Chapter – 4 (Chemical Kinetics)

Exercise Questions:

Question:1 From the rate expression from the following reaction, determine their order of reaction and the dimension of the rate constants.

    i.)   **$2NO(g) \rightarrow N_2O(g)$ 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:

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

Therefore, order of the reaction = 2

$K = Rate / [NO]^2$

Dimension of k = $molL^{-1}s^{-1} / (molL^{-1})^2$

= $molL^{-1}s^{-1} / mol^2L^{-2}$

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

    ii.)   Given rate k = $[H_2O_2][I^{-1}]$

         Therefore order of the reaction = 2

         $K = Rate / [H_2O_2][I^{-1}]$

         Dimension of = $mol^{-1}s^{-1} / (mol/L)(mol/L)$

         = $L^{-1}/mol/s$

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

         Therefore, order of reaction = 3/2

         $K = Rate/[CH_3CH0]^{3/2}$

         Dimension of = $mol^{-1}s^{-1}/mol/L)^{3/2}$

         = $L^{3/2}mol^{-1/2}/s$

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

         Therefore, order of the reaction = 1k = Rate / $[C_2H_5Cl]$

         Dimension of = $molL^{-1}s^{-1} / molL^{-1}$

         = s^{-1}

Question:2 For the reaction:

2A + B → A2B
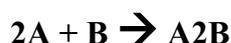
The rate = k[A][B]² with k = 2.0 x 10⁻⁶ mol⁻² L² / s. Calculate the initial rate of the reaction when [A] = 0.1 mol / L, [B] = 0.2 mol / L. Calculate the rate of reaction after [A] is reduced to 0.06 mol / L.

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 mol L^{-1}) $(0.2 \text{ mol L}^{-1})^2$

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

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^{-1} L^{-1} = 0.04 mol L

Therefore, concentration of B reacted= 1/2 x 0.04 mol L^{-1} = 0.02 mol L^{-1}

Then, concentration of B available, [B] = $(0.2 - 0.02)$ mol L^{-1}

= 0.18 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

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

= 3.89 mol L^{-1} s^{-1}

Question:3 The decomposition of NH3 on platinum surface is zero order reaction. What are rates of production of N2 and H2 if k = 2.5 x 10⁻⁴ mol⁻¹ L / s/

Answer:

The decomposition of NH3 is

2NH3 → N2 + 3H2

Rate of reaction,

dx / dt = 1 / 2d[NH3] / dt = d[N2] / dt = 1 / 3d[H2] / dt = k

Where k is the rate constant. Since, reaction is of zero order,

Rate of reaction = dx/dt = d[N2]dt = k

= 2.5×10^{-4} M s^{-1}

But, d[N2] / dt = 1/3d[H2] / dt

: d[H2] / dt = 3 d[N2] / dt

= 3 x 2.5 x 10-4 mol-1L s-1

= 7.5 x 10-4 M s-1

Question:4 The decomposition of dimethyl ether leads to the formation of CH4, H2 and CO and the reaction rate is given by

Rate = k[CH3OCH3]$^{3/2}$

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

Answer:

If the pressure is measured in bar and time in minutes, then unit of rate = bar / min

Rate = k(p CH3OCH3)

k = Rate / (p CH3OCH3)$^{3/2}$

Therefore, unit of rate constants (k) = bar min^{-1} / bar$^{3/2}$

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

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

Answer:

1. Concentration:

On increasing concentration of reactants, the probability of colloisions of molecules increases hence rate of reaction increases.

2. Temperature:

On increasing temperature, the kinetic energy of molecules increases, hence, the number of collision increases. Therefore, the rate of reaction also increases.

3. Pressure:

 On increasing pressure, the molecules of gases come closer to each other. As a result their collisions increase and hence rate of reaction increases.

4. Surface Area of Reactants:

On increasing surface area of reactants, the rate of reaction increases. For example, the powdered metals react faster than the metals in a lump.

5. Nature of reactants:

If the reactants are ionic in nature than the rate of reaction is faster than those in which reactants are molecular in nature.

