

$$P_0 - p = P_0 - [P_t - P_0]$$

$$= 2\ P_0 - P_t$$

For a first order reaction,

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

When $t = 100$ s,

$$k = \frac{2.303}{100}\log\frac{0.5}{2\times 0.5 - 0.6}$$

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

When $P_t = 0.65$ atm,

$P_0 + p = 0.65$

$p = 0.65 - P_0$

$= 0.65 - 0.5$

$= 0.15$ atm

Thus, when the total pressure = 0.65 atm,

Pressure of $SOCl_2$ is, $p_{SOCl_2} = P_0 - p$

$= 0.5 - 0.15$

$= 0.35$ atm

Hence, the rate of equation,

Rate $= k\,(p_{SOCl_2})$

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

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

4.22 The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

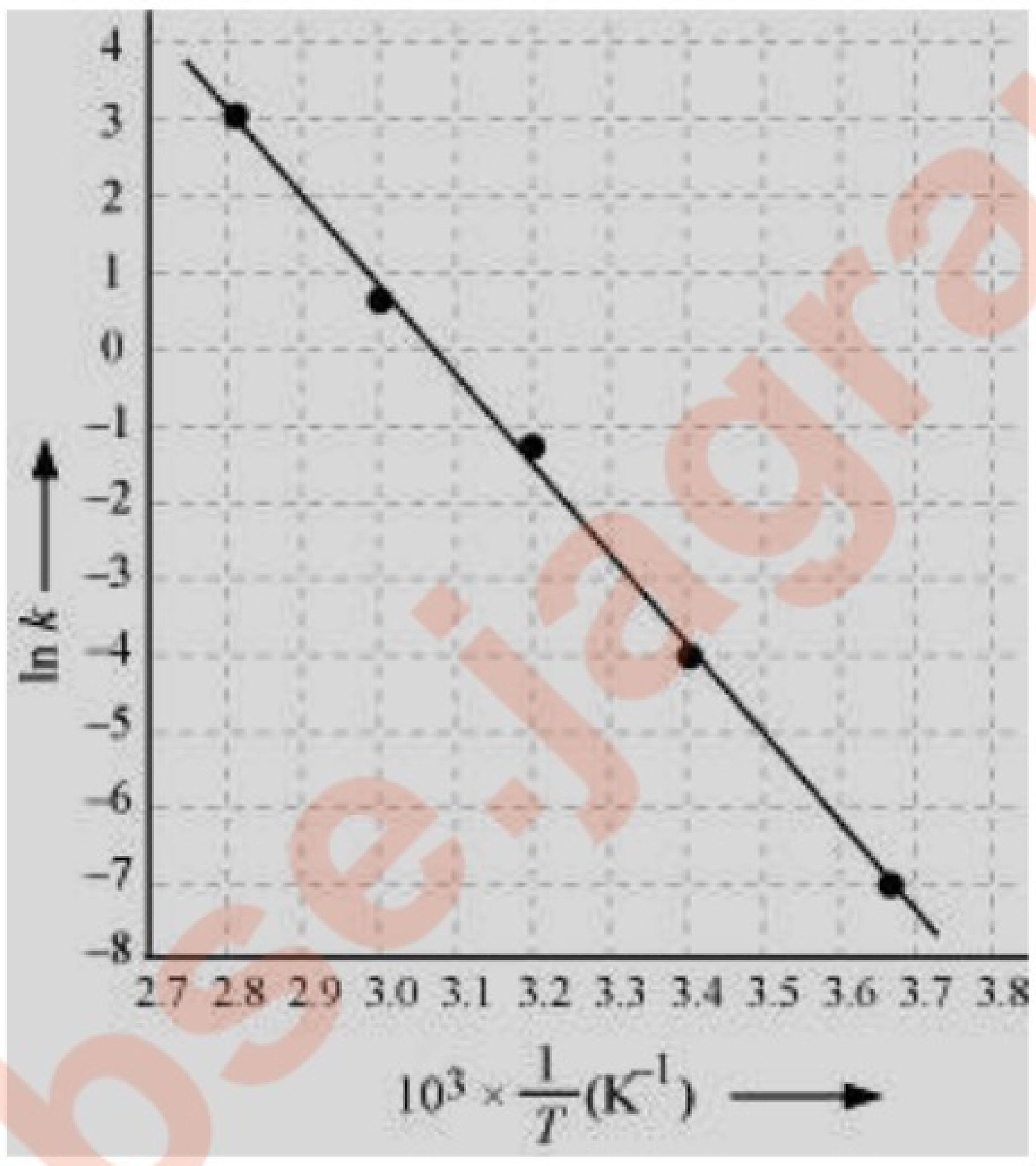
T/°C	0	20	40	60	80
$10^5 \times k / s^{-1}$	0.0787	1.70	25.7	178	2140

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 4.22

We have,

T/°C	0	20	40	60	80
T/K	273	293	313	333	353
$\frac{1}{T}$	3.66×10^{-3}	3.41×10^{-3}	3.19×10^{-3}	3.0×10^{-3}	2.83×10^{-3}
10^5	0.0787	1.70	25.7	178	2140
ln k	−7.147	− 4.075	−1.359	−0.577	3.063



