



Svante August Arrhenius (1859 – 1927)

Svante August Arrhenius was a Swedish scientist. Arrhenius was one of the founders of the science of physical chemistry. He focused his attention on the conductivities of electrolytes. He proposed that crystalline salts dissociate into paired charged ions when dissolved in water, for which he received the Nobel Prize for Chemistry in 1903. He also proposed definitions for acids and bases. He formulated the concept of activation energy.



O Learning Objectives

After studying this unit, the students will be able to

- * define the rate and order of a reaction,
- derive the integrated rate equations for zero and first order reactions,
- describe the half life period,
- describe the collision theory,
- discuss the temperature dependence of the rate of a reaction, and
- explain various factors which affect the rate of a reaction.

INTRODUCTION

We have already learnt in XI standard that the feasibility of a chemical reaction under a given set of conditions can be predicted, using the principles of thermodynamics. However, thermodynamics does not provide an answer to a very important question of how fast a chemical reaction takes place. We know from our practical experience that all chemical reactions take some time for completion. Reaction speeds ranging from extremely fast (in femto seconds) to extremely slow (in years). For example, when the reactants BaCl, solution and dilute H₂SO₄ are just mixed, a white precipitate of BaSO₄ is immediately formed; on the other hand reactions such as rusting of Iron take many years to complete. The answers to the questions such as (i) how fast a chemical change can occur and (ii) What happens in a chemical reaction during the period between the initial stage and final stage are provided by the chemical kinetics. The word kinetics is derived from the Greek word "kinesis" meaning movement.

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

The study of chemical kinetics not only help us to determine the rate of a chemical reaction, but also useful in optimizing the process conditions of industrial manufacturing processes, organic and inorganic synthesis etc.

In this unit, we discuss the rate of a chemical reaction and the factors affecting it. We also discuss the theories of the reaction rate and temperature dependence of a chemical reaction.

7.1 Rate of a chemical reaction:

A rate is a change in a particular variable per unit time. You have already learnt in physics that change in the displacement of a particle per unit time gives its velocity. Similarly in a chemical reaction, the change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.

Let us consider a simple general reaction

$$A \longrightarrow B$$

The concentration of the reactant ([A]) can be measured at different time intervals. Let the concentration of A at two different times t_2 and t_2 , $(t_2>t_1)$ be $[A_1]$ and $[A_2]$ respectively. The rate of the reaction can be expressed as

i.e., Rate =
$$\frac{-([A_2] - [A_1])}{(t_2 - t_1)} = -\left(\frac{\Delta[A]}{\Delta t}\right)$$
 ...(7.1)

During the reaction, the concentration of the reactant decreases i.e. $[A_2] < [A_1]$ and hence the change in concentration $[A_2] - [A_1]$ gives a negative value. By convention the reaction rate is a positive one and hence a negative sign is introduced in the rate expression (equation 7.1)

If the reaction is followed by measuring

the product concentration, the rate is given

by $\left(\frac{\Delta[B]}{\Delta t}\right)$ since $[B_2] > [B_1]$, no minus sign is required here.



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Fig 7.1 change in concentration of A and B for the reaction $A \longrightarrow B$

Unit of rate of a reaction:

unit of rate = $\frac{\text{unit of concentration}}{\text{unit of time}}$

Usually, concentration is expressed in number of moles per litre and time is expressed in seconds and therefore the unit of the rate of a reaction is mol L⁻¹s⁻¹. Depending upon the nature of the reaction, minute, hour, year etc can also be used.

For a gas phase reaction, the concentration of the gaseous species is usually expressed in terms of their partial pressures and in such cases the unit of reaction rate is atm s⁻¹.

7.1.1 Stoichiometry and rate of a reaction:

In a reaction $A \longrightarrow B$, the stoichiometry of both reactant and product are same, and hence the rate of disappearance of reactant (A) and the rate of appearance of product (B) are same.

Now, let us consider a different reaction

$$A \longrightarrow 2B$$

In this case, for every mole of A, that disappears two moles of B appear, i.e., the rate of formation of B is twice as fast as the rate of disappearance of A. Therefore, the rate of the reaction can be expressed as below

Rate =
$$\frac{+d[B]}{dt} = 2\left(\frac{-d[A]}{dt}\right)$$

In other words,

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

For a general reaction, the rate of the reaction is equal to the rate of consumption of a reactant (or formation of a product) divided by its coefficient in the balanced equation

$$xA + yB \longrightarrow lC + mD$$

Rate = $\frac{-1}{x} \frac{d[A]}{dt} = \frac{-1}{y} \frac{d[B]}{dt} = \frac{1}{l} \frac{d[C]}{dt} = \frac{1}{m} \frac{d[D]}{dt}$

7.1.2 Average and instantaneous rate:

Let us understand the average rate and instantaneous rate by considering the isomerisation of cyclopropane.



