



# Rayat Shikshan Sanstha's Annasaheb Awate College Manchar

S.Y. B.Sc.

CH-301 : Physical & Analytical Chemistry

Chapter 1 : Chemical Kinetics

Lecture 04 : Integrated Rate-Laws

by

Prof. Hinge V. B.

NET,SET & GATE

# 1. Chemical Kinetics

## ➤ Introduction to kinetics:

Rates of chemical reactions – definition of rates, rate laws and rate constants, reaction order and molecularity, determination of rate law, factors affecting reaction rates.

## ➤ Integrated rate laws –

Zeroth-order reactions, first-order reactions, second-order reactions (with equal and unequal initial concentration of reactants), half-life period.

➤ **Methods for determination order of a reactions.**

➤ **Arrhenius equation-**

temperature dependence of reaction rates, interpretation of Arrhenius parameters.

➤ **Reaction dynamics**

collision theory and transition-state theory of bimolecular reactions, comparison of the two theories.

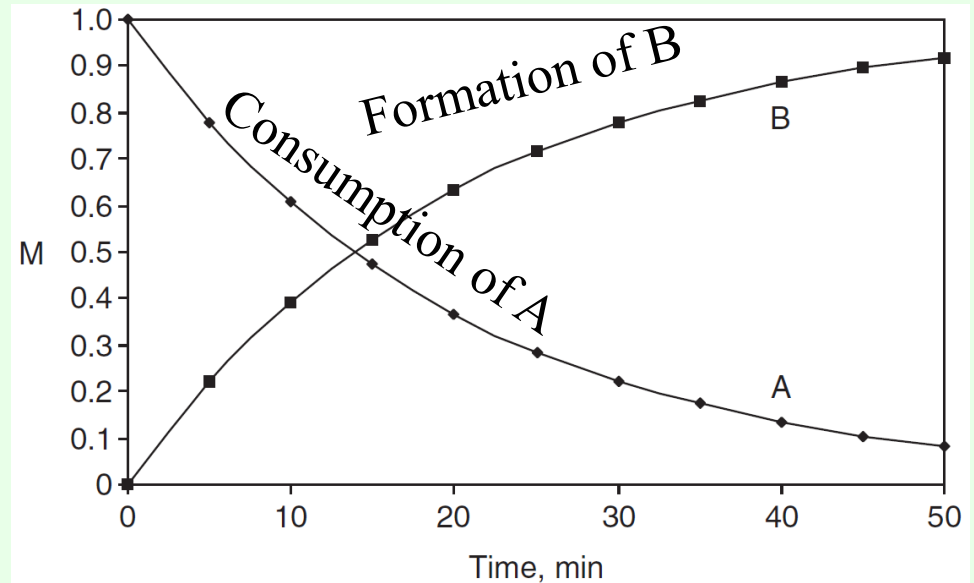
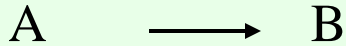
➤ **Problems.**

# Introduction to kinetics

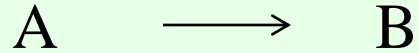
## What is Chemical Kinetics ?

Measurement of **rate of chemical reaction** under the given conditions temperature, pressure & concentration.

Rate of chemical reactions :



## Rate of a reaction



*Change in concentration of a reactant or product in unit time*

### 1. Rate of consumption of reactant

The rate of decrease in concentration of any one of the reactants per unit time.

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

### 2. Rate of formation of product

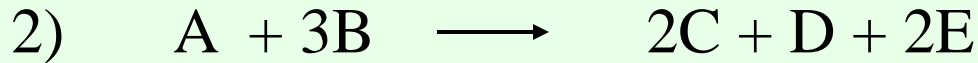
The rate of increase in concentration of any one of the products.

$$r = +\frac{d[B]}{dt}$$

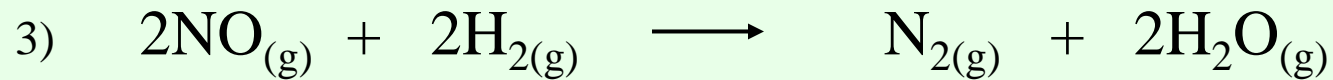
## Reaction rate ?



$$r = -\frac{1}{a} \frac{d[A]}{dt} = -\frac{1}{b} \frac{d[B]}{dt} = +\frac{1}{c} \frac{d[C]}{dt} = +\frac{1}{d} \frac{d[D]}{dt}$$

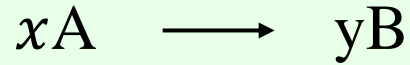


$$r = -\frac{d[A]}{dt} = -\frac{1}{3} \frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = \frac{d[D]}{dt} = \frac{1}{2} \frac{d[E]}{dt}$$



$$r = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{1}{2} \frac{d[\text{H}_2]}{dt} = \frac{d[\text{N}_2]}{dt} = \frac{1}{2} \frac{d[\text{H}_2\text{O}]}{dt}$$

## Rate Law & Rate constant /velocity constant



The rate of reaction is experimentally given by, **Rate-law**

$$r = k[\text{A}]^x$$

k is rate constant / velocity constant of the reaction at the given temperature.

If [A] is unity ;

$$r = k$$





Rate law for this reaction is,

$$r = k[A]^a[B]^b[C]^c$$

If  $[A]=[B]=[C]=1$ , then  $k = r$

Thus **rate constant of reaction**, is the *rate of reaction when concentration of each reactant is unity*.

## Order of reaction

The sum of the concentration power of the reactant molecules in rate-law expression.

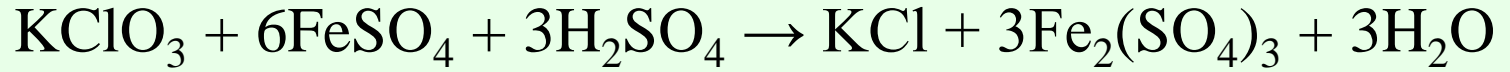
eg,

Reaction	Rate law (experimental quantity)	Order
$A \rightarrow P$	$r = k[A]^0$	Zero
$A \rightarrow P$	$r = k[A]$	First
$2A \rightarrow P$	$r = k[A]^2$	Second

Reaction	Rate law	Order
$A+B \rightarrow P$	$r = k[A][B]$	Second order
$3A \rightarrow P$	$r = k[A]^3$	Third order
$2A+B \rightarrow P$	$r = k[A]^2[B]$	Third order
$A+2B \rightarrow P$	$r = k[A][B]^2$	Third order
$A+B+C \rightarrow P$	$r = k[A][B][C]$	Third order
$A+(1/2)B \rightarrow P$	$r = k[A][B]^{1/2}$	1.5 <sup>th</sup> order

*From this table order may be 0, 1, 2, 3 & fraction.*

- Order of a reaction is a experimental quantity.
- Order of a reaction can be zero , integer or fraction.
- The reactions taking place in one step are called **elementary reactions**. In such reaction by seeing reaction on paper we can find order.
- In **Complex reaction** (which takes place in more than one step) balanced chemical equation never gives us a true order order of a complex reaction.

