Chapter 4
Chemical Kinetics

---

1 Marks Questions

1. Is rate of reaction always constant?

Ans. No. rate of a reaction is not always constant. It depends on many factors such as concentration, temperature etc.

2. Can order of reaction be zero? Give example.

Ans. Yes, decomposition of ammonia on a hot platinum surface is a zero order of reaction at high pressure.

3. What do you understand by rate law expression?

Ans. The rate law is the expression in which rate is given in terms of molar concentration of reactants with each term raised to some power ,which may or may not be same as the stoichiometric coefficient of the reacting species in a balanced chemical equation.

4. Is it possible to determine or predict the rate law theoretically by merely looking at the equation?

Ans. No, the rate law can not be predicted by merely looking at the balanced chemical equation but must be determined experimentally.

5. Define the term chemical kinetics?

Ans. The branch of chemistry that deals with the study of reaction rates and their mechanisms is called chemical Kinetics.

6. Define – Rate of reaction and the factors affecting the rate of reaction.

Ans. Rate of reaction can be defined as the change in concentration of a reactant or product per unit time. Factors affecting the rate of reaction are temperature, concentration of reactants and catalyst.

7. **What is average rate of a reaction? How is it determined?**

Ans. Average rate of a reaction is defined as the change in concentration of a reactant or a product per unit time. It can be determined by dividing the change in concentration of reactant or product by the time interval

For the reaction: A → B R av = $\frac{-\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$

8. What are the units of rate of a reaction?

Ans. The units of rate of a reaction are Mol $L^{-1}S^{-1}$. In gaseous reaction the unit of rate of reaction is atom S^{-1}.

9. Identify the reaction order for from each of the following rate constant –

a) $k = 2.3\times10^{-5} L\ mol-1\, s^{-1}$

b) $k = 3.1\times10^{-4} s^{-1}$

Ans. a) Since the units of rate constant are $Lmol^{-1}s^{-1}$ The reactions is of second order.

b) Since the units of rate constant are s^{-1}, The reaction is of first order.

10. Consider the equation $2NO(q)+2H_2(g)\rightarrow N_2(g)+2H_2O(g)$ **The rate law for this equation is first order with respect to** H_2 **and second order with respect to NO. write the rate law for this reaction.**

Ans. The rate law will be $R = K[NO]^2[H_2]$

11. Give an example of pseudo – first order reaction ?

Ans. Hydrolysis of ethyl acetate when concentration of water is very large , is an example of pseudo first order reaction. $CH_3COO\,C_2H_5 + H_2O \rightarrow CH_3COOH + C_2H_5OH$.

12. Write the expression for half – life period of a first order reaction?

Ans. For a first order reaction, the half life period is $T_{1/2} = \frac{0.693}{k}$

13. A first order reaction is found to have a rate constant $K = 5.5\times10^{-14} sec^{-1}$. **Find half life of reaction?**

Ans. t1/2 = $\frac{0.693}{k} = \frac{0.693}{5.5\times10^{-14}\ sec^{-1}} = 1.26\times10^{13}$ s

14. The time required to decompose SO_2Cl_2 to half of its initial amount is 60 min. If the decomposition is a first order reaction, calculate the rate constant of the reaction?

Ans. $0.011\ 55\ min^{-1}$

15. What is the effect of catalyst on rate constant?

Ans. A catalyst increases the rate constant value.

16. How is activation energy affected on adding a catalyst?

Ans. A catalyst lowers the activation energy by following a different path for the reaction.

17. What do you mean by the term- collision frequency?

Ans. The no. of collisions per second per unit volume of the reaction mixture is known as collision frequency. It is denoted by Z.

18. What is the drawback of collision theory?

Ans. The drawback of collision theory is that it considers the molecules to be hard spheres and ignores their structural aspect.

19. How does the number of collisions change on increasing the temperature?

Ans. The rate of reaction would increase on increasing the temperature as it will increase the no. of collision as well as no. of effective collisions.

20. There is no bar on the no. of collisions among the reaching species. Why most of the reactions do not take place under normal conditions?

Ans. The reactions either do not have required energy or are not properly oriented, then the reaction will not take place.

21. The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate activation energy for such a reaction.

Ans. 52.86 KJ/mol

2 Marks Questions

1. Define the terms – i) Order of a reaction

ii) Molecularity of a reaction.

Ans. i) Order of a reaction.

The sum of powers of the concentration of the reactants in the rate law expression is called order of that reaction.

ii) Molecularity of a reaction.

The number of reacting species which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.

2. What are elementary and complex reactions?

Ans. The reactions taking place in one step are called elementary reactions whereas when a sequence of elementary reactions, called mechanism , gives us the product , it is called complex reaction.

3. Differentiate between order and molecularity of a reaction?

Ans.

Order	Molecularity
i) It can be predicted from equation and cannot be predicted theoretically.	i) it is an experimental parameter theoretically
ii) It cannot be zero.	ii) It can be zero.
iii) It cannot be a fraction. It can only be fraction. A whole number.	iii) It can be a whole number as well as

4. Determine the overall order of a reaction which has the rate law $R = K[A]^{5/2}[B]^{3/2}$

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

Order = x +y

50 order = $\frac{5}{2} + \frac{3}{2} = 4$.

i.e; reaction is fourth order reaction.

5. What are the units of a rate constant of a

a) First order reaction

b) nth order reaction.

Ans. i) First order reaction –

Units of rate constant, $k = sec^{-1}$

ii) For nth order reaction

the units of rate constant, $k = mol^{(1-n)\,(n-1)}Ls^{-1}$

6. What is instantaneous rate of a reaction? How is it determined?

Ans. The rate of a reaction at a particular moment of time is called instantaneous rate of a reaction. For a reaction A → B R inst = $\frac{d[A]}{dt} = \frac{d[B]}{dt}$ Where dt = the smallest possible time interval $(\Delta t \to 0)$

7. For the chemical decomposition of SO_2Cl_2**, its initial concentration is 0.8420 mol/L and final concentration is** $0.215\ mol^{L-1}$ **in 2 hours. What is the average rate of this reaction?**

Ans. Rate of reaction = $\frac{\text{change in concentration}}{\text{time interval}}$

$$= \frac{(0.8420 - 0.2105)\ \text{mol/L}}{2hr} = \frac{0.6315}{2} = 0.3158\ \text{mol /L/hr}.$$

8. In the expression of rate of reaction in terms of reactants, what is the significance of negative sign?

Ans. While writing the expression for rate of a reaction is terms of reactants, there is a negative sign which indicates a decrease in concentration of reactants with time.