The kinetics of the above reaction is followed by measuring the concentration of cyclopropane at regular intervals and the observations are shown below. (Table 7.1)

Table 7.1 Concentration of cyclopropane at various times during its isomerisation at 780K

Time (min)	[cyclopropane] $(mol L^{-1})$
0	2.00
5	1.67
10	1.40
15	1.17
20	0.98
25	0.82
30	0.69

Rate of the reaction = $\frac{-\Delta [cyclopropane]}{\Delta t}$

The rate over the entire 30 min = $\frac{-(0.69-2) \text{ molL}^{-1}}{(30-0) \text{ min}}$

$$= \frac{1.31}{30} = 4.36 \times 10^{-2} \text{ molL}^{-1} \text{min}^{-1}$$

It means that during the first 30 minutes of the reaction, the concentration of the reactant (cyclo propane) decreases as an average of 4.36×10^{-2} mol L⁻¹each minute.

Let us calculate the average rate for an initial and later stage over a short period.

$$(\text{Rate})_{\text{initial}} = \frac{-(1.4-2)}{(10-0)}$$
$$= \frac{0.6}{10} = 6 \text{ x } 10^{-2} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$$
$$(\text{Rate})_{\text{later}} = \frac{-(0.69 - 0.98)}{(30-20)}$$
$$= \frac{0.29}{10} = 2.9 \text{ x } 10^{-2} \text{ mol } \text{L}^{-1} \text{min}^{-1}$$

From the above calculations, we come to know that the rate decreases with time as the reaction proceeds and the average rate cannot be used to predict the rate of the reaction at any instant. The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate. The shorter the time period, we choose, the closer we approach to the instantaneous rate,

As
$$\Delta t \rightarrow 0$$
;

$$\frac{-\Delta [cyclopropane]}{\Delta t} = \frac{-d [cyclopropane]}{dt}$$

A plot of [cyclopropane] Vs (time) gives a curve as shown in the figure 7.2. Instantaneous rate at a particular instant 't' $\frac{-d [cyclopropane]}{dt}$ is obtained by calculating the slope of a tangent drawn to the curve at that instant.

In general, the instantaneous reaction rate at a moment of mixing the reactants (t=0) is calculated from the slope of the tangent drawn to the curve. The rate calculated by this method is called initial rate of a reaction.



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Let us calculate the instantaneous rate of isomerisation cyclopropane at different concentrations: 2 M, 1M and 0.5 M from the graph shown in fig 7.2, the results obtained are tabulated below.

[cyclopropane] mol L ⁻¹	Rate mol L ⁻¹ min ⁻¹	
2	6.92 × 10 ⁻²	
1	3.46 × 10 -2	
0.5	1.73 × 10 -2	

Table 7.2 Rate of isomerisation

7.3 Rate law and rate constant:

We have just learnt that, the rate of the reaction depends upon the concentration of the reactant. Now let us understand how the reaction rate is related to concentration by considering the following general reaction.

 $xA + yB \longrightarrow products$

The rate law for the above reaction is generally expressed as

Rate = $k [A]^m [B]^n$

Where k is proportionality constant called the rate constant. The values of m and n represent the reaction order with respect to A and B respectively. The overall order of the reaction is given by (m+n). The values of the exponents (m and n) in the rate law must be determined by experiment. They cannot be deduced from the Stoichiometry of the reaction. For example, consider the isomerisation of cyclopropane, that we discussed earlier.

The results shown in table 7.2 indicate that if the concentration of cyclopropane is reduced to half, the rate also reduced to half. It means that the rate depends upon [cyclopropane] raised to the first power

$$\Rightarrow \frac{\text{Rate}}{[\text{cyclopropane}]} = k$$

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Rate mol L ⁻¹ min ⁻¹	[cyclopropane] mol L ¹	$k = \frac{Rate}{[cyclopropane]}$
6.92 × 10 ⁻²	2	3.46×10^{-2}
3.46 × 10 -2	1	3.46 × 10 -2
1.73 × 10 -2	0.5	3.46×10^{-2}

Table 7.3 Rate constant for isomerisation

Let us consider an another example, the oxidation of nitric oxide (NO)

 $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

Series of experiments are conducted by keeping the concentration of one of the reactants constant and the changing the concentration of the others.