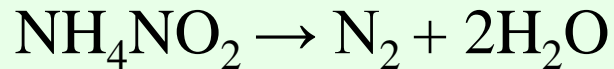


What is the order of given reaction ?

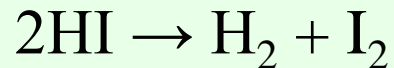
This reaction which apparently **seems to be of tenth order** is actually a **second order reaction**. This shows that this reaction takes place in several steps ie, this is a complex reaction.

## Molecularity of a reaction

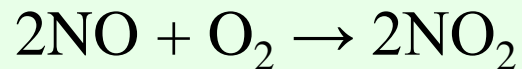
*The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction, which must collide simultaneously in order to bring about a chemical reaction is called molecularity of a reaction.*



Unimolecular reaction



Bimolecular reaction



Trimolecular reaction

# Order of a reaction

# Molecularity of a reaction

The sum of the concentration power of the reactant molecules in rate-law expression

It is experimental quantity

It can be zero, integer or fraction

Order is applicable to elementary as well as complex reactions

The number of reacting species (atoms, ions or molecules) taking part in an elementary reaction

It is theoretical quantity

It is always Integer. can't be fraction or zero.

molecularity is applicable to only for elementary reactions.

# Units of rate constants

## Zero order Rxn

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

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

$$\frac{\text{Concn}}{\text{time}} = k$$

Concn = moles/lit.

Concn = mole/dm<sup>3</sup>

mol.lit.<sup>-1</sup>sec<sup>-1</sup>

mol.dm<sup>-3</sup>sec<sup>-1</sup>



# First order Rxn

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

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

$$\frac{\text{conc}^n}{\text{time concn}}$$

$$\text{Conc}^n = \text{moles/lit.}$$

$$\text{Sec.}^{-1}$$

$$\text{Conc}^n = \text{mole/dm}^3$$

$$\text{Sec.}^{-1}$$

## Second order Rxn

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

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

$$\frac{\text{conc}^n}{\text{time} \cdot (\text{conc}^n)^2} = k$$

$$\text{Conc}^n = \text{moles/lit}$$

$$\text{mol}^{-1}\text{lit}\cdot\text{sec}^{-1}$$

$$\text{Conc}^n = \text{mole/dm}^3$$

$$\text{mol}\cdot^{-1}\text{dm}^3\text{sec}^{-1}$$

# Nth order Rxn

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

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

$$\frac{\text{conc}^n}{\text{time} \cdot (\text{conc}^n)^n} = k$$

$$\text{Conc}^n = \text{moles/lit}$$

$$\text{mol.}^{1-n} \text{lit.}^{n-1} \text{sec}^{-1}$$

$$\text{Conc}^n = \text{mole/dm}^3$$

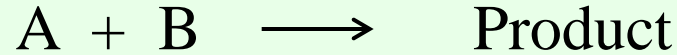
$$\text{mol.}^{1-n} (\text{dm}^3)^{n-1} \text{sec}^{-1}$$

## Unit of Rate constant k

$\text{mol.}^{1-n}\text{lit.}^{n-1}\text{sec}^{-1}$	Order of reaction	Unit of rate constant
n=0	Zero order reaction	$\text{mol.lit.}^{-1}\text{sec}^{-1}$
n=1	First order reaction	$\text{Sec.}^{-1}$
n=2	Second order reaction	$\text{mol}^{-1}\text{lit.sec}^{-1}$
n=3	Third order reaction	$\text{mol}^{1-n}\text{lit.}^{n-1}\text{sec}^{-1}$

# Determination of rate law

## 1. Isolation method



- Concentration of all the reactants except one are in large excess.
- If B is in large excess, that means its concentration is constant throughout the reaction  
then we get rate expression w. r. t. A

- similarly, If A is in large excess, that means its concentration is constant throughout the reaction then we get rate expression w. r. t. B
- By comparing two rate expressions we get the overall rate-law.

Write rate-law & find the order of reaction from the given experimental data ?

Experiment no	[A]	[B]	Overall rate
1	30	30	100
2	60	30	400
3	30	60	200
4	60	60	800

In Experiment 1 & 2 the conc<sup>n</sup> of B is kept constant. Therefore we write rate expression w.r.t. A

$$1. \text{ Rate} = k[A]^a[B]^b$$

$$100 = k30^a30^b$$

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

$$400 = k60^a30^b$$

Divide eq. 2 by 1

$$\frac{400}{100} = \left(\frac{60}{30}\right)^a \left(\frac{30}{30}\right)^b$$

$$4 = 2^a$$

$$a = 2$$

Experiment no	[A]	[B]	Overall rate
1	30	30	100
2	60	30	400
3	30	60	200
4	60	60	800

In Experiment 1 & 3 the conc<sup>n</sup> of A is kept constant. Therefore we write rate expression w.r.t. B



$$1. \text{ Rate} = k[A]^a[B]^b$$

$$100 = k30^a30^b$$

$$3. \text{ Rate} = k[A]^a[B]^b$$

$$200 = k30^a60^b$$

Divide eq. 3 by 1

$$\frac{200}{100} = \left(\frac{60}{30}\right)^b$$

$$2 = 2^b$$

$$b = 1$$

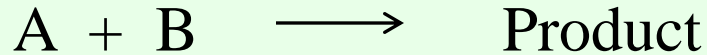
Experiment no	[A]	[B]	Overall rate
1	30	30	100
2	60	30	400
3	30	60	200
4	60	60	800

Overall rate-law is

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

$$\text{Rate} = k[A]^2[B]^1 \quad \& \text{ order is 3.}$$

## 2. Initial rates method



This method is used in conjunction with the isolation method. In this method initial rates of reaction is determined for different  $\text{conc}^n$  of A reactant by keeping B reactant  $\text{conc}^n$  constant