9. For the reaction $2O_3(g) \rightleftharpoons 3O_2(g)$, $-\frac{\Delta[O_3]}{\Delta t}$ was found to be $5.0\times10^{-4}\,atm/s$. Determine the value of $\frac{\Delta[O_2]}{\Delta t}$ in atm /s during this period of time?

Ans. From the equation $2O_3(g) \rightleftharpoons 3O_2(g)$, $-\frac{1}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{1}{3}\frac{\Delta[O_2]}{\Delta t}$

$$\frac{\Delta[O_2]}{\Delta t} = \frac{-3}{2}\frac{\Delta[O_3]}{\Delta t} = \frac{-3}{2} \times (-5.0\times10^{-4}\ \text{atms}^{-1}) = 7.5\times10^{-4}\ \text{atm s}^{-1}$$

10. The rate Law for the reaction A+B → C is rate $= K[A]^2[B]$. What would the reaction rate be when concentration of both A and B are doubled?

Ans. $R_1 = K[A]^2[B]$------------------1)

$R_2 = K[2A]^2[2B]$------------------2)

Dividing 2) by 1)

$$\frac{R_2}{R_1} = \frac{[2A]^2\ [2B]}{[A]^2\ [B]} = \frac{8\ [A]^2\ [B]}{[A]^2\ [B]} = \frac{R_2}{R_1} = 8:1 \text{ or } R_2 = 8R_1$$

The rate of reaction increases eight times.

11. Write the integrated rate equation for –

i) zero order reaction.

ii) first order reaction.

Ans. i) Zero order reaction - $K = \frac{[R_0]\ -[R]}{t}$

ii) First order reaction K = $\frac{2.303}{t} \log \frac{[R_0]}{[R]}$

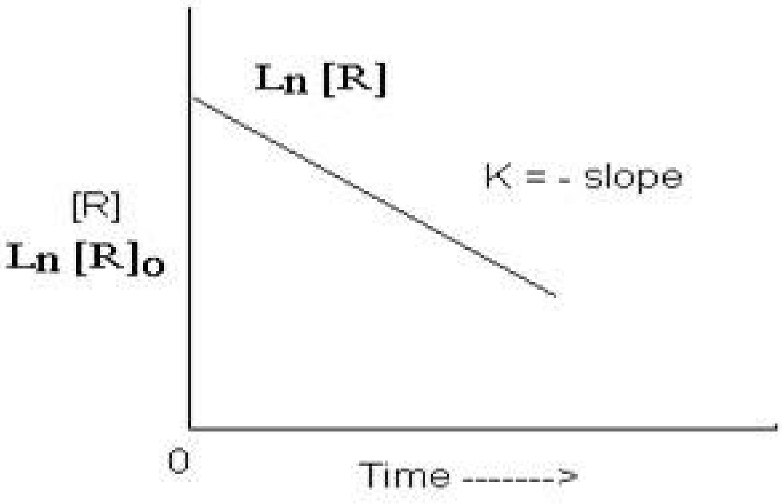
Where R_0 is the initial concentration

R is concentration at time t.

12. From the graph below

i) Identify the order of reaction.

ii) What will be the unit of rate constant?



Ans. From the graph

i) Reaction is first order reaction

ii) The unit of rate constant will be sec^{-1}.

13. What is the use of integrated rate equation?

Ans. Use of integrated rate equation -

1. The value of rate constant can be known when concentration of reactant at different times are known-

2. Order of a reaction can be determined by the knowledge of reaction concentration at different times.

14. For first order reaction - A → B Write

(1) Differential rate law.

(2) Integrated rate law.

Ans. For the reaction A → B, if the order =1

(i) Differential rate law is $\frac{-d[A]}{dt} = \mathrm{K}\,[\mathrm{A}]$

(ii) Integrated rate law is $t = \frac{2.303}{K} \log \frac{[R]_o}{[R]}$

15. The rate constant for the first order decomposition of N_2O_5 at 25^0C is $3\times10^{-2}\,min^{-1}$. It the initial concentration of N_2O_5 is $2\times10^{-3}\,mol/L$, How long will it take to drop the concentration to $5\times10^{-4}\,mol/L$?

Ans. t = $\frac{2.303}{k} \log \frac{[R]_o}{[R]}$

$$= \frac{2.303}{3\times10^{-2}\ \mathrm{min}^{-1}} \log \frac{2\times10^{-3}}{5\times10^{-4}}$$

$= \frac{2.303}{3\times10^{-2}} \log 4 \ (\log 4 = 0.6021)$

= 46.22 min.

16. Write Arrhenius equation.

Ans. Arrhenius equation

$K = A\,e^{-Ea/RT}$

Where K = rate constant , T = absolute temperature

E_a = Activation energy, R = gas constant.

17. If the activation energy of a reaction is zero, will the rate of reaction still depend on temperature?

Ans. $K = A\,e^{-Ea/RT}$

When Ea = 0

$K = A\,e^{-0/RT}$

$= A.\,e^{0}$

K = A

$\therefore$ Rate of reaction will not depend upon the temperature if activation energy is zero.

18. How does collision theory explain formation of products in a chemical reaction?

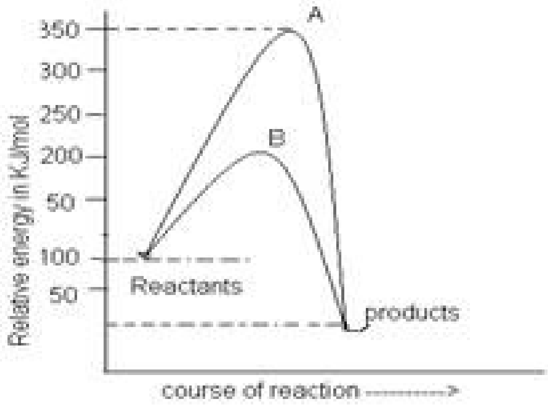
Ans. According to collision theory, the reactant molecules are assumed to be hard spheres and reaction occurs when these molecules collide with each other. The collisions in which molecules collide with sufficient kinetic energy (called threshold energy) and proper orientation, lead to formation of product. Here activation energy and proper orientation of the molecules determine the criteria for effective collision & hence the rate of a reaction.

