Unit-7 Chemical kinetics

Notes

1.Rate = $\frac{\textit{Change in comcentration of reactants or products}}{\textit{time intrerval}}$

2.For reactants

rate = Negative gradient of change in reactant

3.For product

rate = positive gradient of change in products

4. aA + bB → Products

Rate law

rate = K[A]^a[B]^b

5.**Collision rate** Z $[A_2][B_2]$

6. **Fraction of effective collisions**

$$f = e^{\frac{-E_a}{RT}}$$

7.**Arrhenius equation** $k = Ae^{\frac{-E_a}{RT}}$

$\log k = \log A \frac{E_a}{2.303R}(\frac{1}{T})$

8.Intgrated form of first order rate constant

$k = \frac{2.303}{t} \log [A_0] / [A]$

9. Intgrated form of zero order rate constant

$k = \frac{[A_0] - [A]}{t}$

10.half life period for first order reaction

$t_{1/2} = \frac{0.6932}{k}$

11.half life period for first order reaction

$t_{1/2} = \frac{[A_0]}{2k}$

BOOK BACK

Answer the following questions:

1. Define average rate and instantaneous rate.

Average rate

It is defined as change in concentration of a reaction or product of a chemical in a given interval of time

Average rate = $\frac{\textit{Change in comcentration of reactants or products}}{\textit{time intrerval}}$

Instantaneous rate

The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate

2. Define rate law and rate constant.

Rate law

It equates rate of the reaction to the product of its rate constant and the concentration of reactants raised to certain exponential powers

aA + bB → Products

rate = K[A]^a[B]^b

K = rate constant of reaction

a , b = Exponents

Rate constant

It is equal to the rate of the reaction , when the concentration of reactant is unity It is proportionality constant .

3.Derive integrated rate law for a zero order reaction A → product

A reaction in which the rate is independent of the concentration of the reactant over a wide range of concentrations is called as zero order reactions rate law

rate = k[A]^0

$\frac{-d[A]}{dt}$ = k (1) where $[A]^0 = 1$

-d[A] = k dt ………. (1)

Integrate the above equation between the limits of $[A_0]$ at t = 0 and [A] at t = t ,

$- \int_{[A_0]}^{[A]} d\,[A] = k \int_0^t dt$

$[A_0] - [A] = kt$

$\mathbf{k} = \frac{[A_0] - [A]}{t}$

4.Define half life of a reaction. Show that for a first order reaction half life is independent of initial concentration.

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value.

For first order reaction rate constant

$\mathbf{k} = \frac{2.303}{t} \log [A_0] / [A]$ ……….(1)

when $t = t_{½}$ $[A] = [A_0] / 2$

$k = \frac{2.303}{t_{1/2}} \log 2$

$t_{1/2} = \frac{0.6932}{k}$ secs

Equation for half life of first order reaction does not contain any initial concentration term

5. What is an elementary reaction? Give the differences between order and molecularity of a reaction.

Elementary reaction

Each and every single step in a reaction mechanism is called an elementary reaction.

Order of reaction	Molecularity of reaction
It is sum of the power of concentration terms involved in experimentally determined rate law	It is total number of reactant species involved in an elementary step
It can be zero or fractional or integer	It is always whole number , cannot be zero or fractional number
It is assigned for overall reaction	It is assigned for each elementary step of mechanism

6. Explain the rate determining step with an example.

Decomposition of hydrogen peroxide catalysed by I^-

$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

It is experimentally found that the reaction is first order with respect to both **H_2O &** I^- which indicates that I^- is also involved in the reaction.

The mechanism involves the following steps

Step : 1

$H_2O_{2(aq)} + I^{-1}_{(aq)} \rightarrow H_2O_{(l)} + OI^{-1}_{(aq)}$

Step : 2

$H_2O_{2(aq)} + OI^{-1}_{(aq)} \rightarrow H_2O_{(l)} + I^{-1}_{(aq)} + O_{2(g)}$

Overall reaction is

$2H_2O_{2(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)}$

These two reactions are elementary reactions. Adding equation (1) and (2) gives the overall reaction.
Step 1 is the rate determining step, since it involves both **H_2O_2 &** I^- , the overall reaction is bimolecular.

7. Describe the graphical representation of first order reaction.

Reaction in which rate of the reaction depends on the concentrations of one of the reactant only is called first order reaction

A → **Products**

Rate = k [A]

$\frac{-d[A]}{dt}$ = k [A]

$\frac{-d[A]}{[A]}$ = k dt

Integrate the above equation between the limits of $[A_0]$ at t = 0 and [A] at t = t ,

$- \int_{[A_0]}^{[A]} \frac{d[A]}{[A]} = k \int_0^t dt$

ln $\frac{[A_0]}{A}$ = kt …………..(1)

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303

k = $\frac{2.303}{t}$ log $[A_0]$ / [A] ……….(2)