From that we get

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

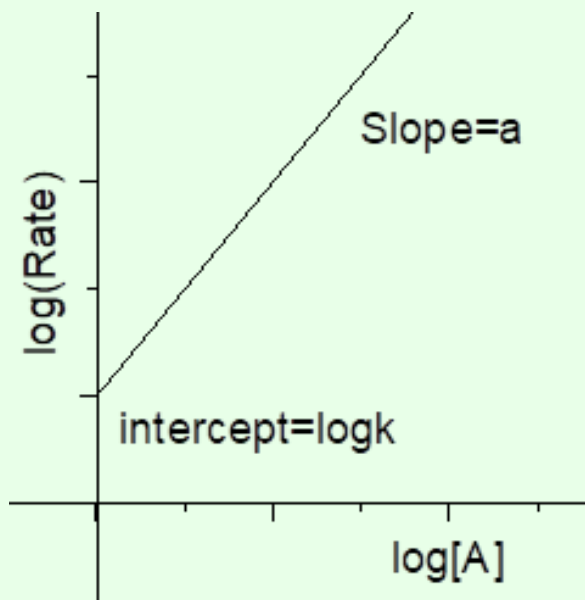
taking log on both sides

$$\log(\text{Rate}) = \log k + a \log[A]$$

$$\log(\text{Rate}) = a \log[A] + \log k$$

$$y = mx + c$$

Plot a graph, we get straight line with intercept  $\log k$  & slope  $a$



lly, by keeping A reactant conc<sup>n</sup> constant....Determine the value of b from slope

Then put value of a & b in rate law expression.

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

A1 Attendance bot: dev(Pavan:p2pdops@gmail.com) on 2020-08-17 : 12:08 :

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
1	Attendance bot: dev(Pavan:p2pdops@gmail.com) on 2020-08-17 : 12:08 :																		
2																			
3	Members :37																		
4																			
5	vikram hinge																		
6	Abhishek Bhor																		
7	aishwarya barve																		
8	Aishwarya Dongare																		
9	ANIKET JADHAV																		
10	Anisha Argade																		
11	Anita Kale																		
12	Damini Talpe																		
13	Dipali Thorat																		
14	Kajal Nighot																		
15	Kaushal Thorat																		
16	Komal Dhumal																		
17	manali gunjal																		
18	Manasi Hinge																		
19	Nikita Shinde																		
20	Pallavi Bokad																		
21	Pradnya Bhor																		
22	Pradnya Karale																		
23	Pranjal Thorat																		
24	Pranjal Thosar																		
25	Pratiksha Pokharkar																		
26	priyanka bhor																		

Meet attendance -(2020-08-17\_

A1 Attendance bot: dev(Pavan:p2pdops@gmail.com) on 2020-08-17 : 12:08 :

	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S
16	Komal Dhupal																		
17	manali gunjal																		
18	Manasi Hinge																		
19	Nikita Shinde																		
20	Pallavi Bokad																		
21	Pradnya Bhor																		
22	Pradnya Karale																		
23	Pranjal Thorat																		
24	Pranjal Thosar																		
25	Pratiksha Pokharkar																		
26	priyanka bhor																		
27	Priyesh Bangar																		
28	Rohit Bhor																		
29	Rutuja Lande																		
30	Rutuja Shewale																		
31	sejal Pingale																		
32	Shivani Lohakare																		
33	shreya bhalerao																		
34	shruti davkhare																		
35	Sujit Awate																		
36	Swati Bhagwat																		
37	Vaishnavi Ghodekar																		
38	Vaishnavi Hinge																		
39	vaishnavi lande																		
40	Varsha Shelkande																		
41	vidya jadhav																		

Meet attendance -(2020-08-17\_

# Factors affecting reaction rates

## 1. Temperature

The rate of reaction increases as temperature increases, the rate of reaction decreases as temperature decreases. Generally rate of reaction get doubled by increasing the temp. by  $10^{\circ}\text{C}$ .

## 2. Catalyst

A catalyst is a substance that can increase the rate of a reaction but which itself unchanged in amount & chemical composition at the end of the reaction.

### **3. Concentration**

Concentration refers to the no of particles in a given volume concentration is like strength of a substance. The higher the concentration of the substance higher the reaction rate.

### **4. Surface area**

An increase in surface area will result in an increase of the exposure ,of reactants to one another.

The greater the exposure , the greater the reaction rate.

### **5. Stirring**

Stirring will also cause an increase in reactant exposure.

Therefore, the more stirring ,the faster the reaction rate.

## Problems

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

$$\begin{aligned} \text{Rate} &= -\frac{d[R]}{dt} \\ &= \frac{(0.03 - 0.02)M}{25 \text{ min}} \\ &= \frac{0.01}{25} M \cdot \text{min}^{-1} \end{aligned}$$



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

$$\text{Rate} = -\frac{d[R]}{dt}$$

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

**4.** 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 ?

**5.** Calculate the overall order of a reaction which has the rate expression

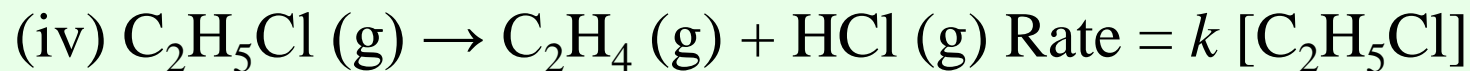
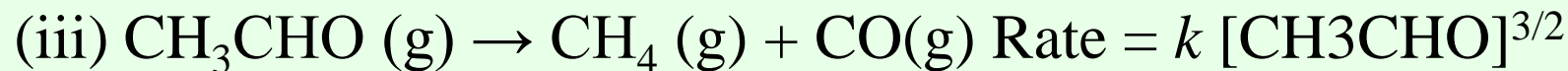
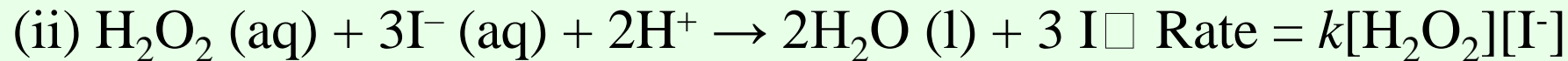
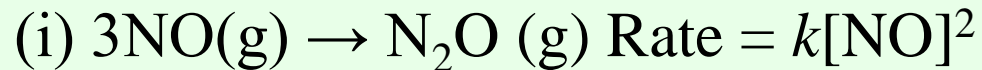
(a)  $\text{Rate} = k [\text{A}]^{1/2} [\text{B}]^{3/2}$

(b)  $\text{Rate} = k [\text{A}]^{3/2} [\text{B}]^{-1}$

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

(i) doubled (ii) reduced to half ?

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



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 <sup>-1</sup>	0.20	0.20	0.40
B/ mol L <sup>-1</sup>	0.30	0.10	0.05
$r_0$ /mol L <sup>-1</sup> s <sup>-1</sup>	$5.07 \times 10^{-5}$	$5.07 \times 10^{-5}$	$1.43 \times 10^{-4}$

What is the order of the reaction with respect to A and B?