19. From the fig. (1)

(a) Calculate ΔE for the reaction, activation energy for forward reaction.

(b) Identify the curve for catalysed reaction.

(c) what is the energy of activation in the presence of catalyst?



Ans. (a) From the figure-

Energy of reactions $E_r = 150 KJ/Mol$

Energy of products, $E_p = 50 Kj/Mol$

Change in energy, $\Delta E = E_P - E_R$

= 50-150 = 100KJ/Mol

Threshold energy, $E_r = 350\ KJ/Mol$

Activation energy, $E_a = E_t - E_r$

= 350-150

= 200 KJ/Mol.

(b) The curve B is for catalysed reaction.

(C) In the presence of catalysts ,

Threshold energy $E_T = 250 KJ/Mol$

Activation energy, $E_a = 250 - 150$

= 100 KJ/Mol.

20. The activation energy of reaction is 75.2 KJ/mol in the absence of a catalyst and 50.14 KJ/Mol in the presence of a catalyst. How many times will the reaction grow in the presence of a catalyst, if the reaction proceeds at $25^0 C$?

Ans. Let the rate constant in the absence of catalyst be K_1, Let the rate constant in the presence of catalyst be K_2 Activation energy in the absence of catalyst, $E_1 = 75.2\ KJ/Mol$ Activation energy in the presence of catalyst, $E_2 = 50.14\ KJ/Mol$.

$$\log \frac{K_2}{K_1} = \frac{E_1 - E_2}{2.303RT}$$

$$= \frac{(75.2 - 50.14) \times 10^3 J/Mol}{2.303 \times 8.314 J/K/mol \times 298K}$$

= 4.391.

$$\frac{K_2}{K_1} = \text{Antilog } 4.391$$

$$\frac{K_2}{K_1} = 24604$$

Or $K_2 = 24604\ K_1$

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

Ans. Average rate $= -\frac{1}{2}\frac{\Delta[A]}{\Delta t}$

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

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

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

= 0.005 mol L - 1 min - 1

= 5 ×10 - 3M min - 1

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

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

$2\frac{1}{2}$

= 2.5

23. Time required to decompose SO_2Cl_2 to half of its initial amount is 60 minutes. If the decomposition is a first order reaction, calculate the rate constant of the reaction.

Ans. We know that for a 1st order reaction,

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

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

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

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

$$0.01155\,\text{min}^{-1}$$

$$=1.155\,\text{min}^{-1}$$

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

Ans. 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

T is the temperature

R is the gas constant

E_a is the activation energy

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

Ans. 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

3 Marks Questions

1. For the reaction A+B $\rightarrow$ C+D, the rate of reaction doubles when the concentration of A doubles, provided the concentration of B is constant. To what order does A enter into the rate expression?

Ans. A+B $\rightarrow$ C+D

$$Rate[A]^x$$

Rate = 1 when [A] = 1 ---------- 1)

Rate = 2 when [A] = 2-----------2)

Dividing equation 2) by 1)

$$\frac{2}{1}\alpha\frac{(2)^x}{1^x}$$

$$2^1\alpha\ (2)^x$$

$$\therefore x=1$$

The reaction is first order reaction.

2. A chemical reaction 2A $\Leftrightarrow$ 4B+C in gas phase occurs in a closed vessel. The concentration of B is found to be increased by $5\times10^{-3}\,mole\,L^{-1}$ in 10 second. Calculate (i) the rate of appearance of B (ii) the rate of disappearance of A?

Ans. 2A $\rightarrow$ 4B +C

$$-\frac{1}{2}\frac{d[A]}{dt}=\frac{1}{4}\frac{d[B]}{dt}=\frac{d[C]}{dt}$$

i) Rate of disappearance of B

$$=\frac{5\times10^{-3}}{10\ 5}\mathrm{mol}/\mathrm{L}^{-1} = 5\times\ 10^{4}\ \mathrm{mol\ L}^{-1}\ \mathrm{s}^{-1}$$

$$\text{ii)}\ \frac{-\mathrm{d}[A]}{dt}=\frac{2}{4}\frac{d[B]}{dt}=\frac{1}{2}\frac{d[B]}{dt}$$

$$=\frac{1}{2}\times5\times10^{-4}\ \mathrm{mol\ L}^{-1}\ \mathrm{s}^{-1} = 2.5\times10^{4}\ \mathrm{mol\ L}^{-1}\ \mathrm{s}^{-1}$$

3. For the following reactions, write the rate of reaction expression in terms of reactants and products?

i) $4NH_3(g)+5O_2(g)4 \rightarrow NO(g)+6H_2O(g)$

ii) $2N_2O_5\ 2NO_2+O_2$

Ans.

In terms of reactant	In terms of products
i) $R_1 - \frac{-1}{4}\frac{\Delta[NH_3]}{\Delta t}$	$R_3=\frac{1}{4}\frac{\Delta[NO]}{\Delta t}$
$R_2=\frac{-1}{5}\frac{\Delta[O_2]}{\Delta t}$	$R_4=\frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$

$$\frac{1}{4}R_1=\frac{1}{5}R_2=\frac{1}{4}R_3=\frac{1}{6}R_4$$

$$-\frac{1}{4}\frac{\Delta[NH_3]}{\Delta t}=-\frac{1}{5}\frac{\Delta[O_2]}{\Delta t}=\frac{1}{4}\frac{\Delta[NO]}{\Delta t}=\frac{1}{6}\frac{\Delta[H_2O]}{\Delta t}$$

II) In terms of reactant	In terms of product
R1 = $-\frac{\Delta[N_2O_5]}{\Delta t}$	$R_2=\frac{\Delta[NO_2]}{\Delta t}$
	$R_3=\frac{\Delta[O_2]}{\Delta t}$

$$\frac{1}{2}R_1 = \frac{1}{2}R_2 = R_3 - \frac{\Delta[N_2O_5]}{\Delta t} = \frac{1}{2}\frac{\Delta[NO_2]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$$

4. The reaction $2N_2O_5(g) \rightarrow 2NO_2(g) + O_2(g)$ was studied and the following data were collected :

S.no (mol/L/min)	$[N_2O_5]\ mol\ L^{-1}$	Rate of disappearance of $[N_2O_5]$ (mol/L/min
1.	1.13×10^{-2}	34×10^{-5}
2.	$0.84\ \times10^{-2}$	25×10^{-5}
3.	0.62×10^{-2}	18×10^{-5}

Determine

i) The order

ii) The rate law.

iii) Rate constant for the reaction.