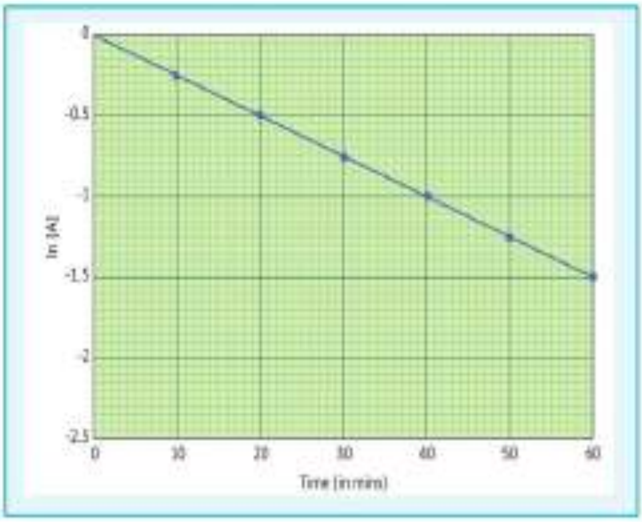
Equation (1) can be rewritten as

ln$[A_0]$ - ln$[A]$ = kt

y = mx + c

If we follow the reaction by measuring the concentration of the reactants at regular time interval‘t’, a plot of ln[A] against ‘t’ yields a **straight line with a negative slope which passes through origin for first order reaction** .

By taking slope k can be found out
For first order reaction k is constant



8. Write the rate law for the following reactions.

(a) A reaction that is 3/2 order in x and zero order in y.

Rate = k $[x]^{3/2} [y]^0$

(b) A reaction that is second order in NO and first order in Br_2.

$2NO + Br_2 \rightarrow$ **2NOBr**

Rate = k $[NO]^2 [Br_2]$

9. Explain the effect of catalyst on reaction rate with an example.

1. A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
2. They may participate in the reaction, but again regenerated and the end of the reaction.
3. In the presence of a catalyst, the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.

Example

To the solution containing 0.1N oxalic acid solution, 0.1N $KMnO_4$ solution

and 5 ml of 2N dilute H_2SO_4 , addition of few crystals of manganese sulphate to that solution pink color of solution fades up

In this case $MnSO_4$ acts as a catalyst and increases the rate of oxidation of $C_2O_2^{2-}$ by MnO_4^-

13.Explain briefly the collision theory of bimolecular reactions.

1. This theory is based on the kinetic theory of gases.
2. According to this theory, chemical reactions occur as a result of collisions between the reacting molecules.

$A_2(g) + B_2(g) \rightarrow 2AB$ (g)

- The reaction between A_2 and B_2 molecules proceeds through collisions between them, then the rate would be proportional to the number of collisions per second.

Rate ∝ number of molecules colliding per litre per second (collision rate)
The number of collisions is directly proportional to the concentration of both A_2 and B_2 .

Collision rate = Z $[A_2][B_2]$
Where, Z is a constant.

- The collision rate in gases can be calculated from kinetic theory of gases
- Thus, if every collision resulted in reaction, the reaction would be complete in 10^{-9} second.
- In actual practice this does not happen. It implies that all collisions are not effective to lead to the reaction.

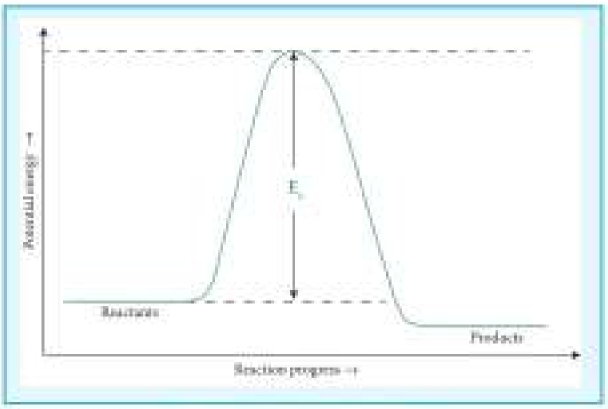


Fig 7.3 progress of the reaction

- In order to react, the colliding molecules must possess a minimum energy called activation energy. The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

Fraction of effective collisions **$f = e^{\frac{-E_a}{RT}}$**
E_a = 100 kJ mol $^{-1}$ T = 300 K
f = 4×10^{-18}

- Thus, out of 10^{18} collisions only four collisions are sufficiently energetic to convert reactants to products.
- This fraction of collisions is further reduced due to orientation factor i.e., even if the reactant collide with sufficient energy, they will not react unless the orientation of the reactant molecules is suitable for the formation of the transition state.

The fraction of effective collisions (f) having proper orientation is given by the steric factor p.