Slope of the line $= \dfrac{y_2 - y_1}{x_2 - x_1} = -12.301\ K$

Arrhenius equation,

$$slope = -\frac{E_a}{R}$$
$$E_a = -slope \times R$$

$= -(2.301) \times 8.314$

$= 102.27\ kj/mol$

Again,

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

T = 273 K

$\ln k = -7.147$

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

$= 37.91$

$A = 2.91 \times 10^6$

$T = 30 + 273K$

$= 303\ K$

$$\frac{1}{T} = 0.0033K = 3.3 \times 10^{-3} K$$
$\ln k = -2.88$

$k = 6.08 \times 10^{-2} \sec^{-1}$

$T = 50 + 273 = 323K$

$$\frac{1}{T} = 0.0031K = 3.1 \times 10^{-3} K$$
$\ln k = -0.5$

$k = 0.607 \sec^{-1}$

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

Answer 4.23

E_a = 179.9 kJ mol^{-1} = 179.9 × 10^3 J mol^{-1}

k = 2.418 × 10^{-5} s^{-1}

T = 546 K

Using Arrhenius equation,

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

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

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

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

$$= \log\left(2.418\times10^{-5}\right) + \frac{179.9\times10^3}{2.303\times8.314\times546}$$

= (0.3835 − 5) + 17.2082

= 12.5917

A = antilog (12.5917)

= 3.9 × 10^{12} s^{-1} (approx.)

4.24 Consider a certain reaction A → Products with k = 2.0 × 10^{-2} s^{-1}. Calculate the concentration of A remaining after 100 s if the initial concentration of A is 1.0 mol L^{-1}.

Answer 4.24

$[A]_o = 1.0 \text{ moL}^{-1}$

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

$T = 100$ s

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

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

$$2\times10^{-2} = \frac{2.303}{100}\log\frac{1}{[A]}$$

$$2\times10^{-2} = \frac{2.303}{100}[-\log A]$$

$$[-\log A] = \frac{2\times10^{-2}\times100}{2.303}$$

$$[A] = anti\log\left[-\frac{2\times10^{-2}\times100}{2.303}\right]$$

$$[A] = anti\log\left[-\frac{2}{2.303}\right]$$

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

Thus, the remaining concentration of A is 0.135 mol/ L.

4.25 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 sample of sucrose remains after 8 hours?

Answer 4.25

Given, $t_{1/2}$ = 3.00 hours

For a first order reaction,

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

$$= \frac{0.693}{3}$$

$$= 0.231\ h^{-1}$$

Now,

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

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

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

$$\frac{[R]_0}{[R]} = anti\log(0.8024)$$

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

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

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

4.26 The decomposition of hydrocarbon follows the equation

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

Calculate E_a.

Answer 4.26

We have

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

Arrhenius equation is,

$k = Ae^{-E_a/RT}$ .... (2)

On comparing both the equations, we get

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

$E_a = 8.314 \times 28000$ K

= 232792 J/mol

= 232.792 kJ / mol

4.27 The rate constant for the first order decomposition of H_2O_2 is given by the following equation:

Log k = 14.34 − 1.25 × 10^4 K/T

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

Answer 4.27

Arrhenius equation is,

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

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

$$\log k = \log A - \frac{E_a}{2.303RT} \text{........................(1)}$$

Given equation is,

$$\log k = 14.34 - 1.25 \times 10^4 \ K/T \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

On comparing both equations, we get

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

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

$$= 239.34 \text{ kJ mol}^{-1}$$

Now, $t_{1/2} = 256$ minutes,

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

$$= \frac{0.693}{256}$$

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

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

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

$$\log\left[4.51 \times 10^{-5}\right] = 14.34 - \frac{1.25 \times 10^4 K}{T}$$

$$\left[0.654 - 5\right] = 14.34 - \frac{1.25 \times 10^4 K}{T}$$

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

$$T = 669K$$

4.28 The decomposition of A into product has value of k as 4.5×10^3 s^{-1} at 10°C and energy of activation 60 kJ mol^{-1}. At what temperature would k be 1.5×10^4 s^{-1}?

Answer 4.20

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

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

$T_1 = 273 + 10 = 283\ K$

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

Using Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log\frac{1.5\times10^4}{4.5\times10^3} = \frac{6\times10^4}{2.303\times8.314}\left[\frac{T_2 - 283}{283T_2}\right]$$

$$0.5229 = 3133.627\left[\frac{T_2 - 283}{283T_2}\right]$$

$$T_2 = 297\ K$$

$= 24°C$

4.29 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. The value of A is $4 \times 10^{10}\ s^{-1}$. Calculate k at 318 K and E_a.

Answer 4.29

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,

$$t' = \frac{2.303}{k'} \log \frac{100}{75}$$
$$= \frac{0.2877}{k'}$$

Now, as per the question

$$t' = t$$

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

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

From Arrhenius equation,

$$\log \frac{k'}{k} = \frac{E_a}{2.303R} \left[\frac{T' - T}{TT'} \right]$$
$$\log 2.7296 = \frac{E_a}{2.303 \times 8.314} \left[\frac{308 - 298}{298 \times 308} \right]$$
$$E_a = \frac{2.303 \times 8.314 \times 298 \times 308 \times \log 2.7296}{10}$$
$$= 76.64\ kj / mol$$

Now we can calculate *k* at 318 K,

We have

$$A = 4 \times 10^{10} \sec^{-1}$$
$$T = 318\ K$$

Again, use Arrhenius equation,

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

$$= 10.6021 - 12.5876$$

$$= -1.9855$$

Thus,

$$k = anti\log\left(-1.9855\right)$$
$$= 1.034 \times 10^{-2} \sec^{-1}$$

4.30 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.

Answer 4.30

$$k_2 = 4k_1$$
$$T_1 = 293\ K$$
$$T_2 = 313\ K$$

From Arrhenius equation,

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\log\frac{k_2}{k_1}=\frac{E_a}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\frac{4k_1}{k_1}=\frac{E_a}{2.303\times8.314}\left[\frac{313-293}{293\times313}\right]$$

$$0.6021=\frac{20\times E_a}{2.303\times8.314\times293\times313}$$

$$E_a=52863.33\ J/mol$$

$$=52.86\ kj/mol$$