Ans. Let the order of reaction be x

$$Rate = K[N_2O_5]^x$$

i) From the data -

$34\times10^{-5} = \left(1.13\times\ 10^{-2}\right)^x$ ----------1)

$25\times10^{-5} = \left(0.84\times\ 10^{-2}\right)^x$ ----------2)

$18\times10^{-5}=\left(0.62\times10^{-2}\right)^{x}$ ----------3)

Dividing 1) by 2)

$$\frac{34\times10^{-5}}{25\times10^{-5}}=\left(\frac{1.13\times10^{-2}}{0.84\times10^{-2}}\right)^{x}$$

(1.36) = $(1.35)^{x}$

X=1

The order of reaction with respect with respect to N_2O_5 is 1

ii) Rate law $R=K\ [N_2O_5]$

iii) Rate constant , K = $\frac{Rate}{[N_2O_5]}$ = $\frac{18\times10^{-5}\ \text{mol/L/min}}{0.62\times10^{-2}\ \text{mol/L}}$ = $0.29\ min^{-1}$

5. The following experimental data was collected for the reaction:

$Cl_2(g)+2NO(g)\rightarrow2NOCl(g)$

Trial	Intial conc. Of $Cl_2\ (mol/L)$	[NO] mol/L	Initial Rate,(mol/L/s)
1	0.10	0.010	1.2×10^{-4}
2	0.10	0.030	10.8×10^{-4}
3	0.20	0.030	21.6×10^{-4}

Construct the rate equation for the reaction.

Ans. Order of NO is 2

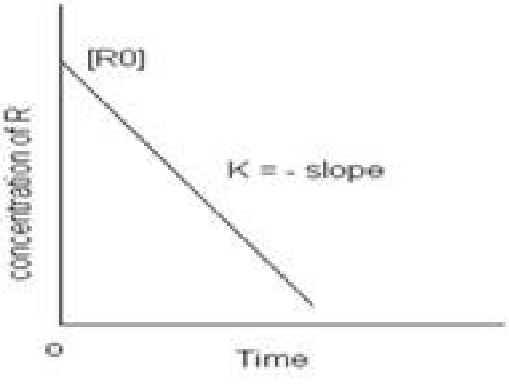
Rate law = $K\ [Cl_2]\ [NO]^2$

6. Draw a graph for

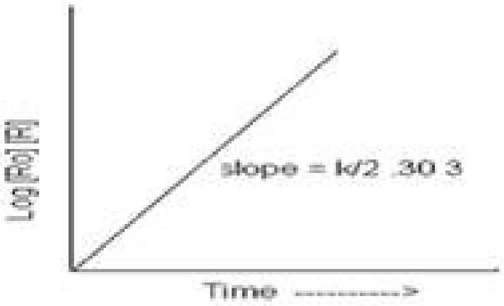
a) Concentration of reactant against time for a zero order reaction.

b) Log [Ro]/ [R] against time for a first order reaction.

Ans.



(a)



(b)

7. In general it is observed that the rate of a chemical reaction doubles with every 10^0 rise in temperature. If this generalization holds for a reaction in the temperature range295K to 305K, what would be the activation energy for this reaction? $\left(R = 8.314 Jk^{-1} mol^{-1}\right)$

Ans. $T_1 = 295K \; T_2 = 305K$

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

$$K_2 = 2k_1$$

$$E_a = 2.303 \times 8.314 \times \left[\frac{305 \times 295}{305 - 295}\right] \log \frac{2k_1}{k_1}$$

= $2.303 \times 8.314 \times 8997.5K \log 2$

= 51855.2 J/mol (log2 = 0.3010)

8. The rate constant for a reaction is $1.5\times10^{7}s^{-1}$ at $50^{0}C$ and $4.5\times10^{7}s^{-1}$ at $100^{0}C$.

Calculate the value of activation energy for the reaction $R=8.314\ JK^{-1}mol^{-1}$?

Ans. $\log\frac{k_2}{k_1}=\frac{Ea}{2.303_R}\left(\frac{T_2-T_1}{T_1T_2}\right)$

$$\log\frac{4.5\times10^{7}}{1.5\times10^{7}}=\frac{Ea}{2.303\times3.314}\left(\frac{373-323}{373\times323}\right)$$

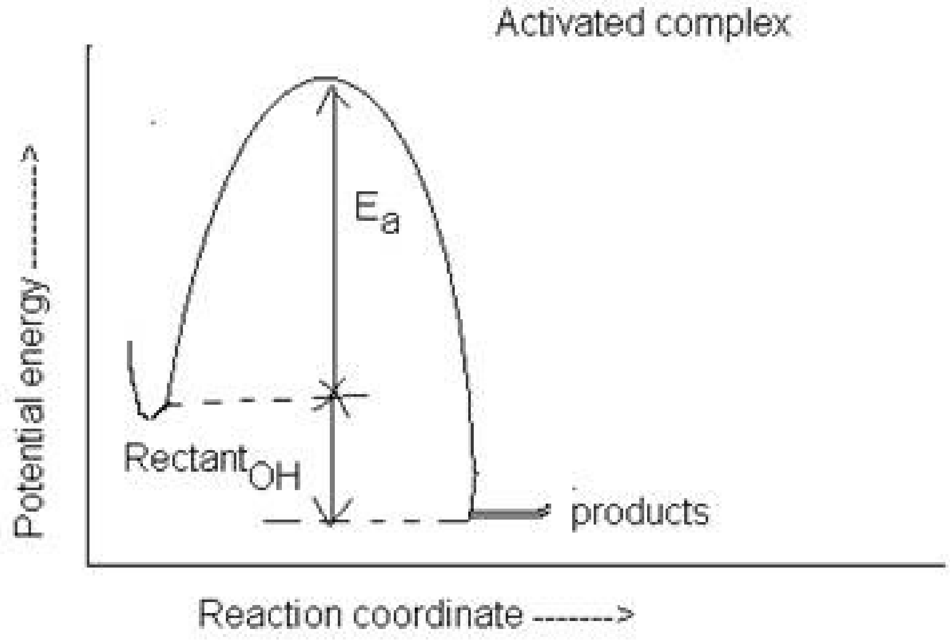
$$\log1.5=\frac{Ea}{2.303\times3.314}\left(\frac{50}{373\times323}\right)$$

$$Ea=\left(\frac{2.303\times3.314\times373\times323}{50}\right)\times\log1.5$$

$$=22\ KJ/mol$$

9. Plot a graph showing variation of potential energy with reaction. coordinate?

Ans.