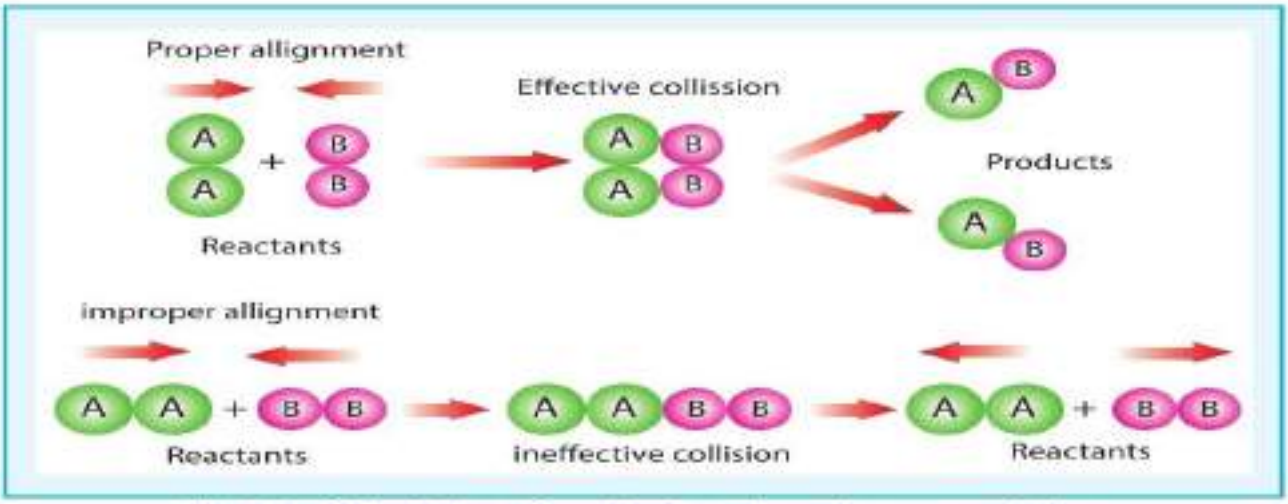


Fig 7.6 - Orientation of reactants - schematic representation

Rate = p x f x collision rate

$= Z\,[A_2][B_2] \times p \times e^{\frac{-E_a}{RT}}$ ……. **(1)**

Rate = k $[A_2][B_2]$ ………**(2)**

From (1) & (2)

$k = p\,Z\,e^{\frac{-E_a}{RT}}$

14. Write Arrhenius equation and explains the terms involved.

$k = A e^{\frac{-E_a}{RT}}$

A = Frequency factor or Arrhenius factor

E_a = Activation energy

R = gas constant

T = temperature

16. Hydrolysis of methyl acetate in aqueous solution has been studied by titrating the liberated acetic acid against sodium hydroxide. The concentration of an ester at different temperatures is given below.

t(min)	0	20	40	60	α
V(mL)	20.2	25.6	29.5	32.8	50.4

$k = \frac{2.303}{t} \log \left(\frac{V_\alpha - V_0}{V_\alpha - V_t}\right)$

$V_\alpha - V_0 = 50.4 - 20.2 = 30.2$

t = 20 mins V_t = 20.2

$k = \frac{2.303}{20} \log \left(\frac{30.2}{50.4-25.6}\right)$

$= 0.1151 \times 0.086$

$= \mathbf{9.8 \times 10^{-3}\ min^{-1}}$

t = 40 V_t = 29.5

$k = \frac{2.303}{40} \log \left(\frac{30.2}{50.4-29.5}\right)$

$= 0.0576 \times 0.1598$

$= \mathbf{9.20 \times 10^{-3}\ min^{-1}}$

t = 60 V_t = 32.8

$k = \frac{2.303}{60} \log \left(\frac{30.2}{50.4-32.8}\right)$

$= 0.03838 \times 0.2344$

$= \mathbf{9.0 \times 10^{-3}\ min^{-1}}$

k is found to be constant , so reaction is first order

17. Explain pseudo first order reaction with an example.

Second order reaction can be altered to a first order reaction by taking one of the reactant in large excess, such reaction is called pseudo first order reaction

Acid hydrolysis of an ester,

$CH_3COOCH_{3\,(aq)} + H_2O \rightarrow CH_3COOH_{(aq)} + CH_3OH$

If the reaction is carried out with the large excess of water, there is no significant change in the concentration of water during hydrolysis. i.e.,concentration of water remains almost a constant.

$k [H_2O] = k'$

rate = k $[CH_3COOCH_3]$

Thus it follows first order kinetics

18.Identify the order for the following

(i) Rusting of Iron

First order reaction

(ii) Radioactive disintegration of $_{92}U^{238}$

First order reaction

(iii) $2A + 3B \rightarrow$ **Products ; rate = k $[A]^{1/2} [B]^2$**

Pseudo First order reaction

19. A gas phase reaction has energy of activation 200 kJ mol^{-1} . If the frequency factor of the reaction is 1.6 × 10^{13} s^{-1}. Calculate the rate constant at 600 K.

E_a = 200 kJ mol^{-1} A= 1.6 × 10^{13} s^-

T = 200 K R = 8.314 K^{-1} mol^1

$k = Ae^{\frac{-E_a}{RT}}$

$= 1.6 \times 10^{13} \times e^{-(40.1)}$

$= 1.6 \times 10^{13} \times 3.8 \times 10^{-18}$

= 6.21 × 10^{-5} s^{-1}

21. How do concentrations of the reactant influence the rate of reaction?

- The rate of a reaction increases with the increase in the concentration of the reactants.
- The effect of concentration is explained on the basis of collision theory of reaction rates.
- According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules.
- Higher the concentration, greater is the possibility for collision and hence the rate.

22. How do nature of the reactant influence rate of reaction.

- Chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the product.
- The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.
- The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants

For example, reaction of sodium metal with iodine vapours is faster than the reaction between solid sodium and solid iodine.

Book inside

Short answers

1. Differences between rate and rate constant of a reaction:

Rate of a reaction	Rate constant of a reaction
It represents the speed at which the reactants are converted into products at any instant.	It is a proportionality constant
It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants in unity
It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

2.Define molecularity of a reaction

An elementary step is characterized by its molecularity.

The total number of reactant species that are involved in an elementary step is called molecularity of that particular step

3. Half life for an nth order reaction involving reactant A and $n \neq 1$

$$t_{1/2} = \frac{2^{n-1}-1}{(n-1)k[A_0]^{n-1}}$$

4.How does surface area of the reactant affects the rate of reaction

1. In heterogeneous reactions, the surface areas of the solid reactants play an important role in deciding the rate.
2. For a given mass of a reactant, when the particle size decreases surface area increases. Increase in surface area of reactant leads to more collisions per litre per second, and hence the rate of reaction is increased.