Experiment	[NO] X 10 ⁻² (mol L ⁻¹)	[O ₂] X 10 ⁻² (mol L ⁻¹)	Initial rate x 10 ⁻² (mol L ⁻¹ min ⁻¹)
1	1.3	1.1	19.26
2	1.3	2.2	38.40
3	2.6	1.1	76.80

Rate = $k [NO]^{m} [O_{2}]^{n}$ For experiment 1, the rate law is $\operatorname{Rate}_{1} = k [\operatorname{NO}]^{m} [\operatorname{O}_{2}]^{n}$ 19.26 X10⁻² = k $[1.3]^{m}[1.1]^{n}$...(1)

Similarly for experiment 2

 $\operatorname{Rate}_{2} = \operatorname{k} [\operatorname{NO}]^{m} [\operatorname{O}_{2}]^{n}$

 $38.40 \text{ X10}^{-2} = \text{k} [1.3]^{\text{m}} [2.2]^{\text{n}}$...(2)

For experiment 3

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Rate₃ = k [NO]^m[O₂]ⁿ
76.8 × 10⁻² = k [2.6]^m[1.1]ⁿ ...(3)

$$\frac{(2)}{(1)} \Rightarrow \frac{38.40 \times 10^{-2}}{19.26 \times 10^{-2}} = \frac{k [1.3]^{m} [2.2]^{n}}{k [1.3]^{m} [1.1]^{n}}$$

$$2 = \left(\frac{2.2}{1.1}\right)^{n}$$
2=2ⁿ i.e., n=1

Therefore the reaction is first order with respect to O₂

$$\frac{(3)}{(1)} \Rightarrow \frac{76.8 \times 10^{-2}}{19.26 \times 10^{-2}} = \frac{k [2.6]^{m} [1.1]^{n}}{k [1.3]^{m} [1.1]^{n}}$$
$$4 = \left(\frac{2.6}{1.3}\right)^{m}$$
$$4 = 2^{m} \text{ i.e., m=2}$$

Therefore the reaction is second order with respect to NO

The rate law is $Rate_1 = k [NO]^2 [O_2]^1$ The overall order of the reaction = (2 + 1) = 3

Differences between rate and rate constant of a reaction:

s.no	Rate of a reaction	Rate constant of a reaction
1	It represents the speed at which the reactants are converted into products at any instant.	It is a proportionality constant

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s.no	Rate of a reaction	Rate constant of a reaction
2	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 is unity
3	It depends on the initial concentration of reactants.	It does not depend on the initial concentration of reactants.

7.4 Molecularity:

Kinetic studies involve not only measurement of a rate of reaction but also proposal of a reasonable reaction mechanism. Each and every single step in a reaction mechanism is called an elementary 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. Let us recall the hydrolysis of t-butyl bromide studied in XI standard. Since the rate determining elementary step involves only t-butyl bromide, the reaction is called a Unimolecular Nucleophilic substitution (S_N^{-1}) reaction.

Let us understand the elementary reactions by considering another reaction, the decomposition of hydrogen peroxide catalysed by I^- .

 $2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$

It is experimentally found that the reaction is first order with respect to both

 H_2O_2 and I⁻, which indicates that I⁻ is also involved in the reaction. The mechanism involves the following steps.

Step:1

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 $\mathrm{H}_{2}\mathrm{O}_{2}(\mathrm{aq}) + \mathrm{I}^{-}(\mathrm{aq}) \longrightarrow \mathrm{H}_{2}\mathrm{O}(l) + \mathrm{OI}^{-}(\mathrm{aq})$

Step:2

 $\mathrm{H_2O_2(aq)} + \mathrm{OI}^{-}(\mathrm{aq}) \rightarrow \mathrm{H_2O}(l) + \mathrm{I}^{-}(\mathrm{aq}) + \mathrm{O_2(g)}$

Overall reaction is

$$2H_2O_2(aq) \longrightarrow 2H_2O(l) + O_2(g)$$

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

Differences between order and molecularity:

s.no	Order of a reaction	Molecularity of a reaction
1	It is the sum of the powers of concentration terms involved in the experimentally determined rate law.	It is the total number of reactant species that are involved in an elementary step.
2	It can be zero (or) fractional (or) integer	It is always a whole number, cannot be zero or a fractional number.
3	It is assigned for a overall reaction.	It is assigned for each elementary step of mechanism.