10. 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?

Ans. 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 mol^{-1}, then equation (1) can be written as:

$$\text{Rate}_1 = k.(a)_2$$

= ka_2

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

Now, the rate equation will be:

Rate = $k(3a)_2$

$$= 9(ka^2)$$

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

11. A first order reaction has a rate constant $1.1510^{-3}\ S^{-1}$. How long will 5 g of this reactant take to reduce to 3 g?

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

Initial amount = 5 g

Final concentration = 3 g

Rate constant = $1.15\ 10^{-3}\,s^{-1}$

We know that for a 1storder reaction,

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

$$= \frac{2.303}{1.15 \times 10^{-3}} \log \frac{5}{3}$$

$$= \frac{2.303}{1.15 \times 10^{-3}} \times 0.2219$$

= 444.38 s

= 444 s (approx)

12. For the reaction $R \rightarrow P$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes. Calculate the average rate of reaction using units of time both in minutes and Pseconds.

Ans. Average rate of reaction $-\frac{\Delta[R]}{\Delta t}$

$$= -\frac{[R]_2 - [R]_1}{t_2 - t_1}$$

$$= -\frac{0.02 - 0.03}{25} \text{M min}^{-1}$$

$$= -\frac{-0.01}{25} \text{M min}^{-1}$$

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

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

$$= 6.67 \times 10^{-6} \text{M s}^{-1}$$

13. For the reaction: $2A + B \rightarrow A_2B$ the rate = $k[A][B]_2$ with $k = 2.0 \times 10^{-6} \text{mol}^{-2} \text{L}^2 \text{s}^{-1}$. Calculate the initial rate of the reaction when $[A] = 0.1 \text{mol L}^{-1}$, $[B] = 0.2 \text{mol L}^{-1}$. Calculate the rate of reaction after [A] is reduced to 0.06mol L^{-1}.

Ans. The initial rate of the reaction is

Rate = $k[A][B]_2$

$$=\left(2.0\times10^{-6}\,mol^{-2}L^{2}s^{-1}\right)\left(0.1\,mol\,L^{-1}\right)\left(0.2\,mol\,L^{-1}\right)^{2}$$

$$=8.0\times10^{-9}\,mol^{-2}L^{2}s^{-1}$$

When [A] is reduced from $0.1\ mol\ L^{-1}$ to $0.06\ mol^{-1}$, the concentration of A reacted = $(0.1-0.06)\,mol\,L^{-1}=0.004\,mol\,L^{-1}$

Therefore, concentration of B reacted $=\frac{1}{2}\times0.04\,mol\,L^{-1}=0.02\,mol\,L^{-1}$

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

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

After [A] is reduced to $0.06\ mol^{-1}$, the rate of the reaction is given by,

Rate = $k[A][B]_2$

$$=\left(2.0\times10^{-6}\,mol^{-2}L^{2}s^{-1}\right)\left(0.06\,mol\,L^{-1}\right)\left(0.18\,mol\,L^{-1}\right)^{2}$$

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

14. 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?

Ans. Letthe concentration of the reactant be [A] = *a*

Rate of reaction, $R=k\left[A\right]_2$

$$=ka^{2}$$

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

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

$$= 4ka^2$$

= 4 R

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 $R' = k\left(\frac{1}{2}a\right)^2$

$$= \frac{1}{4}ka^2$$

$$= \frac{1}{4}R$$

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

15. 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?

Ans. (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

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

$$=9.k[A][B]^2$$

Therefore, the rate of reaction will increase 9 times.

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

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

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

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

Therefore, the rate of reaction will increase 8 times.

16. 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**

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

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

$=3.4\times10^{-3}\,s$ (approximately)

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

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

= 0.35 min (approximately)

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

$= \frac{0.693}{4\,\text{years}^{-1}}$

= 0.173 years (approximately)

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

Ans. Here, $k = \frac{0.693}{t_{1/2}}$

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

It is known that,

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

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

= 1845 years (approximately)

Hence, the age of the sample is 1845 years.

18. 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 1/16thvalue?

Ans. It is known that,

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

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

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

$=4.6\times10^{-2}\ \mathrm{s}$ (approximately)

Hence, the required time is $4.6\times10^{-2}\mathrm{s}$.

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

Ans. For a first order reaction,

$$t_1=\frac{2.303}{k}\log\frac{[R]_0}{[R]}$$

$$k=\frac{2.303}{40\,\mathrm{min}}\log\frac{100}{100-30}$$

$$=\frac{2.303}{40\,\mathrm{min}}\log\frac{10}{7}$$

$$=8.918\times10^{-3}\,\mathrm{min}^{-1}$$

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

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

$$=\frac{0.693}{8.918\times10^{-3}}\mathrm{min}$$

= 77.7 min (approximately)

20. Consider a certain reaction A $\rightarrow$ Products with $k=2.0\times10^{-2}\,s^{-1}$. Calculate the concentration of *A* remaining after 100 s if the initial concentration of *A* is $1.0\,\mathrm{mol\,L^{-1}}$.

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

T= 100 s

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

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

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

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

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

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

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

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

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

4 Marks Questions

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

Ans. It is given that *T*1 = 298 K

Therefore, $T_2 = (298+10)K$

= 308 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, $R = 8.314\,JK^{-1}\,mol^{-1}$

Now, substituting these values in the equation:

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

We get:

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

$$\log 2 = \frac{E_a}{2.303\times 8.314}\left[\frac{10}{298\times 308}\right]$$

$$E_a = \frac{2.303\times 8.314\times 298\times 308\times \log 2}{10}$$

$$= 52897.78\,J\,mol^{-1}$$
$$= 52.9\,k\,J\,mol^{-1}$$

2. The activation energy for the reaction $2HI_{(g)} \rightarrow H_2 + I_{2(g)}$ is $209.5\,k\,J\,mol^{-1}$ at 581K. Calculate the fraction of molecules of reactants having energy equal to or greater than activation energy?