For example, powdered calcium carbonate reacts much faster with dilute HCl than with the same mass of $CaCO_3$ as marble

5.What is chemical kinetics ?

Chemical kinetics is the study of the rate and the mechanism of chemical reactions, proceeding under given conditions of temperature, pressure, concentration etc.

6.What is rate of reaction

The change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.

7.What are the factors affecting rate of the reaction ?

1. Nature and state of the reactant
2. Concentration of the reactant
3. Surface area of the reactant
4. Temperature of the reaction
5. Presence of a catalyst

8.Define activation energy

In order to react, the colliding molecules must possess a minimum energy called activation energy. The molecules that collide with less energy than activation energy will remain intact and no reaction occurs.

9.Factors affecting rate of the reaction

Nature and state of the reactant:

- Chemical reaction involves breaking of certain existing bonds of the reactant and forming new bonds which lead to the product.
- The net energy involved in this process is dependent on the nature of the reactant and hence the rates are different for different reactants.
- The physical state of the reactant also plays an important role to influence the rate of reactions. Gas phase reactions are faster as compared to the reactions involving solid or liquid reactants

Concentration of the reactants

- The rate of a reaction increases with the increase in the concentration of the reactants.
- The effect of concentration is explained on the basis of collision theory of reaction rates.
- According to this theory, the rate of a reaction depends upon the number of collisions between the reacting molecules.
- Higher the concentration, greater is the possibility for collision and hence the rate.

Effect of surface area of the reactant:

- In heterogeneous reactions, the surface areas of the solid reactants play an important role in deciding the rate.
- For a given mass of a reactant, when the particle size decreases surface area increases. Increase in surface area of reactant leads to more collisions per litre per second, and hence the rate of reaction is increased.

Effect of presence of catalyst:

- A catalyst is substance which alters the rate of a reaction without itself undergoing any permanent chemical change.
- They may participate in the reaction, but again regenerated and the end of the reaction.
- In the presence of a catalyst, the energy of activation is lowered and hence, greater number of molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.

SAIVEERA ACADEMY – REVOLUTION FOR LEARNING
PEELAMEDU – COIMBATORE 8098850809
12TH CHEMISTRY UNIT – 7 WISDOM TEST

Marks : 90 **Duration : 1 hr 30min**

I.Choose the correct answers **10 × 1 = 10**

1. After 2 hours, a radioactive substance becomes $(\frac{1}{4})^{th}$ of the original amount .Then half life (in min) is

a) 60 minutes b) 120 minutes c) 30 minutes d) 15 minutes

2. The half life period of a radioactive element is 140 days. After 420 days , 1 g of element will be reduced to

a) 1/2 *g* b) 1/4 *g* c) 1/8 *g* d) 1 /16 *g*

3. If 87.5% of a first order reaction was completed in 60 minutes , 50% of the same reaction under the same conditions would be completed in

a) 20 minutes b) 30 minutes c) 35 minutes d) 75 minutes

4. If the initial concentration of the reactant is doubled, the time for half reaction is remains same . Then the order of the reaction is

a) Zero b) one c) Fraction d) none

5. The rate constant of a reaction is 7.8 mol $l^{-1}s^{-1}$.The order of the reaction is

a) First order b) zero order c) Second order d) Third order

6. Assertion: rate of reaction doubles when the concentration of the reactant is doubles if it is a first order reaction.

Reason: rate constant is independent of temperature

a) Both assertion and reason are true and reason is the correct explanation of assertion.

b) Both assertion and reason are true but reason is not the correct explanation of assertion.

c) Assertion is true but reason is false.

d) Both assertion and reason are false

7. In a first order reaction $x \rightarrow y$; if k is the rate constant and the initial concentration of the reactant x is 0.1M, then, the half life is

a) (log 2 / k) *g* b) (0.6931 / (0.1)k)

c) 0.6931 / k d) (ln 2 / (0.1) k)

8. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 100K to 200K? (R = 8.314 JK^{-1} mol^{-1})

a) 23465 $kJK^{-1}mol^{-1}$ b) 43465 $kJK^{-1}mol^{-1}$

c) 43465 $JK^{-1}mol^{-1}$ d) 217.32 $JK^{-1}mol^{-1}$

9. The addition of a catalyst during a chemical reaction alters which of the following quantities

a) Enthalpy b) Activation energy c) Entropy d) Internal energy

10. The decomposition of phosphine (PH_3) on tungsten at low pressure is a first order reaction. It is because the

a) rate is proportional to the surface coverage

b) rate is inversely proportional to the surface coverage

c) rate is independent of the surface coverage

d) rate of decomposition is slow

II.Knowledge Based Questions **$10 \times 1 = 10$**

1.For the reaction $A \rightarrow B$, the concentration of a reactant changes from 0.03 M to 0.02 M in 25 minutes .Calculate average rate in minute .

2.Rate law for a reaction is rate = k [A] $[B]^{3/2}$Can the reaction be an elementary process ? Explain .

3.Draw a schematic graph showing how the rate of a first order reaction changes in concentration of reactants

4. rate = k [A] [B] . Find the unit of rate constant

5.Explain with suitable examples , how the molecularity of a reaction is different from order of reaction .