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Example 1

Consider the oxidation of nitric oxide to form NO₂

 $2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$

(a). Express the rate of the reaction in terms of changes in the concentration of $NO_{,}O_{2}$ and NO_{2} .

(b). At a particular instant, when $[O_2]$ is decreasing at 0.2 mol L⁻¹s⁻¹ at what rate is $[NO_2]$ increasing at that instant?

Solution:

a) Rate =
$$\frac{-1}{2} \frac{d[NO]}{dt} = \frac{-d[O_2]}{dt} = \frac{1}{2} \frac{d[NO_2]}{dt}$$

b) $\frac{-d[O_2]}{dt} = \frac{1}{2} \frac{d[NO_2]}{dt}$
 $\frac{d[NO_2]}{dt} = 2x \left(\frac{-d[O_2]}{dt}\right) = 2 \times 0.2 \text{ mol } L^4 s^4$
= 0.4 mol $L^4 s^4$

Evaluate yourself 1

1). Write the rate expression for the following reactions, assuming them as elementary reactions.

i)
$$3A + 5B_2 \longrightarrow 4CD$$

ii)
$$X_2 + Y_2 \longrightarrow 2XY$$

2). Consider the decomposition of $N_2O_5(g)$ to form $NO_2(g)$ and $O_2(g)$. At a particular instant N_2O_5 disappears at a rate of 2.5×10^{-2} mol dm⁻³s⁻¹. At what rates are NO_2 and O_2 formed? What is the rate of the reaction?

Example 2

1. What is the order with respect to each of the reactant and overall order of the following reactions?

(a).
$$5Br^{-}(aq) + BrO_{3}^{-}(aq) + 6H^{+}(aq)$$

 \longrightarrow 3Br₂(l) + 3H₂O(l)

The experimental rate law is

Rate = k $[Br^{-}][BrO_{3}^{-}][H^{+}]^{2}$

(b). $CH_3CHO(g) \xrightarrow{\Delta} CH_4(g) + CO(g)$ the experimental rate law is Rate = k $[CH_3CHO]^{\frac{3}{2}}$

Solution:

- a) First order with respect to Br^- , first order with respect to BrO_3^- and second order with respect to H^+ . Hence the overall order of the reaction is equal to 1 + 1 + 2 = 4
- b) Order of the reaction with respect to acetaldehyde is $\frac{3}{2}$ and overall order is also $\frac{3}{2}$

Example 3

2. The rate of the reaction $x + 2y \rightarrow \text{product}$ is $4 \times 10^{-3} \text{ mol } \text{L}^{-1}\text{s}^{-1}$, if [x]=[y]=0.2 M and rate constant at 400K is $2 \times 10^{-2} \text{s}^{-1}$, What is the overall order of the reaction.

Solution :

Rate = $k [x]^n [y]^m$

4 x 10⁻³ mol L⁻¹s⁻¹ = 2 x 10⁻²s⁻¹ (0.2mol L⁻¹)ⁿ (0.2mol L⁻¹)^m

$$\frac{4 \times 10^{-3} \operatorname{mol} L^{-1} s^{-1}}{2 \times 10^{-2} s^{-1}} = (0.2)^{n+m} \left(\operatorname{mol} L^{-1} \right)^{n+m}$$
$$0.2 \left(\operatorname{mol} L^{-1} \right) = (0.2)^{n+m} \left(\operatorname{mol} L^{-1} \right)^{n+m}$$

Comparing the powers on both sides

The overall order of the reaction n + m = 1

Evaluate yourself 2

 For a reaction, X + Y → product; quadrupling [x], increases the rate by a factor of 8. Quadrupling both [x] and [y],

increases the rate by a factor of 16. Find the order of the reaction with respect to x and y. what is the overall order of the reaction?

2). Find the individual and overall order of the following reaction using the given data.

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

ent	Initial concentra	tion	Initial rate
Experiment	NO	Cl ₂	NOCl mol L ⁻¹ s ⁻¹
1	0.1	0.1	7.8 x10 ⁻⁵
2	0.2	0.1	3.12 x10 ⁻⁴
3	0.2	0.3	9.36 x10 ⁻⁴

7.5 The integrated rate equation:

We have just learnt that the rate of change of concentration of the reactant is directly proportional to that of concentration of the reactant. For a general reaction,

 $A \longrightarrow \text{product}$ The rate law is

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

Where k is the rate constant, and x is the order of the reaction. The above equation is a differential equation, $\frac{-d[A]}{dt}$, so it gives the rate at any instant. However, using the above expression, we cannot answer questions such as how long will it take for a specific concentration of A to be used up in the reaction? What will be the concentration of

reactant after a time 't'?. To answer such questions, we need the integrated form of the above rate law which contains time as a variable.