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



10.

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



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

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

- 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]/ mol L <sup>-1</sup>	[B]/ mol L <sup>-1</sup>	Initial rate/ mol L <sup>-1</sup> min <sup>-1</sup>
I	0.1	0.1	$2.0 \times 10^{-2}$
II	-	0.2	$4.0 \times 10^{-2}$
III	0.4	0.4	-
IV	-	0.2	$2.0 \times 10^{-2}$

**12.** Which of the following statements is correct?

- (i) The rate of a reaction decreases with passage of time as the concentration of reactants decreases.
- (ii) The rate of a reaction is same at any time during the reaction.
- (iii) The rate of a reaction is independent of temperature change.
- (iv) The rate of a reaction decreases with increase in concentration of reactant(s).

13. Rate law for the reaction  $A + 2B \longrightarrow C$  is found to be

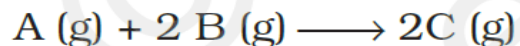
$$\text{Rate} = k [A][B]$$

Concentration of reactant 'B' is doubled, keeping the concentration of 'A' constant, the value of rate constant will be\_\_\_\_\_.

- (i) the same
- (ii) doubled
- (iii) quadrupled
- (iv) halved

14.

Compounds 'A' and 'B' react according to the following chemical equation.



Concentration of either 'A' or 'B' were changed keeping the concentrations of one of the reactants constant and rates were measured as a function of initial concentration. Following results were obtained. Choose the correct option for the rate equations for this reaction.

Experiment	Initial concentration of [A]/mol L <sup>-1</sup>	Initial concentration of [B]/mol L <sup>-1</sup>	Initial rate of formation of [C]/mol L <sup>-1</sup> s <sup>-1</sup>
1.	0.30	0.30	0.10
2.	0.30	0.60	0.40
3.	0.60	0.30	0.20

- (i) Rate =  $k [A]^2 [B]$
- (ii) Rate =  $k [A] [B]^2$
- (iii) Rate =  $k [A] [B]$
- (iv) Rate =  $k [A]^2 [B]^0$

Meet attendance -

File Home Insert Page Layout Formulas Data Review View H

NOTICE Most features are disabled because your Office product is inactive. To use for free,

A1 Attendance bot: dev(Pavan:p2pdops@gmai

	A	B	C	D	E	F	G	H
1	Attendance bot: dev(Pavan:p2pdops@gmail.com) on 2020-08-18 : 13:40 :							
2								
3	Members :37							
4								
5	vikram hinge							
6	Abhishek Bhor							
7	aishwarya barve							
8	Aishwarya Dongare							
9	ANIKET JADHAV							
10	Anita Kale							
11	Damini Talpe							
12	Fiza Jamadar							
13	Harshada Thorat							
14	kajal dhmal							
15	Rudra Thorat							
16	Rutuja Lande							
17	Rutuja Shewale							
18	Sagar Chinchpure							
19	shraddha kunjir							
20	shreya bhalerao							
21	shruti davkhare							
22	Sujit Awate							
23	Vaishnavi Ghodekar							
24	Vaishnavi Hinge							
25	vaishnavi lande							

Meet attendance -(2020-08-18 \_

Meet attendance -

File Home Insert Page Layout Formulas Data Review View H

NOTICE Most features are disabled because your Office product is inactive. To use for free,

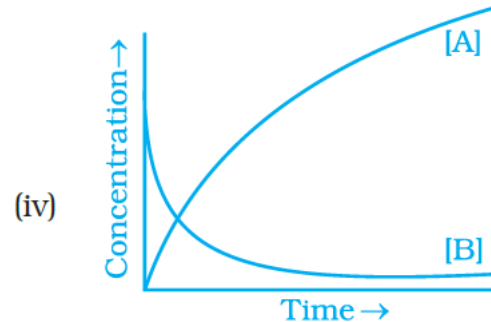
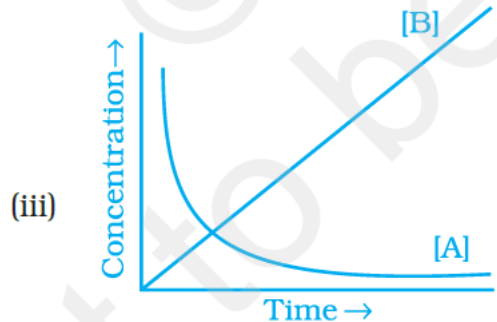
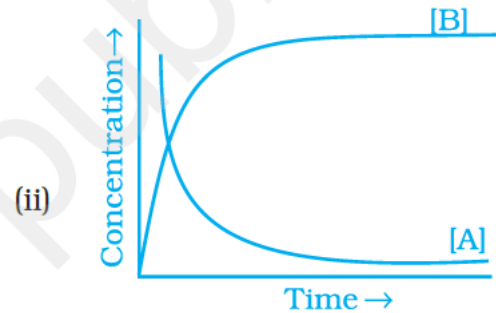
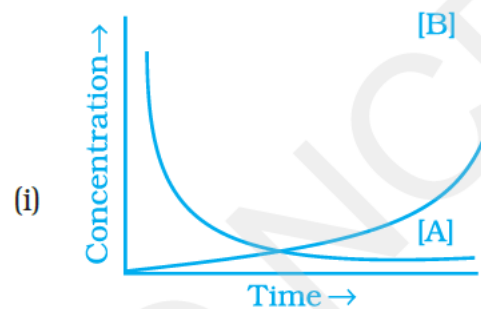
A1 Attendance bot: dev(Pavan:p2pdops@gmai

	A	B	C	D	E	F	G	H
18	Sagar Chinchpure							
19	shraddha kunjir							
20	shreya bhalerao							
21	shruti davkhare							
22	Sujit Awate							
23	Vaishnavi Ghodekar							
24	Vaishnavi Hinge							
25	vaishnavi lande							
26	vidya jadhav							
27	Pujan Bhor							
28	Rohit Bhor							
29	Priyesh Bangar							
30	Pratiksha Pokharkar							
31	priyanka bhor							
32	Pranjal Thorat							
33	Pranjal Thosar							
34	Pradnya Bhor							
35	Pradnya Litke							
36	Kaushal Thorat							
37	manali gunjal							
38	Manasi Hinge							
39	Nikita Shinde							
40	Pallavi Bokad							
41	Kajal Nighot							
42								

Meet attendance -(2020-08-18 \_

15.

Consider the reaction  $A \rightleftharpoons B$ . The concentration of both the reactants and the products varies exponentially with time. Which of the following figures correctly describes the change in concentration of reactants and products with time?