6. For the reaction $A \rightarrow B$. rate = k $[A]^2$ [B] i.How is rate of reaction affected if the concentration of A is doubled ? ii.What is overall order of reaction if B is present in large excess

7.How does change in temperature affect the rate of reaction ? How can this effect the rate constant of the reaction represented quantitatively

8.For a chemical reaction $A \rightarrow B$, the variation in the concentration ln[A] vs time t plot is given as .For this reaction i)What is order of reaction ii) What is unit of rate constant k ?

9.A reaction is second order in A and first order in B .Write the differential rate reaction .

10.Identify the order of reaction if its unit are L^{-1} mol s^{-1} and L mol^{-1} s^{-1}

III.Knowledge based problems (25 marks)

1.A first order reaction takes 10 minutes for 25 % decomposition .Calculate $t_{½}$ for the reaction Given log 2 = 0.3010 , log 3 = 0.4771 log 4 = 0.6021) **3m**

2.The rate constant for a first order reaction increases from 2×10^{-2} to 8×10^{-2} when the temperature changes from 300 K TO 320 K .Calculate activation energy (log 2 = 0.3010 , log 3 = 0.4771 log 4 = 0.6021) **2m**

3.For the hydrolysis of methyl acetate in aqueous solution , the following result were obtained

t (s)	0	30	60
$[CH_3COOCH_3]$ mol L^{-1}	0.60	0.30	0.15

Show its follows pseudo first order reaction as the concentration of water remains constant **3m**

4.Show that time required for 99% completion is double the time required for the completion of 90% reaction. **3m**

5.If half life period of first order reaction is x and ¾ th life period of same reaction is y .How are x and y related **2m**

6.Reaction is second order with repect to a reactant .How its rate affected if the concentration of the reactant is i)doubled ii)reduced to half . **2m**

7.The experimental date for decomposition of N_2O_5 [$2 N_2O_5 \rightarrow 4NO_2 + O_2$] in gas phase at 318K are given below

t (s)	0	800	1600	2400	3200
Log $[N_2O_5]$	-1.79	-1.94	-2.11	-2.28	-2.46

i)Draw a graph between log$[N_2O_5]$ and t . ii)Calculate rate constant iii)What is rate law ?**5m**

8. From the following data, show that the decomposition of hydrogen peroxide is a reaction of the first order:

t (min)	0	10	20
V (ml)	46.1	29.8	19.3

Where *t* is the time in minutes and V is the volume of standard KMnO4 solution required for titrating the same volume of the reaction mixture. **2m**

9. **3m**

For the reaction

$$2NO(g) + Cl_2(g) \rightarrow 2NOCl(g)$$

the following data were collected. All the measurements were taken at 263 K:

Experiment No.	Initial [NO](M)	Initial $[Cl_2]$(M)	Initial rate of disappearance of Cl_2(M/min)
1.	0.15	0.15	0.60
2.	0.15	0.30	1.20
3.	0.30	0.15	2.40
4.	0.25	0.25	?

(a) Write the expression for rate law.

(b) Calculate the value of rate constant and specify its units.

IV. Very short answers **10 × 2 = 20**

1.Define rate constant and write unit & examples for zero order reaction

2.Define i. Collision frequency ii.Activation energy

3.Define elementary reaction in a process & rate of a reaction

4. Derive integrated rate law for a zero order reaction A $\rightarrow$ product

5. Define rate law & instantaneous rate.

6. Write the rate law for the following reactions.

(a) A reaction that is 3/2 order in x and zero order in y.

(b) A reaction that is second order in NO and first order in Br_2.

7. The rate law for a reaction of A, B and C has been found to be rate k = $[A]^2 [B]^2 [L]^{3/2}$. How would the rate of reaction change when

(i) Concentration of [L] is quadrupled (ii) Concentration of both [A] and [B] are doubled

8. Write Arrhenius equation and explains the terms involved

9. Identify the order for the following reactions

(i) Rusting of Iron ii) Radioactive disintegration of ${}_{92}U^{238}$

10. . Write expression for Half life for an n^{th} order reaction involving reactant A and $n \neq 1$ and give examples for first order reaction

V. Short answers **5 × 3 = 15**

1.Write differences between order and molecularity of reaction

2.Define half life of a reaction . Prove that half life for first order is independent of initial concentration

3.Explain pseudo first order reaction with examples

4. Give the differences between rate of a reaction & rate constant

5.Derive integrated rate law for a first order reaction A $\rightarrow$ product

VI.Long answers **5 × 2 = 10**

1.Explain the factors affecting rate of the reaction

2. Explain briefly the collision theory of bimolecular reactions

To study the
abnormal is the best way of
understanding the normal

SAIVEERA ACADEMY
8098850809
12TH CHEMISTRY UNIT – 7
WISDOM TEST KEY

I.Choose the best answers

1, a) 60 min
At end of first $t_{1/2}$ ½ remains
At the end of 2nd $t_{1/2}$ ¼ remains
$2t_{1/2}$ = 2 hours = 120 min
$t_{1/2}$ = 60 min

2. c) 1/8 g
In 140 days initial concentration reduced to ½ g
In 280 days initial concentration reduced to ¼ g
In 420 days initial concentration reduced to 1/8 g

3.a) 20 min
At end of first $t_{1/2}$ 50% remains
At end of second $t_{1/2}$ 25% remains
At end of third $t_{1/2}$ 12.5 remains
For 87.5 % , 3 $t_{1/2}$ needed
$t_{87.5\%} = 3t_{50\%}$
$t_{50\%} = t_{87.5\%} / 3 = 60 / 3 = 20$ min

4. b) one
For first order $t_{1/2} = 0.6931 / k$
$t_{1/2}$ is independent of initial concentration
So its is first order reaction order is one

5. b) zero order
For zero order $k = A_0 – A /t$
Unit of $k = mol\ lit^{-1} / s$

6. b) Both assertion and reason are true but reason is not the correct explanation of assertion.