Question: 6 A reaction in 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:

Let the concentration of the reactant be [A] = a

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

$= ka^2$

i.) If the concentration of the reaction is double 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 increased by 4 times.

ii.) If the concentration of the reactants is reduced to half i.e., [A] = ½ a the rate of the reaction would be

$R = k(1/2a)^2$

$= 1/4ka$

$= 1/4R$

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

Question: 7 What is the effect of temperature on the rate constant of a reaction? How can this temperature effect on the 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,

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

where, k is the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

T is the temperature, and

Ea is the energy of activation for the reaction

Question:8 In the 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 rate of reaction between the time interval 30 to 60 second.**

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 = d[Ester] / dt

= 0.31 – 0.17 / 60 – 30

= 0.14 / 30

ii.) For a pseudo first order reaction,

$K = 2.303 / t \log [R]_0 / [R]$

For t = 30s, k1 = 2.303 / 30 log 0.55/0.31

= 1.91 x 10^{-1} / s

For t = 60, k2 = 2.303 / 60 log 0.55 / 0.17

= 1.96 x 10^{-2} / s

For t = 90, k3 = 2.303 / 90 log 0.55 / 0.085

= 2.07 x 10^{-2} / s

Then average rate constant, k = k1 = k2 + k3 / 3

1.98 x 10^{-2} / s

Question: 9 A reaction in first order in A and second order in B.

   i.)   Write the different rate equation.

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

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

Answer:

   i.)   The different rate equation will be = d[r] / dt = $k[A][B]^2$

   ii.)   If the concentration of B is increased three times, then $-d[R]$ / dt = $k[A][3B]^2$ = $9.k[A][B]^2$

          Therefore, the rate of reaction will becomes 9 times.

   iii.) When the concentration of both A and B are doubled, $-d[R]$ / dt = $k[A][B]^2$

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

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

          Therefore, the rate of reaction will increase 8 times.

Question :10 In a reaction between A and B, the initial rate of reaction was measured for different initial concentration of A and B as given below:

A/ mol / L	0.20	0.20	0.40
B/ mol /L	0.30	0.10	0.05
r_0/ mol /L / s	5.07 x 10^{-5}	5.07 x 10^{-5}	1.43 x 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 x and with respect to B be y

Therefore,

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

   5.07 x 10^{-5} = $k[0.20]^x[0.30]^y$….i

5.07 x 10^{-5} = k$[0.20]^x[0.10]^y$…..ii

1.43 x 10^{-5} = k$[0.40]^x[0.05]^y$…..iii

Dividing equation I by ii, we obtain

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

= $[0.30]^y$ / $[0.10]^y$

= $(0.30/0.10)^x$ = $(0.30 / 0.10)^y$

Dividing equation iii. By ii, we obtain

1.43 x 10^{-5} / 5.07 x 10^{-5} = k$[0.40]^x[0.05]^y$ / k$[0.20]^x[0.10]^y$

= 2.821 = 2^x

Log2.821 = x log2[taking log on both sides]

X = log2.821 / log 2

= 1.496

= 1.5 (approx.)

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

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

2A + B ➔ C + D

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

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

Answer:

Let the equation is,

Rate = k [A]x [B]y

Then According to given data.

(rate)I = 6.0 x 10-3 = k(0.1)x (0.1)y.

(rate)II = 7.2 x 10-2 = k(0.3)x (0.2)y

(rate)III = 2.88 x 10-1 = k(0.3)x (0.4)y

(rate)IV = 2.40 x 10-2 = k(0.4)x (0.1) y

From equation (2) and (3) y = 2

(rate)II / (rate)III = 7.2 x 10^{-2} / 288 x 10^{-1}

= k/k (0.3/0.3)^x (0.2 / 0.4)^y

$^=$ 7.2 x 10^{-2} / 288 x 10^{-1} = (0.2 / 0.4)^y

0.72 x 10^{-1}/ 0.288 = (½)^y

¼ = ½)^y

(1/2)^2 = (1/2)^y

Y = 2

From equation (1) and (4) x = 1

(rate)I / (rate)Iv = 6.0 x 10^{-3} / 2.40 x 10^{-2}

K / (0.1 / 0.4)^x(0.1 / 0.1)^y

0.6 / 2.4 = (1/4)^x

(¼)^1 = (1/4)^x

X = 1

Hence, rate = k [A] [B]2 because x = 1, y = 2.