# Integrated rate-laws

```
graph TD; A[Integrated rate-laws] --> B[Zero order reaction]; A --> C[First order reaction]; A --> D["Second order reaction (with equal initial concentration)"]; A --> E["Second order reaction (with unequal initial concentration)"];
```

**Zero order reaction**

**First order reaction**

**Second order reaction** (with equal initial concentration)

**Second order reaction** (with unequal initial concentration)



## Zero order reaction :

The reaction in which the rate of reaction is independent of initial concentration of reactant molecule.



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

$$-\frac{d[A]}{dt} = k[A]^0$$

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

$$-d[A] = kdt$$

Taking integration on both sides

$$\int_{[A]_0}^{[A]_t} -d[A] = k \int_{t=0}^{t=t} dt$$

$[A]_0$  is initial conc<sup>n</sup> of A

$[A]_t$  is conc<sup>n</sup> of A at time t

Time is from t= 0 to t=t

$$\{-[A]\}_{[A]_0}^{[A]_t} = k\{t\}_0^t$$

$$-\{[A]_t - [A]_0\} = k\{t - 0\}$$

$$- [A]_t + [A]_0 = kt$$
$$[A]_0 - [A]_t = kt \quad \text{—————} \quad (1)$$

$$\boxed{k = \frac{[A]_0 - [A]_t}{t}} \quad \text{—————} \quad (2)$$

From equation (1)

$$- [A]_t = kt - [A]_0$$

$$[A]_t = -kt + [A]_0$$

Compare this with equation of line

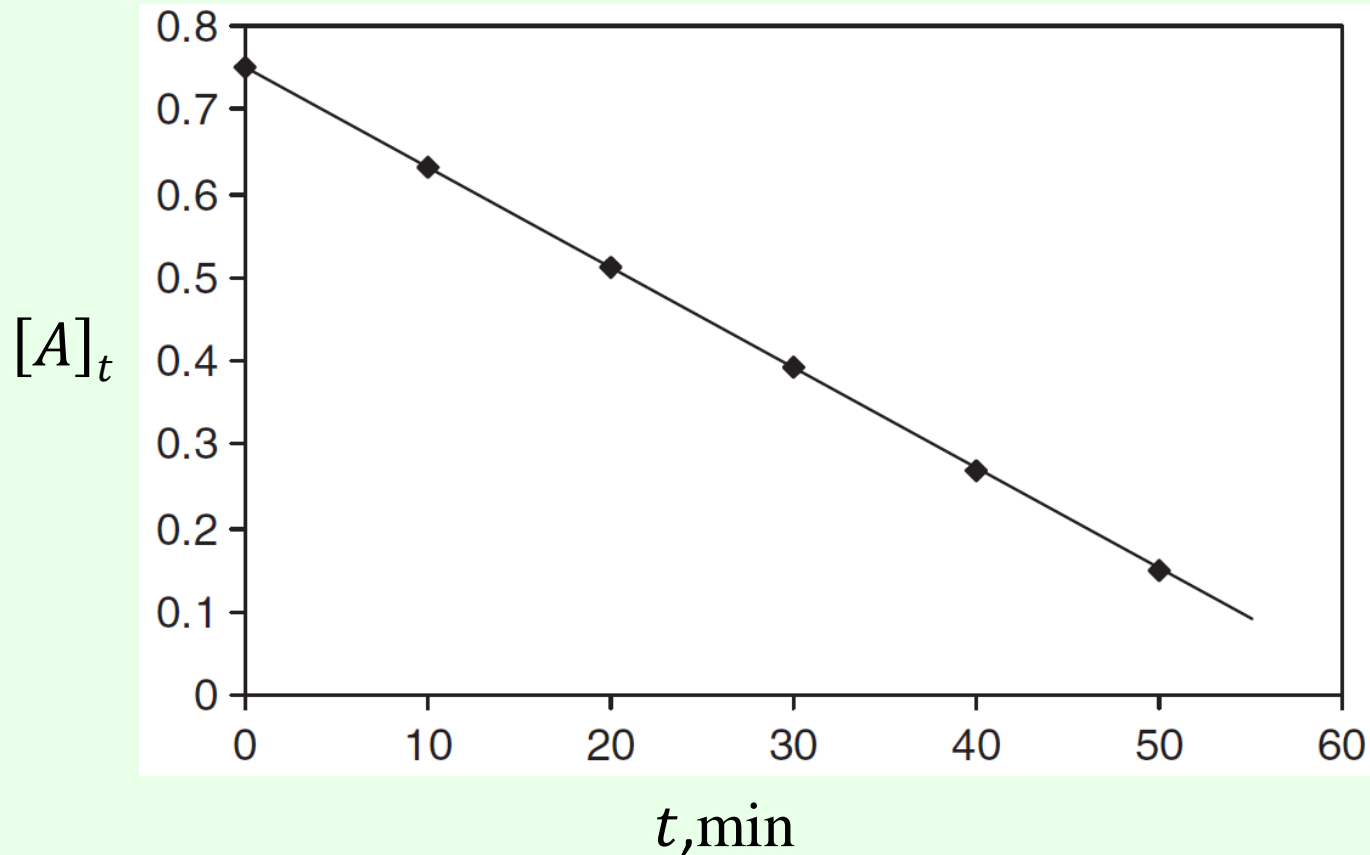
$$y = mx + c$$

*y axis =  $[A]_t$*

*x axis =  $t$*

*Slope =  $m = -k$*

*Intercept =  $c = [A]_0$*



## Half life of zero order reaction:

The time at which only 50% of reactant get converted into product.

or

The time at which only half of the reactant get converted into product.

$\therefore$  Put  $[A]_t = \frac{[A]_0}{2}$  in equation (2) &  $t = t_{1/2}$

$$k = \frac{[A]_0 - \frac{[A]_0}{2}}{t_{1/2}}$$

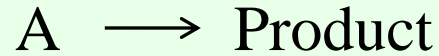
$$k = \frac{[A]_0}{2t_{1/2}}$$

*The half life of zero order reaction is directly proportional to initial concentration of reactant molecule*

$$\therefore t_{1/2} = \frac{[A]_0}{2k}$$

## First Order Reaction:

The reaction in which rate of reaction is depends on first power of the reactant molecule.