7. c) 0.6931 / k
$k = \frac{21}{t} \ln [A_0] / [A]$
$[A_0] = 0.1$ $[A] = 0.05$
$t_{1/2} = \ln 2 / k = 0.6931 / k$

8. d) 217.32 $JK^{-1}\ mol^{-1}$
$\log(k_2/k_1) = 2.303\ E_a /R\ (T_2 - T_1 / T_1 T_2)$

T_1 = 100 K T_2 = 200K
$k_2 = 2k_1$
E_a = 217.32 $JK^{-1}\ mol^{-1}$

9. b) Activation energy

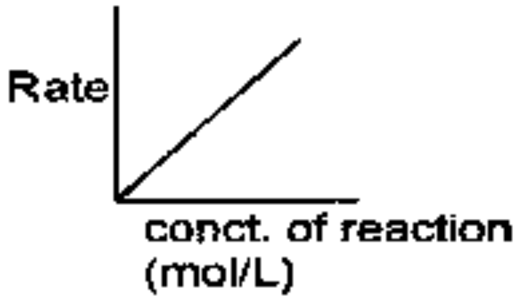
10. c) rate is independent of the surface coverage

II.Knowledge Based Questions

1.Average rate = - Change in reactant / change in time
= - (0.02 – 0.03) / 25
= 4×10^{-4} M min^{-1}

2.No an elementary process would have a rate law with order which is different from molecularities

3.



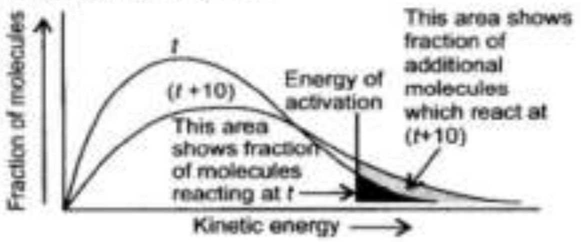
4.rate = k [A] [B]
k = rate / [A] [B]
= mol lit^{-1} s^{1} / (mol $lit^{-1})^2$
= mol^{-1} lit s^{-1}

5.nA + mB → Products
rate = k $[A]^n [B]^m$
Order = n + m
In simple bimolecular reaction n & m = 1
Therefore order = 2
Mechanism in which a molecule of reactant A and one of B incorporated in the transition state of rate determining step .
For this n = 2 and m = **0 (also second order)**
But molecularity is one

6. rate = k $[A]^2$ [B]
A = 2A
rate = k $[2A]^2$ [B]
= 4 (k $[A]^2$[B])
Increases by four times order **n = 3**

7.

Rate of reaction increases with increase in temperature. The rate of reaction nearly doubles with 10° rise in temperature as shown in following diagram



Distribution curve showing temperature dependece of a rate of reaction.

8.Since graph is straight line with negative slope therefore order is **first**

For first order unit of **k = s^1**

9. dx /dt = $k[A]^2 [B]$

10.i.Zero order $k = A_0 - A /t$

Unit of k = mol lit^{-1} / s

ii.second order k = rate / $[A]^2$

Unit of k = L $mol^{-1} s^{-1}$

IV. Very short answers

1. It is equal to the rate of the reaction , when the concentration of reactant is unity

It is proportionality constant

Unit of zero order ; mol lit^{-1} / s

Decomposition of N_2O on hot platinum surface

Or Iodination of acetone in acid medium

2.It is defined as number of collisions between

Between A and B occurring in container per unit volume per unit time

Activation energy

In order to react, the colliding molecules must possess a minimum energy

3.Elementary reaction

Each and every single step in a reaction mechanism

Rate of a reaction

It represents the speed at which the reactants are converted into products at any instant

4. rate law

rate = $k[A]^0$

$\frac{-d[A]}{dt}$ = k (1) where $[A]^0 = 1$

-d[A] = k dt ………. (1)

Integrate the above equation between the limits of $[A_0]$ at t = 0 and [A] at t = t ,

$- \int_{[A_0]}^{[A]} d\,[A] = k \int_0^t dt$

$[A_0] - [A] = kt$

k $= \frac{[A_0] - [A]}{t}$

5. It equates rate of the reaction to the product of its rate constant and the concentration of reactants raised to certain exponential powers

aA + bB → Products

rate = $K[A]^a[B]^b$

K = rate constant of reaction

a , b = Exponents

Instantaneous rate

The rate of the reaction, at a particular instant during the reaction

6. **(a) A reaction that is 3/2 order in x and zero order in y.**

Rate = k $[x]^{3/2} [y]^0$

(b) A reaction that is second order in NO and first order in Br_2.