Rate law is rate = k [A] [B]2

Hence calculation of rate constant with the help of eq (1) rate = k [A] [B]2

6.0 x 10-3 = k(0.1)(0.1)2

k = 6.0×10−310−36.0×10−310−3

k = 6.0 mol-2 L2 min^{-1}

Question:12 The reaction between A and B in 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	[B] / mol / L	Initial rate / mol /L min^{-1}
I	0.1	0.1	2.0 x 10^{-2}
II	-	0.2	4.0 x 10^{-2}
III	0.4	0.4	-
IV	-	0.2	2.0 x 10^{-2}

Answer:

The given 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

Rate = k = [A]

From experiment I, we obtain

2.0 x 10^{-2}mol L^{-1} min^{-1} = k(0.1 mol /L)

K = 0.2 / min

From experimentII, we obtain

4.0 x 10^{-2}mol / L/ min = k(0.2 mol /L)

[A] = 0.2 mol /L

From experiment III, we obtain

Rate = 0.2 /min x 0.4 mol / L

= 0.08 mol /L /min

From experiment IV, we obtain

2.0×10^{02} mol / L / min = 0.2 / min[A]

[A] = 0.1 mol / L

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

   i.)   **$200s^{-1}$**

   ii.)   **$2\ min^{-1}$**

   iii.)   **$4\ years^{-1}$**

Answer:

   i.)   Half life , t = 0.693 / k = $0.693 / 200s^{-1}$

           = $0.346 \times 10^{-2} = 3.46 \times 10^{-3}$s

   ii.)   Half life, $t_{1/2}$ = 0.693 / k = 0.693 / 2/min

           = 0.346 min

   iii.)   Half – life,$t_{1/2}$ = 0.693 / k = 0.693/years

           = 0.173 years.

Question: 14 The experimental data for decomposition of N2O5
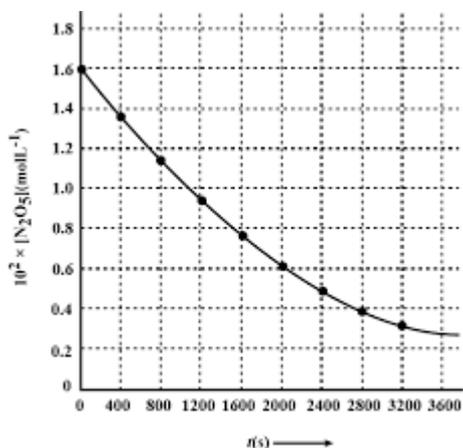
[2N2O5 → 4NO2 + O2]

In gas phase at 318K are given below:

t/s	0	400	800	1200	1600	2000	2400	2800	3200
10^2 x [N2O5]/mol /L	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

   i.)   **Plot [N2O5] against t.**

   ii.)   **Ii.) Find the half-life period for the reaction.**

   iii.)   **Draw a graph between lof[N2O5] 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 (ii).**

Answer:

i.)

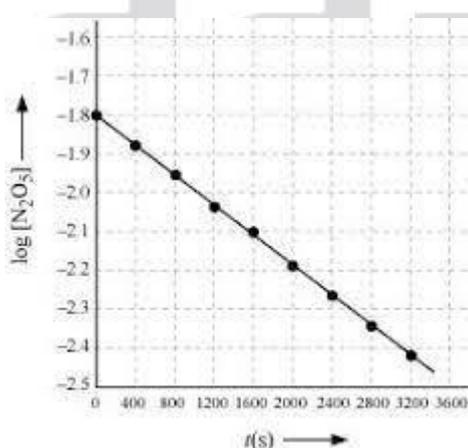
ii.) Time corresponding to the concentration, $1.630 \times 10^{-2} / 2$ mol / L = 0.815×10^{-2} mol / L is the half life

From the graph, the half life is obtained as 1440s.

iii.)

t(s)	10^2 x [N2O5] / mol / L	Log[N2O5]
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 first order as the plot, log [N2O5] v/s t, is a straight line.

Therefore, the rate law of the reaction is

Rate = k[N2O5]

v.)   From, the plot [N2O5] v/s t, we obtain

Slope = 2.46 – (-1.79) / 3200 – 0

= -0.67 / 3200

Again, slope of the line of the plot log[N2O5] v/s t, is given by = k/ 2.303

Therefore, we obtain, - k /2.303 = 0.67 / 3200

= 4.82×10^{-4} mol / L / s

vi.)   Half – life is given by

$T_{1/2}$ = 0.639 / k = 0.693 / 4.82×10^{-4} s

= 1.438×10^{3} s

= 1438 s

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

Question:15 The half life for radioactive decay of^{14}C is 5730 years. An archeological containing wood had only 80% of ^{14}C found in a living tree. Estimate the age of the sample.