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

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

$$-\frac{d[A]}{[A]} = kdt$$

Taking integration on both sides

$$-\int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]} = k \int_0^t dt$$

$$-\left\{ \ln[A] \right\}_{[A]_0}^{[A]_t} = k \{t\}_0^t$$

$$-\{ \ln[A]_t - \ln[A]_0 \} = k \{t - 0\}$$

$$-\ln[A]_t + \ln[A]_0 = kt$$

$$\ln[A]_0 - \ln[A]_t = kt$$

$$kt = \ln[A]_0 - \ln[A]_t$$

$$kt = \ln[A]_0 - \ln[A]_t \longrightarrow$$

$$kt = \ln \frac{[A]_0}{[A]_t}$$

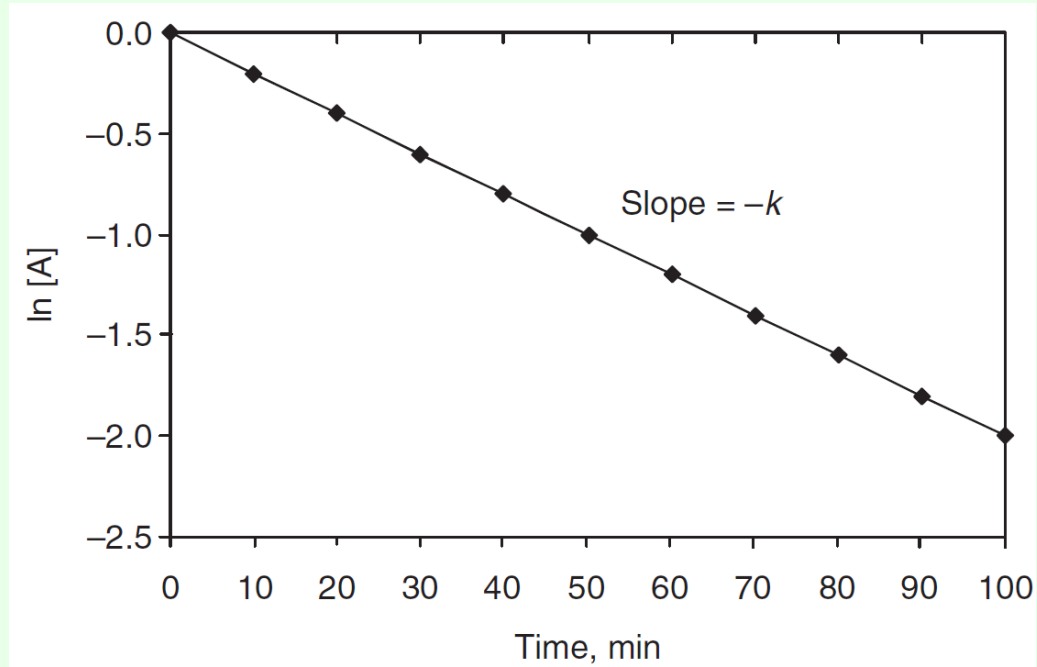
$$k = \frac{1}{t} \ln \frac{[A]_0}{[A]_t}$$

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

$$-\ln[A]_t = kt - \ln[A]_0$$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$y = mx + c$$



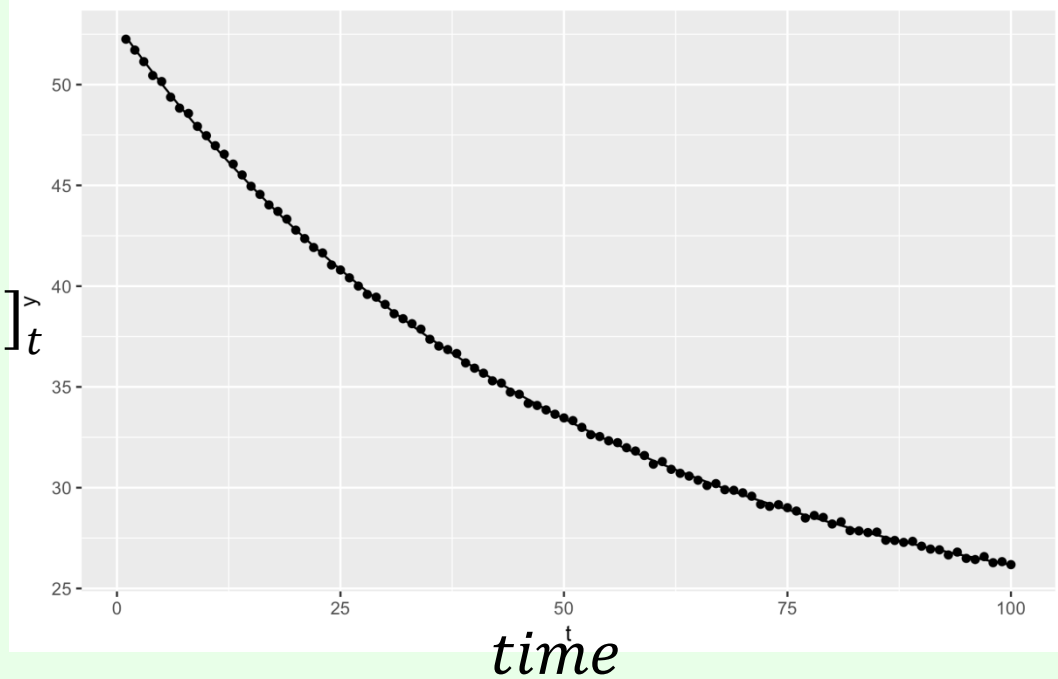


$$\ln[A]_t = -kt + \ln[A]_0$$

$$\ln[A]_t = \ln[A]_0 - kt$$

$$[A]_t = [A]_0 e^{-kt}$$

$[A]_t$



From this equation, it can be seen that the concentration of A decreases with time in an exponential way. Such a relationship is sometimes referred to as an exponential decay.

## Half life of first order reaction:

The time at which only 50% of reactant get converted into product.

or

The time at which only half of the reactant get converted into product.

∴ Put  $[A]_t = \frac{[A]_0}{2}$  in First order equation &  $t = t_{1/2}$

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

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

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

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

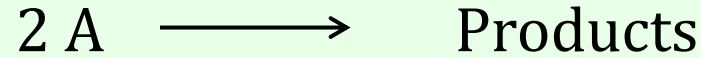
$$t_{1/2} = \frac{2.303}{k} * 0.3010$$

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

The half life of first order reaction is independent of initial concentration of reactant molecule

## Second order Reaction (with equal initial concentration of reactant )

The reaction in which rate of reaction is depends on Second power of the reactant molecule.