$2NO + Br_2$ → **2NOBr**

Rate = k $[NO]^2 [Br_2]$

7. **rate = $k[A]^2 [B]^2 [L]^{3/2}$**

i) L = 4L

rate = $k[A]^2 [B]^2 [4L]^{3/2}$

rate = $k[A]^2 [B]^2 [2L]^3$

rate =8($k[A]^2 [B]^2 [L]^{3/2}$)

i.e rate is increased by 8 times

ii) A = 2A , B = 2B

rate = $k[2A]^2 [2B]^2 [L]^{3/2}$

rate = 16($k[A]^2 [B]^2 [L]^{3/2}$)

i.e rate is increased by 8 times

8.k = $Ae^{\frac{-E_a}{RT}}$
A = Frequency factor or Arrhenius factor
E_a = Activation energy
R = gas constant
T = temperature
9.i)First order
ii)Second order
10. $t_{1/2} = \frac{2^{n-1}-1}{(n-1)k[A_0]^{n-1}}$
Write the examples as question of 9

V.Short answers
1.

Order of reaction	Molecularity of reaction
It is sum of the power of concentration terms involved in experimentally determined rate law	It is total number of reactant species involved in an elementary step
It can be zero or fractional or integer	It is always whole number , cannot be zero or fractional number
It is assigned for overall reaction	It is assigned for each elementary step of mechanism

2. The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value.
For first order reaction rate constant

$$\mathbf{k = \frac{2.303}{t} \log [A_0] / [A]} \quad \text{..........(1)}$$

when **t = t½ [A] = [A₀] / 2**

$$k = \frac{2.303}{t_{1/2}} \log 2$$

$$t_{1/2} = \frac{0.6932}{k} \text{ secs}$$

Equation for half life of first order reaction does not contain any initial concentration term

3. Second order reaction can be altered to a first order reaction by taking one of the reactant in large excess, such reaction is called pseudo first order reaction

Acid hydrolysis of an ester,
$CH_3COOCH_{3\,(aq)} + H_2O \rightarrow CH_3COOH_{(aq)} + CH_3OH$
If the reaction is carried out with the large excess of water, there is no significant change in the concentration of water during hydrolysis. i.e.,concentration of water remains almost a constant.
$k[H_2O] = k'$
rate = k $[CH_3COOCH_3]$
Thus it follows first order kinetics

4.

Rate of a reaction	Rate constant of a reaction
It represents the speed at which the reactants are converted into products at any instant.	It is a proportionality constant
It is measured as decrease in the concentration of the reactants or increase in the concentration of products.	It is equal to the rate of reaction, when the concentration of each of the reactants in unity

It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

5. first order reaction.

Reaction in which rate of the reaction depends on the concentrations of one of the reactant only is called first order reaction

A → **Products**

Rate = k [A]

$\frac{-d[A]}{dt}$ = k [A]

$\frac{-d[A]}{[A]}$ = k dt

Integrate the above equation between the limits of $[A_0]$ at t = 0 and [A] at t = t ,

$- \int_{[A_0]}^{[A]} \frac{d[A]}{[A]} = k \int_0^t dt$

ln $\frac{[A_0]}{A}$ = kt …………..(1)

This equation is in natural logarithm. To convert it into usual logarithm with base 10, we have to multiply the term by 2.303

k = $\frac{2.303}{t}$ log $[A_0]$ / [A] ……….(2)

VI.Long answers

1.refer book or study material

2.refer book 0or study material

III.Knowledge based problems (25 marks)

1.

$t_{25\%} = 10$ min.

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

$$t_{25\%} = \frac{2.303}{k}\log\frac{[R]_0}{\frac{3}{4}[R]_0}$$

$$\left[\begin{array}{l}\because \text{ 25\% of reactants has been changed into products} \\ [R] = [R]_0 - \frac{25}{100}[R]_0 = \frac{75}{100}[R]_0 = \frac{3}{4}[R]_0\end{array}\right]$$

$\Rightarrow$ $$k = \frac{2.303}{10\text{ min}}[\log 4 - \log 3]$$

$\Rightarrow$ $$k = \frac{2.303}{10}\times(0.6021-0.4771) = \frac{2.303}{10}\times 0.1250$$

Now, $$t_{1/2} = \frac{2.303}{k}\log\frac{[R]_0}{[R]_0/2} = \frac{2.303}{k}\log 2$$

$\Rightarrow$ $$t_{1/2} = \frac{2.303\times 10}{2.303\times 0.1250}\times 0.3010 = \frac{3.010}{0.1250} = 24.08\text{ min}.$$

2.

Given: $k_2 = 8\times 10^{-2}$, $k_1 = 2\times 10^{-2}$, $T_1 = 300$ K, $T_2 = 320$ K

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)$$

$\Rightarrow$ $$\log\frac{8\times 10^{-2}}{2\times 10^{-2}} = \frac{E_a}{2.303\times 8.314}\left(\frac{1}{300}-\frac{1}{320}\right)$$

$\Rightarrow$ $$\log 4 = \frac{E_a}{19.147}\times\frac{20}{300\times 320}$$

$\Rightarrow$ $$E_a = \frac{19.147\times 0.6021\times 300\times 320}{20} \quad [\because \log 4 = 0.6021]$$

$$= \frac{19.147\times 0.6021\times 4800\text{ kJ mol}^{-1}}{1000}$$

$\Rightarrow$ $$E_a = 55.3364\text{ kJ mol}^{-1}.$$

3.

(i) $$k = \frac{2.303}{t}\log\frac{[R]_0}{[R]} = \frac{2.303}{30}\log\frac{0.60}{0.30} = \frac{2.303}{30}\times 0.301 = 2.31\times 10^{-2}\,s^{-1}$$

Also, $$k = \frac{2.303}{60}\log\frac{0.60}{0.15} = \frac{2.303}{60}\times 0.6021 = 2.31\times 10^{-2}\,s^{-1}$$

Since 'k' is constant, it shows that it follows pseudo first order reaction.