Answer:

Radioactive decay follows first order kinetics. Therefore, decay constant

λ = 0.693 / $t_{1/2}$

= 0.693 / 5730 / years

t = 2.303 / λ log $[R]_0$/ [R]

t = 2.303 x 5730 / 0.693 log 100/ 80

= 1845 years

Hence, the age of the sample is 1845 years.

Question:16 The rate constant for a first order reaction is 60/s. How much time will it take to reduce the initial concentration of the reactant to its 1/6th value?

Answer:

It is known that, t = 2.303 / k log $[R]_0$ / [R]

= 2.303 / 60 /s log 1/1

= 4.62×10^{-2}s (appox0

Hence, the required time is 4.62×10^{-2}s.

Question:17 During nuclear explosion one of the products is ^{90}Sr with half – life of 28.1 years. If 1$\mathcal{U}_g$ 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:

$K = 0.693/t_{1/2} = 0.693 / 28.1 / y$

Here,

It is known that

$T = 0.303/kl \log [R]_0 /[R]$

$10 = 0.303 \times 28.1 / 0.693 \log 1 / [R]$

$10 = \log[R] = 10 \times 0.303 / 2.303 \times 28.1$

$[R] = \text{anti log } (-0.1071)$

$= 0.7814ug$

Therefore, 0.7814 ug of ^{90}Sr will remain after 10 years

Again, $t = 2.303 / k \log[R]_0 / [R]$

$= 60 = 2.303 \times 28.1 / 0.693 \log 1/[R]$

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

$= 0.2278$ ug

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

Quiestion: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:

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

$t1 = 2.303/k \log100/100-99$

$= 2.303 /k \log100$

$= 2 \times 2.303/k$

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

$t2 = 2.303 /k \log100/100-99$

$2.303/k \log10$

$= 2.303 / k$

Therefore, $t1 = 2t2$

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.

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

Answer:

For a first order reaction ,

$T = 2.303/k \log[R]_0 / [R]$

$K = 2.303 / 40 \min \log 100/100 - 30$

$2.303/40 \min \log 10 / 7$

= 8.918 x 10^{-3}min^{-1}

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

$T_{1/2}$ = 0.693/k = 0.693 min/ 8.918 x 10^{-3}

= 77.7 min.

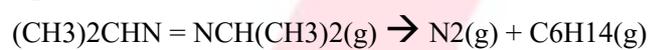**Question:20 For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.**

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

Calculate the rate constant.

Answer:

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

(CH3)2CHN = NCH(CH3)2(g) $\rightarrow$ N2(g) + C6H14(g)

At t = 0 P_0 0   0

At t = t P_0 – P   p   p

After time, t, total pressure, Pt = (Pº - p) + p + p

$\Rightarrow$ Pt = (Pº + p)

$\Rightarrow$ p = Pt - Pº

Therefore, Pº - p = Pº - Pt - Pº

= 2 Pº - Pt

For a first order reaction,

k = 2.303/t Log Pº / Pº - p

= 2.303/t Log Pº / 2 Pº - Pt

When t = 360 s, k = 2.303 / 360s log 35.0 / 2 x 35.0 - 54.0

= 2.175 × 10^{-3} s^{-1}

When t = 720 s, k = 2.303 / 720s log 35.0 / 2x35.0 - 63.0

= 2.235 × 10^{-3} s^{-1}

Hence, the average value of rate constant is

k = (2.175 × 10^{-3} + 2.235 × 10^{-3}) / 2   s^{-1}

= 2.21 × 10^{-3} s^{-1}

Question:21 The following data were obtained during the first order thermal decomposition of SO2Cl2 at a constant volume.

SO2Cl2(g) → SO2(g) + Cl2(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 0.63 atm.

Answer:

The thermal decomposition of SO2Cl2at 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, Pt = (Pº - p) + p + p

$\Rightarrow$ Pt = (Pº + p)

$\Rightarrow$ p = Pt - Pº

Therefore, Pº - p = Pº - Pt - Pº

= 2 Pº - Pt

For a first order reaction,

k = 2.303/t Log Pº / Pº - p

= 2.303/t Log Pº / 2 Pº - Pt

When t = 100 s,

k = 2.303 / 100s log 0.5 / 2x0.5 - 0.6

= 2.231 × 10^{-3} s^{-1}

When Pt= 0.65 atm,

P^0 + p = 0.65

$\Rightarrow$ p = 0.65 – P^0

= 0.65 - 0.5

= 0.15 atm

Therefore, when the total pressure is 0.65 atm, pressure of SOCl2 is

pSOCL2 = P^0 - p

= 0.5 - 0.15

= 0.35 atm

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

Rate = k(pSOCL2)