Ans. In the given case:

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

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:

$$x = e^{-Ea/RT}$$

In $x = -E_a / RT$

$$\log x = -\frac{E_a}{2.303\,RT}$$

$$\log x = \frac{209500\,J\,mol^{-1}}{2.303 \times 8.314\,J\,K^{-1}mol^{-1} \times 581}$$ =18.8323

Now, x = Anti log (18.8323)

= Anti log $\overline{19}.1677$

$$1.471 \times 10^{-19}$$

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

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

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

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

(iv) $C_2H_5Cl(g) \rightarrow C_2H_2(g) + HCl(g)\ Rate = k[C_2H_5Cl]$

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

Therefore, order of the reaction = 2

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

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

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

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

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

Therefore, order of the reaction = 2

Dimension of $k = \frac{\text{Rate}}{[H_2O_2][I^-]}$

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

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

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

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

Dimension of $k = \frac{\text{Rate}}{[CH_3CHO]^{\frac{3}{2}}}$

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

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

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

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

Therefore, order of the reaction = 1

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

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

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

4. 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 $k = 2.5 \times 10^{-4}\ \text{mol}^{-1}\ \text{L s}^{-1}$?

Ans. The decomposition of NH_3 on platinum surface is represented by the following equation.

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

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

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

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

Therefore, $= 2.5\times10^{-4}\,\text{mol}\,L^{-1}s^{-1}$

Therefore, the rate of production of N_2 is

$$\frac{d[N_2]}{dt} = 2.5\times10^{-4}\,\text{mol}\,L^{-1}s^{-1}$$

And, the rate of production of H_2 is

$$\frac{d[H_2]}{dt} = 3\times2.5\times10^{-4}\,\text{mol}\,L^{-1}s^{-1}$$

$$= 7.5\times10^{-4}\,\text{mol}\,L^{-1}s^{-1}$$

5. 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., $\text{Rate} = k\left(P_{CH_3OCH_3}\right)^{3/2}$ If the pressure is measured in bar andtime in minutes, then what are the units of rate and rate constants?

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

Unit of rate = $\text{bar}\,\text{min}^{-1}$

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

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

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

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

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

Ans. 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, *k* is the rate constant,

A is the Arrhenius factor or the frequency factor,

R is the gas constant,

T is the temperature, and

E_a is the energy of activation for the reaction

7. 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.

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

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

$= \frac{0.14}{30}$

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

(ii) For a pseudo first order reaction,

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

For *t*= 30 s, $k_1 = \frac{2.303}{30}\log\frac{0.55}{0.31}$

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

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

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

For *t*= 90 s,

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

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

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

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

$$= 1.98 \times 10^{-2} s^{-1}$$

8. 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?

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

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

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

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

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

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

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

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

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

y = 0

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

$$\frac{1.43\times10^{-4}}{5.07\times10^{-5}}=\frac{k[0.40]^x[0.05]^y}{k[0.20]^x[0.30]^y}$$

$$\frac{1.43\times10^{-4}}{5.07\times10^{-5}}=\frac{[0.40]^y}{[0.20]^y}\quad\begin{bmatrix}\text{Since } y=0,\\ [0.05]^y=[0.30]^y=1\end{bmatrix}$$

$$2.821=2^x$$

$$\log 2.821 = x\log 2 \qquad \text{(Taking log on both sides)}$$

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

= 1.496

= 1.5 (approximately)

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

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

$$2A+B\rightarrow C+D$$

Experiment	$A\ /\ \text{mol L}^{-1}$	$B\ /\ \text{mol L}^{-1}$	Initial rate of formation of $D\ /\ \text{mol L}^{-1}\ \text{min}^{-1}$
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.

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

Therefore, rate of the reaction is given by,

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

According to the question,

$6.0\times10^{-3} = k[0.1]^x[0.1]^y$ ....(i)

$7.2\times10^{-2} = k[0.3]^x[0.2]^y$ ....(ii)

$2.88\times10^{-1} = k[0.3]^x[0.4]^y$ ....(iii)

$2.40\times10^{-2} = k[0.4]^x[0.1]^y$ ....(iv)

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

$$\frac{2.40\times10^{-2}}{6.0\times10^{-3}} = \frac{k[0.4]^x[0.1]^y}{k[0.1]^x[0.1]^y}$$

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

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

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

x = 1

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

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

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

$$4 = 2^y$$

$$2^2 = 2^y$$

y = 2

Therefore, the rate law is

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

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

From experiment I, we obtain

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

$$= 6.0\ \text{L}^2\ \text{mol}^{-2}\ \text{min}^{-1}$$

From experiment II, we obtain,

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

$$= 6.0\ \text{L}^2\text{mol}^{-2}\ \text{min}^{-1}$$

From experiment III, we obtain

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

$$= 6.0\ \text{L}^2\text{mol}^{-2}\ \text{min}^{-1}$$

From experiment IV, we obtain

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

$$= 6.0\ \text{L}^2\text{mol}^{-2}\ \text{min}^{-1}$$

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

11. 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	$A / \text{mol L}^{-1}$	$B / \text{mol L}^{-1}$	Initial rate / $\text{mol L}^{-1}\text{min}^{-1}$
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}

Ans. 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,

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

Rate = k [A]

From experiment I, we obtain

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

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

From experiment II, we obtain

$$4.0 \times 10^{-2} \text{mol L}^{-1} \text{min}^{-1} = 0.2 \text{min}^{-1}[A]$$

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

From experiment III, we obtain

$$\text{Rate} = 0.2 \text{min}^{-1} \times 0.4 \text{mol L}^{-1}$$

$$= 0.08 \text{mol L}^{-1} \text{min}^{-1}$$

From experiment IV, we obtain

$$2.0\times10^{-2}\,\text{mol L}^{-1}\,\text{min}^{-1} = 0.2\,\text{min}^{-1}[\text{A}]$$

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

12. The experimental data for decomposition of N_2O_5 $\left[2N_2O_5 \rightarrow 4NO_2 + O_2\right]$ in gas phase at 318K are given below:

t(s)	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [N_2O_5] molL^{-1}$	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.