4.

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

$$t_{99\%} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0 \times \frac{1}{100}} \qquad \left[\because [R] = [R]_0 - \frac{99}{100}[R]_0\right]$$

$$\Rightarrow \quad t_{99\%} = \frac{2.303}{k} \log 100 = \frac{2.303 \times 2}{k} \qquad \ldots(i)$$

Also, $$t_{90\%} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0 \times \frac{10}{100}} \qquad \left[\because [R] = [R_0] - \frac{90}{100}[R]_0\right]$$

$$\Rightarrow \quad t_{90\%} = \frac{2.303}{k} \log 10 = \frac{2.303}{k} \qquad \ldots(ii)$$

From equations (i) and (ii)

$$t_{99\%} = 2 \times t_{90\%}.$$

5.

(i) $$t_{1/2} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/2} = \frac{2.303}{k} \log 2 = \frac{2.303}{k} \times 0.3010$$

$$\Rightarrow \quad t_{1/2} = \frac{0.693}{k} = x \qquad \ldots(i)$$

$$t_{3/4} = \frac{2.303}{k} \log \frac{[R]_0}{[R]_0/4}$$

$$= \frac{2.303}{k} \log 4 = \frac{2.303}{k} \times 0.6021$$

$$\Rightarrow \quad t_{3/4} = \frac{1.386}{k} = y \qquad \ldots(ii)$$

From (i) and (ii), we get

$$y = 2x \qquad [\because t_{3/4} = 2t_{1/2}]$$

6.

$$\frac{dx}{dt} = k[A]^2$$

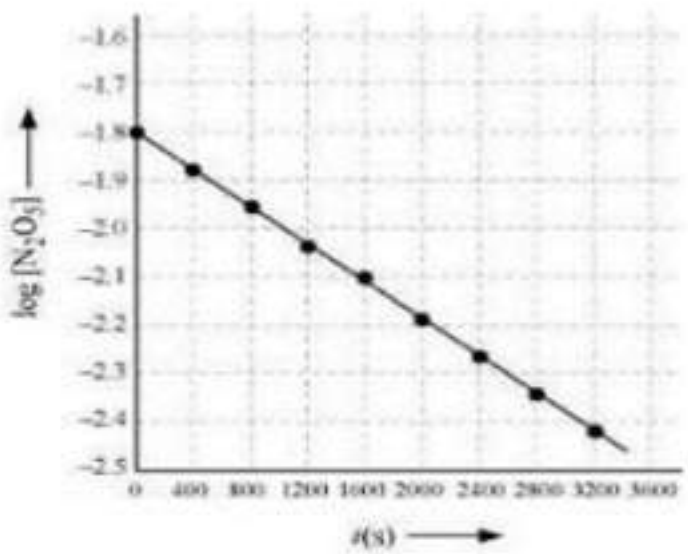
(i) rate $= k[2A]^2 = 4k[A]^2$

The rate will become four times.

(ii) rate $= k\left[\frac{A}{2}\right]^2 = k \times \frac{[A]^2}{4}$

The rate will become $\frac{1}{4}$ (one fourth).

7.



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

$\Rightarrow = 4.82 \times 10^{-4} molL^{-1}s^{-1}$

(vi) Half-life is given by

$t_{1/2} = \frac{0.639}{k} = \frac{0.639}{4.82\times10^{-4}}$ s

= 1.438×10^{3} s

= 1438 s

8. **k = $\frac{2.303}{t}$ log [V₀] / [Vₜ]**

V_0 = 46.1 ml V_t = 29.8 t = 10
k = 0.0436 min^{-1}

V_0 = 46.1 ml V_t = 19.3 t = 20
k = 0.04365min^{-1}
k found to be constant .Hence its is nearly constant

9.

$$\frac{dx}{dt} = k[A]^x [B]^y = k[NO]^x [Cl_2]^y$$

where 'x' is order w.r.t [NO] and 'y' is order w.r.t to $[Cl_2]$

$\Rightarrow \quad 0.60 = k\ (0.15)^x\ (0.15)^y$ ....(*i*)

Also, $1.20 = k\ (0.15)^x\ (0.30)^y$ ...(*ii*)

Dividing (*i*) by (*ii*) we get

$$\frac{1}{2} = \frac{1}{2^y} \Rightarrow 2^y = 2^1 \Rightarrow y = 1$$

Also, $2.40 = k(0.30)^x\ (0.15)^y$ ...(*iii*)

Dividing (*i*) by (*iii*) we get

$$\frac{1}{4} = \frac{1}{2^x} \Rightarrow 2^x = 2^2 \Rightarrow x = 2$$

(*a*) $\frac{dx}{dt} = k\ [NO]^2\ [Cl_2]^1$, where $\frac{dx}{dt}$ is represents rate of reaction.

(*b*) $0.60 = k(0.15)^2\ (0.15)$ [Putting values of expt. 1]

$$\Rightarrow k = \frac{0.60}{(0.15)^2\ (0.15)} = 177.78\ L^2\ mol^{-2}\ min^{-1}$$

$$k = 1.78 \times 10^2\ L^2\ mol^{-2}\ min^{-1}$$

where '*k*' is rate constant.