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

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

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

If the equation is integrated between limits on concentration of  $[A]_0$  at  $t=0$  and  $[A]_t$  at time  $t$ , we have

$$- \int_{[A]_0}^{[A]_t} \frac{d[A]}{[A]^2} = k \int_0^t dt$$

$$\int x^n = \frac{x^{n+1}}{n+1}$$

$$- \int_{[A]_0}^{[A]_t} \frac{1}{[A]^2} d[A] = k \int_0^t dt$$

$$- \int_{[A]_0}^{[A]_t} [A]^{-2} d[A] = k \int_0^t dt$$

$$\left\{ \frac{[A]^{-2+1}}{-2+1} \right\} = k\{t\}$$

$$-\left\{ \frac{[A]^{-2+1}}{-2+1} \right\}_{[A]_0}^{[A]_t} = k \{t\}_0^t$$

$$\left\{ \frac{1}{[A]_t} - \frac{1}{[A]_0} \right\} = kt$$

$$-\left\{ \frac{[A]^{-1}}{-1} \right\}_{[A]_0}^{[A]_t} = k(t - 0)$$

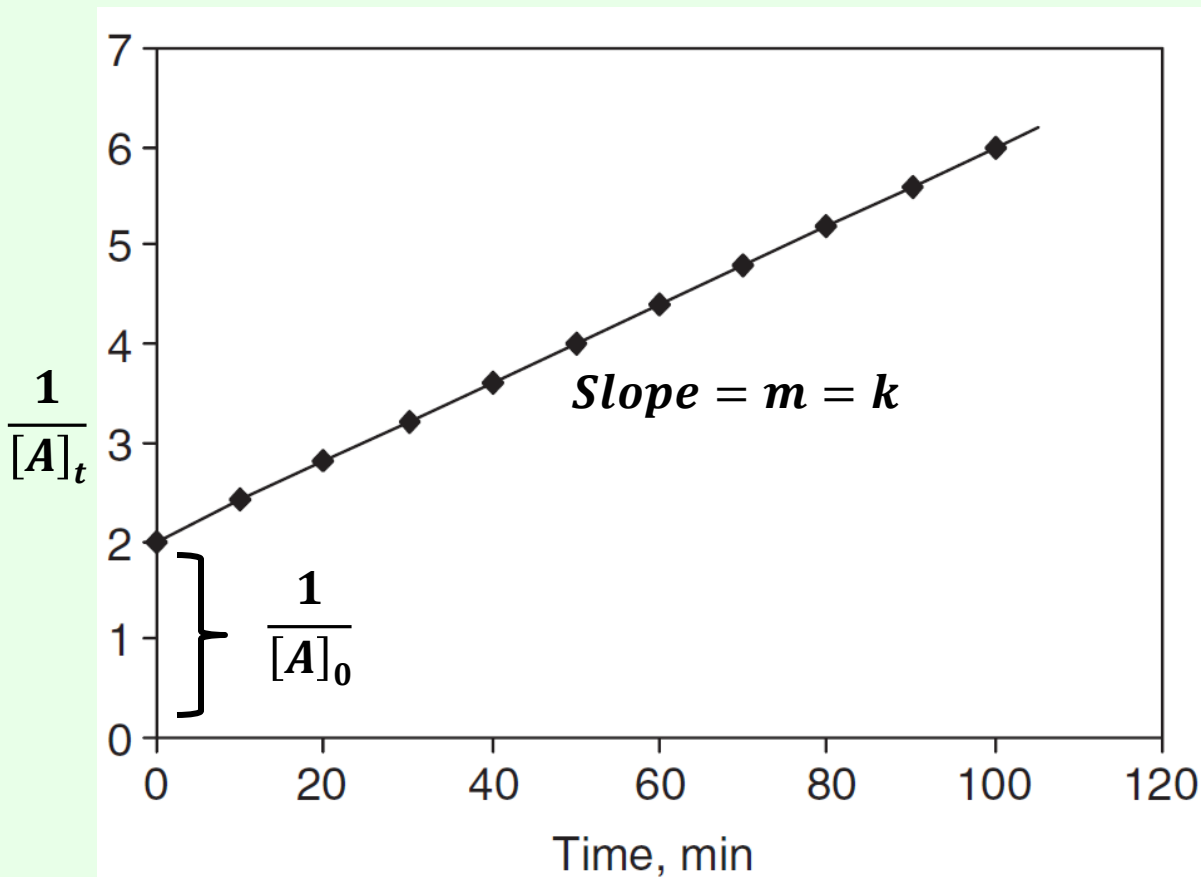
$$k = \frac{1}{t} \left\{ \frac{1}{[A]_t} - \frac{1}{[A]_0} \right\}$$

$$\left\{ \frac{1}{[A]} \right\}_{[A]_0}^{[A]_t} = kt$$

$$\left\{ \frac{1}{[A]_t} - \frac{1}{[A]_0} \right\} = kt$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$y = mx + c$$



## Half life of Second order reaction:

The time at which only 50% of reactant get converted into product.

or

The time at which only half of the reactant get converted into product.

$\therefore$  Put  $[A]_t = \frac{[A]_0}{2}$  in Second order equation &  $t = t_{1/2}$

$$k = \frac{1}{t} \left\{ \frac{1}{[A]_t} - \frac{1}{[A]_0} \right\}$$



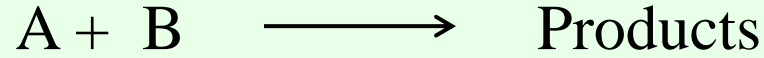
$$k = \frac{1}{t_{1/2}} \left\{ \frac{1}{\frac{[A]_0}{2}} - \frac{1}{[A]_0} \right\}$$

$$t_{1/2} = \frac{1}{k} \left\{ \frac{2}{[A]_0} - \frac{1}{[A]_0} \right\}$$

$$t_{1/2} = \frac{1}{k[A]_0}$$

Half life of Second order reaction inversely proportional to initial concentration of reactant molecule.

**Second order reaction:** (with unequal initial concentration of reactants )

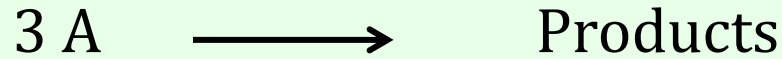


$$\text{Rate} = k[A][B]$$

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

$$k = \frac{1}{t([B]_0 - [A]_0)} \left\{ \ln \frac{[A]_0}{[B]_0} + \ln \frac{[B]_t}{[A]_t} \right\}$$

**Third order reaction:** The reaction in which rate of reaction is depends on third power of the reactant molecule.



$$\text{Rate} = k[A]^3$$

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

$$k = \frac{1}{2t} \left\{ \frac{1}{[A]_t^2} - \frac{1}{[A]_0^2} \right\}$$

## Half life of third order reaction:

The time at which only 50% of reactant get converted into product.

or

The time at which only half of the reactant get converted into product.