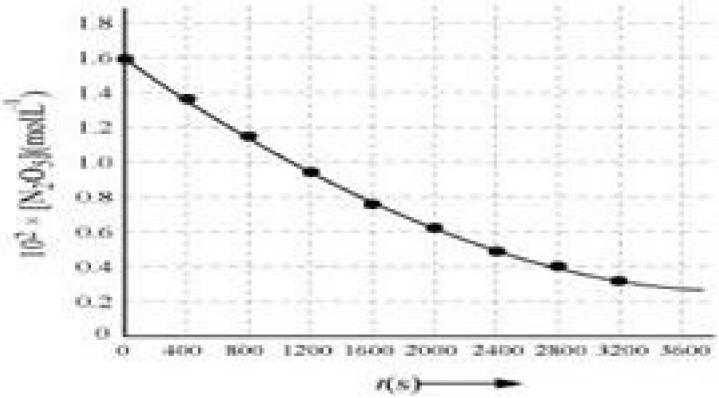
(iii) Draw a graph between log $[N_2O_5]$ and *t*.

(iv) What is the rate law?

(v) Calculate the rate constant.

(vi) Calculate the half-life period from k and compare it with (ii).

Ans.

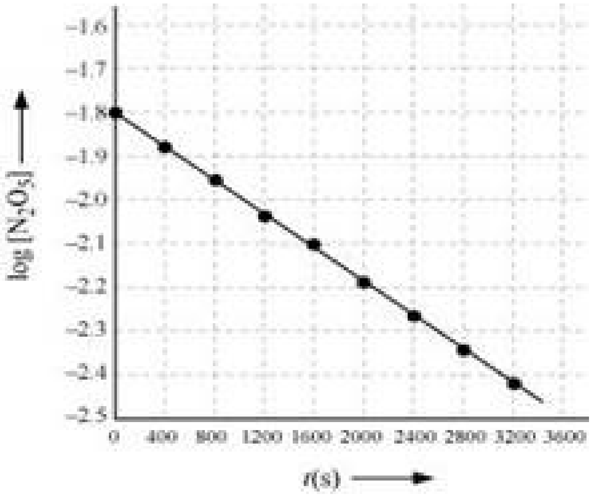


(ii) Time corresponding to the concentration, $\frac{1.630\times10^{2}}{2}\,\text{mol L}^{-1} = 81.5\,\text{mol L}^{-1}$ is the half life. From the graph, the half life is obtained as 1450 s.

(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 $\text{Rate} = k[N_2O_5]\text{s}$



(v) From the plot, $\log[N_2O_5]$ v/s *t*, we obtain

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

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

Again, slope of the line of the plot $\log[N_2O_5]$ v/s *t* is given by $-\frac{k}{2.303}$ Therefore, we obtain,

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

13. During nuclear explosion, one of the products is ^{90}Sr with half-life of 28.1 years. If $1\mu g$ 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.

Ans. Here, $k=\frac{0.693}{t_{1/2}}=\frac{0.693}{28.1}y^{-1}$

It is known that, $t=\frac{2.303}{k}\log\frac{[R]_0}{[R]}$

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

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

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

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

$$=\text{anti}\log\left(\bar{1}.8929\right)$$

$$=0.7814\mu g$$

Therefore, $=0.7814\mu g$ of ^{90}Sr will remain after 10 years.

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

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

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

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

$$= \text{anti}\log\left(\bar{1}.3575\right)$$

$$= 0.2278 \mu g$$

Therefore, $0.2278 \mu g$ of ^{90}Sr will remain after 60 years.

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

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

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

$$= \frac{2.303}{k} \log 100$$

$$= 2 \times \frac{2.303}{k}$$

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

$$t_2 = \frac{2.303}{k} \log \frac{100}{100-99}$$

$$= \frac{2.303}{k} \log 10$$

$$=\frac{2.303}{k}$$

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.

15. For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

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

Calculate the rate constant.

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

$$\begin{array}{lccccc} & (CH_3)_2CHN=NCH(CH_3)_{2(g)} & \longrightarrow & N_{2(g)} & + & C_6H_{14(g)} \\ \text{At } t=0 & P_0 & & 0 & & 0 \\ \text{At } t=t & P_0-p & & p & & p \end{array}$$

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

$$P_t = P_0 + p$$

$$p = P_t - P_0$$

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

$$= 2P_0 - P_t$$

For a first order reaction,

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

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

When t = 360 s, $k = \frac{2.303}{360\,s}\log\frac{35.0}{2\times35.0-54.0}$

$$= 2.175\times10^{-3}s^{-1}$$

When t = 720 s, $k = \frac{2.303}{720\,s}\log\frac{35.0}{2\times35.0-63.0}$

$$= 2.235\times10^{-3}s^{-1}$$

Hence, the average value of rate constant is

$$k = \frac{\left(2.175\times10^{-3}\right)+\left(2.235\times10^{-3}\right)}{2}s^{-1}$$

$$= 2.21\times10^{-3}s^{-1}$$

16. 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.

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

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

$$\begin{array}{lcccccc} & SO_2Cl_{2(g)} & \longrightarrow & SO_{2(g)} & + & Cl_{2(g)} \\ \text{At } t=0 & P_0 & & 0 & & 0 \\ \text{At } t=t & P_0-p & & p & & p \end{array}$$

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

$$P_t = P_0 + p$$

$$p = P_t - P_0$$

Therefore,

$$P_0 - p = P_0 - (P_t - P_0)$$

$$= 2P_0 - P_t$$

For a first order reaction,

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

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

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

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

When $P_t = 0.65$ atm ,

$$P_0 + p = 0.65$$

$$p = 0.65 - P_0$$

= 0.65 – 0.5

= 0.15 atm

Therefore, when the total pressure is 0.65 atm, pressure of $SOCl_2$ is

$P_{SOCl_2} = P_0 - p$

= 0.5 – 0.15

= 0.35 atm

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

$\text{Rate} = k(P_{SOCl_2})$

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

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

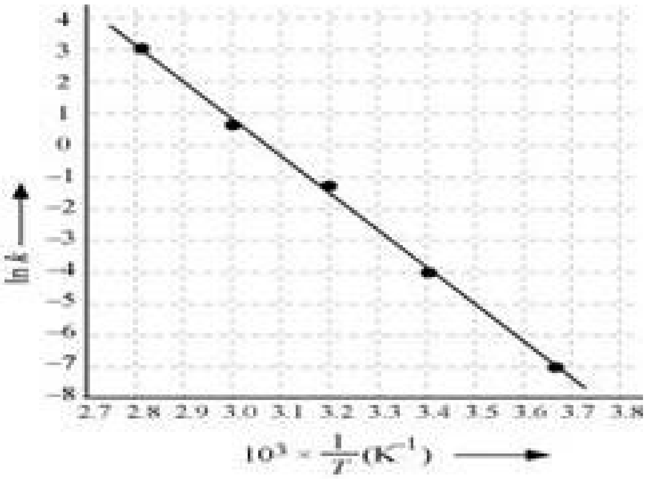
17. The rate constant for the decomposition of N_2O_5 at various temperatures is given below:

$T / °C$	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 $50°C$.