= (2.23 × 10^{-3} s^{-1}) (0.35 atm)

= 7.8 × 10^{-4} atm s^{-1}

Question:22 The rate constant for the decomposition of N2O5 at various temperatures is given below:

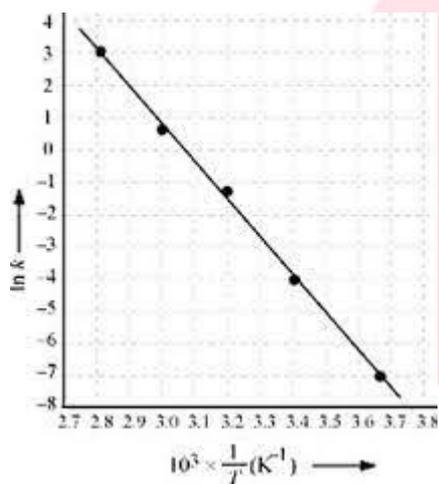| T/^{0}C	0	20	40	60	80
10^5 x k/s^{-1}	0.0787	1.70	25.7	178	2140

Draw a graph between ln k and 1/T and calculate the values of A and E$_a$. predict the rate constant at 30^0 and 50^0 C.

Answer:

For the given data:

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

Slop of the line,

y1 – y2 / x2 - x1 = -12.301 K

According to Arrhenius equation,

Slope = -E$_a$ /R

E$_a$ = -slope x R

= -(-12.301K) x (8.314JK^{-12}/mol)

= 102.27 KJ/mol

Again,

ln k = ln A .E$_a$ / ET

When, T = 273K

ln k = -7.147

Then, ln A = -7.147 + 102.27 x 10^3 / 8.314 x 273 = 37.911

Therefore, A = 2.91 x 10^6

When T = 30 + 273K = 303K

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

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

ln k = -2.8

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

Again , when T = 50 + 273K = 323K

$1/T = 0.0031K \; 3.1 \times 10^{-3}K$

ln k = -0.5

therefore, k = 0.607/s

Question:23 The rate constant for the decomposition of hydrocarbons is 2.418 x 10^{-5} / s at 546 K. if the energy of activation is 179.9kJ/mol, what will be the value of pre-exponential factor.

Answer:

$k = 2.418 \times 10^{-5} s^{-1}$

T= 546 K

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

According to the Arrhenius equation,

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

$\ln k = \ln A - Ea/RT$

$\log k = \log A - Ea / 2.303RT$

$\log A = \log k + Ea / 2.303 \, RT$

$= (0.3835 – 5) + 17.2082$

$= 12.5017$

Therefore, A = antilog (12.5917)

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

Question:24 Consider a certain reaction A→ Products with k = 2.0 x 10^{-2} / s. Calculate the concentration of A remaining after 100s if the initial concentration of A is 1.0 mol /L.

Answer:

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

T= 100 s

$[A]^0 = 1.0 \, molL^{-1}$

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

Therefore, $k = 2.303/t \; \log \; [A]^o / [A]$

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

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

$\Rightarrow - \text{Log } [A] = - (2.0 \times 10^{-2} \times 100) / \ 2.303$

$\Rightarrow [A] = \text{antilog } [- (2.0 \times 10^{-2} \times 100) / \ 2.303]$

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

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

Question: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:

For a first order reaction,

$k = 2.303/t \ \text{Log } [R]^o / [R]$

It is given that, t1/2 = 3.00 hours

Therefore, k = 0.693 / t1/2

$= 0.693 / 3 \ \text{h}^{-1}$

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

Then, $0.231 \text{ h}^{-1} = 2.303 / 8h \ \text{Log } [R]^o / [R]$

$\text{Log}[R]_0/[R] = 0.231 \text{ h}^{-1} \times 8h / 2.303$

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

$[R]_0 / [R] = 6.3445$

$[R] / [R]_0 = 0.1576$ (approx.)

$= 0.158$

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

Question:26 The decomposition of hydrocarbon follows the equation

K = (4.5 x 10^{11}/ s) e$^{-28000K /T}$

Calculate E$_a$.