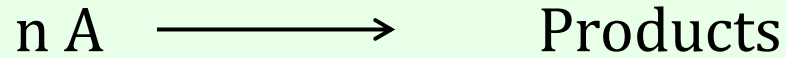
$\therefore$  Put  $[A]_t = \frac{[A]_0}{2}$  in third order equation &  $t = t_{1/2}$

$$k = \frac{1}{2t} \left\{ \frac{1}{[A]_t^2} - \frac{1}{[A]_0^2} \right\}$$

$$t_{1/2} = \frac{1}{2k} \left\{ \frac{1}{([A]_0/2)^2} - \frac{1}{[A]_0^2} \right\}$$

$$t_{1/2} = \frac{3}{2k[A]_0^2}$$

## Nth Order reaction:



$$\text{Rate} = k[A]^3$$

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

$$k = \frac{1}{t(n-1)} \left\{ \frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$$

## Half life of nth order reaction:

Put  $[A]_t = \frac{[A]_0}{2}$  in third order equation &  $t = t_{1/2}$

$$k = \frac{1}{t(n-1)} \left\{ \frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$$

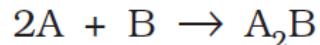
$$t_{1/2} = \frac{1}{k(n-1)} \left\{ \frac{1}{\left(\frac{[A]_0}{2}\right)^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$$

$$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$$

n	Order	Equation	Unit of rate Constant	Half life
n	n <sup>th</sup>	$k = \frac{1}{t(n-1)} \left\{ \frac{1}{[A]_t^{n-1}} - \frac{1}{[A]_0^{n-1}} \right\}$	$\text{mol}^{1-n} \text{lit.}^{n-1} \text{sec}^{-1}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$
0	0 <sup>th</sup>	Put value of $n = 0$ in nth order eq <sup>n</sup>		
2	2nd	Put value of $n = 2$ in nth order eq <sup>n</sup>		
3	3rd	Put value of $n = 3$ in nth order eq <sup>n</sup>		
1	1st	$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]_t}$		$t_{1/2} = \frac{0.693}{k}$

# Problems

**4.2** For the reaction:



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  $0.06 \text{ mol L}^{-1}$ .

**4.3** The decomposition of  $\text{NH}_3$  on platinum surface is zero order reaction. What are the rates of production of  $\text{N}_2$  and  $\text{H}_2$  if  $k = 2.5 \times 10^{-4} \text{ mol}^{-1} \text{ L s}^{-1}$ ?

**4.4** The decomposition of dimethyl ether leads to the formation of  $\text{CH}_4$ ,  $\text{H}_2$  and  $\text{CO}$  and the reaction rate is given by

$$\text{Rate} = k [\text{CH}_3\text{OCH}_3]^{3/2}$$

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.,

$$\text{Rate} = k p_{\text{CH}_3\text{OCH}_3}^{3/2}$$

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



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

**4.8** In a pseudo first order hydrolysis of ester in water, the following results were obtained:

t/s	0	30	60	90
[Ester]/mol L <sup>-1</sup>	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.
- 4.9** A reaction is first order in A and second order in B.
- (i) Write the differential rate equation.
- (ii) How is the rate affected on increasing the concentration of B three times?
- (iii) How is the rate affected when the concentrations of both A and B are doubled?

**4.13** Calculate the half-life of a first order reaction from their rate constants given below:

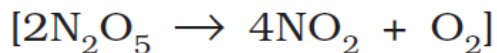
(i)  $200 \text{ s}^{-1}$

(ii)  $2 \text{ min}^{-1}$

(iii)  $4 \text{ years}^{-1}$

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

**4.15** The experimental data for decomposition of  $\text{N}_2\text{O}_5$



in gas phase at 318K are given below:

$t/\text{s}$	0	400	800	1200	1600	2000	2400	2800	3200
$10^2 \times [\text{N}_2\text{O}_5]/\text{mol L}^{-1}$	1.63	1.36	1.14	0.93	0.78	0.64	0.53	0.43	0.35

(i) Plot  $[\text{N}_2\text{O}_5]$  against  $t$ .

(ii) Find the half-life period for the reaction.

(iii) Draw a graph between  $\log[\text{N}_2\text{O}_5]$  and  $t$ .

(iv) What is the rate law ?

(v) Calculate the rate constant.

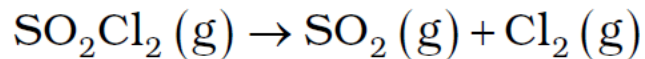
(vi) Calculate the half-life period from  $k$  and compare it with (ii).

- 4.16** The rate constant for a first order reaction is  $60 \text{ s}^{-1}$ . How much time will it take to reduce the initial concentration of the reactant to its  $1/16^{\text{th}}$  value?
- 4.17** During nuclear explosion, one of the products is  $^{90}\text{Sr}$  with half-life of 28.1 years. If  $1\mu\text{g}$  of  $^{90}\text{Sr}$  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.
- 4.18** For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.
- 4.19** A first order reaction takes 40 min for 30% decomposition. Calculate  $t_{1/2}$ .
- 4.20** For the decomposition of azoisopropane to hexane and nitrogen at 543 K, the following data are obtained.

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

Calculate the rate constant.

**4.21** The following data were obtained during the first order thermal decomposition of  $\text{SO}_2\text{Cl}_2$  at a constant volume.



Experiment	Time/ $\text{s}^{-1}$	Total pressure/atm
1	0	0.5
2	100	0.6

Calculate the rate of the reaction when total pressure is 0.65 atm.

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

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

	A	B	C	D	E	F	G
1	Attendance bot: dev(Pavan:p2pdops@gmail.com) on 2020-08-25 : 13:28 :						
2							
3	Members :28						
4							
5	vikram hinge						
6	Abhishek Bhor						
7	Aishwarya Dongare						
8	ANIKET JADHAV						
9	Anisha Argade						
10	Damini Talpe						
11	Harshada Thorat						
12	Indrajeet Saswade						
13	Jostna Pokharkar						
14	kajal dhumal						
15	Pranjal Thosar						
16	Pratiksha Pokharkar						
17	Pujan Bhor						
18	Sagar Chinchpure						
19	sejal Pingale						
20	Sujit Awate						
21	Tanaya Bangar						
22	Vaishanvi Waykar						
23	Vaishnavi Ghodekar						
24	vidya jadhav						
25	Pradnya Karale						
26	Pradnya Litke						
27	Pranjal Thorat						
28	Nikita Shinde						
29	piyush thorat						
30	Pradnya Bhor						
31	Kaushal Thorat						
32	Manasi Hinge						