Ans. From the given data, we obtain

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



Slope of the line,

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

According to Arrhenius equation,

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

= $E_a = -\text{Slope} \times R$

$$= -(-12.301\text{K}) \times (8.134\text{JK}^{-1}\text{mol}^{-1})$$

$$= 102.27\,\text{kJ mol}^{-1}$$

Again,

$$\text{In k} = \text{In A} - \frac{E_a}{RT}$$

$$\text{In A} = \text{In k} + \frac{E_a}{RT}$$

When T = 273 K

In k = –7.147

Then, In A = $-7.147+\frac{102.27\times10^{3}}{8.314\times273}$

=37.911

Therefore, A = 2.91×10^{6}

When, T = 30 + 273K = 303 K

$$\frac{1}{T}=0.0033K=3.3\times10^{-3}K$$

Then, at $\frac{1}{T}=3.3\times10^{-3}K$,

In k = –2.8

Therefore, k = $6.08\times10^{-2}s^{-1}$

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

18. The rate constant for the decomposition of hydrocarbons is $2.418\times10^{-5}s^{-1}$ at 546 K. If the energy of activation is 179.9 kJ/mol, what will be the value of pre-exponential factor.

Ans. $k=2.418\times10^{-5}s^{-1}$

T= 546 K

$$E_a=179.9kJmol^{-1}$$
$$=179.9\times10^{3}J\,mol^{-1}$$

According to the Arrhenius equation,

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

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

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

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

$$= \log\left(2.418\times10^{-5}\,s^{-1}\right) + \frac{179.9\times10^{3}\,J\,mol^{-1}}{2.303\times8.314\,Jk^{-1}mol^{-1}\times546K}$$

= (0.3835 - 5) + 17.2082

= 12.5917

Therefore, A = antilog (12.5917)

= $3.9\times10^{12}\,s^{-1}$ (approximately)

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

Ans. For a first order reaction, $k = \frac{2.303}{t}\log\frac{[R]_0}{[R]}$

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

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

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

= $0.231h^{-1}$

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

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

$$\frac{[R]_0}{[R]} = \text{antilog}\left(0.8024\right)$$

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

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

= 0.158

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

20. The decomposition of hydrocarbon follows the equation $k = \left(4.5\times10^{11}s^{-1}\right)e^{-28000}K/T$. Calculate E_a.

Ans. The given equation is $k = \left(4.5\times10^{11}s^{-1}\right)e^{-28000}K/T$ ....(i)

Arrhenius equation is given by,

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

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

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

$$E_a = R\times 28000\,K$$

$$= 8.314\,JK^{-1}mol^{-1}\times 28000\,K$$

$$= 232792\,J\,mol^{-1}$$

$$= 232.792\,J\,mol^{-1}$$

21. The rate constant for the first order decomposition of H_2O_2 is given by the following equation: $\log k = 14.34 - 1.25 \times 10^4 \text{ K} / \text{T}$ Calculate E_a for this reaction and at what temperature will its half-period be 256 minutes?

Ans. Arrhenius equation is given by,

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

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

$$\text{In}\, k = \log A - \frac{E_a}{RT}$$

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

The given equation is

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

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

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

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

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

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

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

Also, when $k_{1/2} = 256 \text{ min utes}$

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

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

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

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

It is also given that, $\log k = 14.34 - 1.25 \times 104\,\text{K} / \text{T}$

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

$$\log\left(0.654 - 05\right) = 14.34 - \frac{1.25 \times 10^{4}\,\text{K}}{\text{T}}$$

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

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

= 668.95 K

= 669 K (approximately)

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

Ans. From Arrhenius equation, we obtain $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

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

T_1 =273 + 10 = 283 K

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

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

Then, $\log \frac{1.5\times10^4}{4.5\times10^3} = \frac{6.0\times10^4\ \text{Jmol}^{-1}}{2.303\times8.314\ \text{JK}^{-1}\text{mol}^{-1}}\left(\frac{T_2-283}{283T_2}\right)$

$$0.5229 = 3133.6279\left(\frac{T_2-283}{283T_2}\right)$$

$$\frac{0.5229\times283T_2}{3133.627} = T_2-283$$

$$0.0472T_2 = T_2-283$$

$$0.9528T_2 = 283$$

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

= 297 K

= $24°\text{C}$

Hence, *k* would be $1.5\times10^4 \text{s}^{-1}$ at $24°\text{C}$.

23. 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 $4\times10^{10}\text{s}^{-1}$. Calculate *k* at 318 K and E_a.

Ans. 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,

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

$$= \frac{2.2877}{k'}$$

According to the question, t = t’

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

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

From Arrhenius equation, we obtain

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

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

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

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

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

To calculate *k* at 318 K,

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

Again, from Arrhenius equation, we obtain

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

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

=(0.6021+10) – 12.5876

= –1.9855

Therefore, k = Antilog (–1.9855)

$= 1.034 \times 10^{-2} s^{-1}$

24. The rate of a reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation of the reaction assuming that it does not change with temperature.

Ans. From Arrhenius equation, we obtain $\log \frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$

It is given that, $k_2 = 4k_1$

$$T_1 = 293K$$
$$T_2 = 313K$$

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

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

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

$$= 52863.33\,J\,mol^{-1}$$

$$= 52.86\,kJ\,mol^{-1}$$

Hence, the required energy of activation is $52.86\,kJ\,mol^{-1}$.