Answer:

The given equation is

$k = (4.5 \times 10^{11} \text{ s}^{-1}) e^{-28000} / KT$ … (i)

Arrhenius equation is given by,

$k = Ae^{-E_a /RT}$ ……………….. (ii)

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

$E_a / RT = 28000K / T$

$\Rightarrow E_a = R \times 28000K$

= 8.314 J K^{-1} mol^{-1} × 28000 K

= 232792 J mol^{-1}

= 232.792 kJ mol^{-1}

Question:27 The rate constant for the first order decomposition of H2O2 is given by the following equation:

Log k = 14.34 – 1.25 x 10^4 K/T

Calculate E$_a$ fir this reaction and at what temperature will its half-period be 256 minutes?

Answer:

Arrhenius equation is given by,

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

$\Rightarrow$In k = In A - Ea/RT

$\Rightarrow$In k = Log A - Ea/RT

$\Rightarrow$ Log k = Log A - Ea/2.303RT   (i)

The given equation is

Log k = 14.34 - 1.25 104 K/T   (ii)

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

Ea/2.303RT = 1.25 104 K/T

$\Rightarrow$ Ea =1.25 × 104K × 2.303 × R

= 1.25 × 104K × 2.303 × 8.314 J K^{-1} mol^{-1}

= 239339.3 J mol^{-1} (approximately)

= 239.34 kJ mol^{-1}

Also, when t1/2= 256 minutes,

k = 0.693 / t1/2

= 0.693 / 256

= 2.707 × 10^{-3} min^{-1}

= 4.51 × 10^{-5} s^{-1}

It is also given that, log k= 14.34 - 1.25 × 104K/T

Log(4.51 x 10^{-3}0 = 14.34 – 1.25 x 10^4 K/ T

1.25 x 10^{4}K / T = 18.686

T = 1.25 x 10^4 K/ 18.686

668.95 K

= 669 (approx.)

Question:28 The decomposition of A into product has value of k as 4.5 x 10^3 / s at 10^0C and the energy of activation 60 kJ / mol. At what temperature would k be 1.5 x 10^4 / s?

Answer:

From Arrhenious equation, we obtain

Log K2/K1 = Ea /2.303R (T2 – T1 / T1T2)

Also, k1 = 4.5 x 10^3/s

T1 = 273 + 10 = 283K

k2 = 1.5 x 10^4 / s

Ea = 60 kJ /mol = 6.0 x 10^4 J / mol

Then log $\frac{1.5 \times 10^4}{4.5 \times 10^3}$ = $\frac{6.0 \times 10^4 \text{ J / mol}}{2.303 \times 8.314 \text{ J/ K / mol}}$ ($\frac{\text{T2} – 283}{283\text{T2}}$)

= $\frac{0.5229 \times 283\text{T2}}{3133.627}$ = T2 - 283

0.9528 T2 = 283

T2 = 297.019K

2967 K

= 24^0C

Question :29 The time required for 10% completion of a first order reaction at 298K is equal to that required for its 25% completion at 308K. if the value of A is 4 x 10^{10}/s. Calculate k at 318K and E_a.

Answer:

For a first order reaction,

t = 2.303 / k log a / a - x

At 298 K,

t = 2.303 / k log 100 / 90

= 0.1054 / k

At 308 K,

t' = 2.303 / k' log 100 / 75

= 2.2877 / k'

According to the question,

t = t'

⟹ 0.1054 / k = 2.2877 / k'

⟹ k' / k = 2.7296

From Arrhenius equation,we obtain

Log k'/k = Ea / 2.303 R (T' – T/TT')

Log(2.7296) = Ea /2.303 x 8.314 (308 – 298 / 298 x 308)

Ea = 2.303 x 8.314 x 298 x308 x log(2.7296) / 308 – 298

= 76640.096 J /mol

76.64 kJ /mol

To calculate k at 318 K,

It is given that, A = 4 x 1010 s-1, T = 318K

Again, from Arrhenius equation, we obtain

Therefore, k = Antilog (-1.9855)

= 1.034 x 10^{-2} s $^{-1}$

Question:30 The rate of a reaction quadraples when the temperature changes from 293K to 313K. Calculate the energy of activation of the reaction assuming theat it does not change with temperature.

Answer:

For Arrhenius equation, we obtain

Log log k2 / k1 = Ea /2.303 (T2 – T1/ T2 T1)

It is given that k2 = 4k1

T1 = 293K

T2 = 313 K

Therefore, log 4 k1/ k1 = Ea / 2.303 x 8.314 (313 – 293 / 313 x 293)

Ea = 0.6021 x 2.303 x 8.314 x 293 x 313 / 20

= 52.86 kJ / mol

Hence, the required energy of activation is 52.86 kJ / mol.