7.5.1 Integrated rate law for a first order reaction

A reaction whose rate depends on the reactant concentration raised to the first power is called a first order reaction. Let us consider the following first order reaction,

 $A \longrightarrow product$

Rate law can be expressed as

Rate = $k [A]^{l}$

Where, k is the first order rate constant.

$$\frac{-d[A]}{dt} = k [A]^{1}$$

$$\Rightarrow \frac{-d[A]}{[A]} = k dt$$
...(1)

Integrate the above equation between the limits of time t = 0 and time equal to t, while the concentration varies from the initial concentration [A₀] to [A] at the later time.

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

$$\left(-\ln[A]\right)_{[A_0]}^{[A]} = k(t)_0^t$$

$$-\ln[A] - \left(-\ln[A_0]\right) = k (t-0)$$

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

$$\ln\left(\frac{[A_0]}{[A]}\right) = kt$$
...(2)

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

$$2.303 \log\left(\frac{[A_0]}{[A]}\right) = kt$$

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Fig: 7.3 A plot of $\ln[A]$ Vs t for a first order reaction, A \longrightarrow product with initial concentration of [A] = 1.00 M and $k = 2.5 \times 10^{-2} \text{min}^{-1}$.

$$k = \frac{2.303}{t} \log\left(\frac{[A_0]}{[A]}\right) -\dots (3)$$

Equation (2) can be written in the form y = mx + c as below

$$ln[A_0] - ln[A] = kt$$
$$ln[A] = ln[A_0] - kt$$
$$\Rightarrow y = c + mx$$

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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. From this, the rate constant is calculated.

Examples for the first order reaction

(i) Decomposition of dinitrogen pentoxide

$$N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$$

- (ii) Decomposition of sulphurylchloride; $SO_2Cl_2(l) \longrightarrow SO_2(g) + Cl_2(g)$
- (iii) Decomposition of the H_2O_2 in aqueous solution; $H_2O_2(aq) \longrightarrow H_2O(l) + \frac{1}{2}O_2(g)$
- (iv) Isomerisation of cyclopropane to propene.

Pseudo first order reaction:

Kinetic study of a higher order reaction is difficult to follow, for example, in a study of a second order reaction involving two different reactants; the simultaneous measurement of change in the concentration of both the reactants is very difficult. To overcome such difficulties, A 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. Let us consider the acid hydrolysis of an ester,

 $(\mathbf{0})$

$$CH_3COOCH_3$$
 (aq) + $H_2O(l) \xrightarrow{H} CH_3COOH$ (aq) + CH_3OH (aq)

Rate = $k [CH_3COOCH_3] [H_2O]$

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.

Now, we can define $k [H_2O] = k'$; Therefore the above rate equation becomes

Rate =
$$k'$$
 [CH₃COOCH₃]

Thus it follows first order kinetics.

7.5.2 Integrated rate law for a zero order reaction:

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. Such reactions are rare. Let us consider the following hypothetical zero order reaction.

$$A \longrightarrow product$$

The rate law can be written as,

Rate = k [A]⁰
$$\frac{-d[A]}{dt} = k (1) \qquad (:: [A]0 = 1)$$

 $\Rightarrow -d[A] = k dt$

Integrate the above equation between the limits of $[A_0]$ at zero time and [A] at some later time 't',

$$-\int_{[A_0]}^{[A]} d[A] = k \int_0^t dt$$
$$-([A])_{[A_0]}^{[A]} = k (t)_0^t$$

 $[A_0] - [A] = kt$

$$k = \frac{[A_0] - [A]}{4}$$

Equation (2) is in the form of a straight line y = mx + c

Ie., $[A] = -kt + [A_0]$

$$\Rightarrow$$
 y = c + mx

A plot of [A] Vs time gives a straight line with a slope of -k and y - intercept of $[A_0]$.

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Fig 7.4 : A plot of [A] Vs time for a zero order reaction A \longrightarrow product with initial concentration of [A] = 0.5M and k = $1.5 \times 10^{-2} \text{mol}^{-1} \text{L}^{-1} \text{min}^{-1}$

Examples for a zero order reaction:

- 1. Photochemical reaction between H₂ and Cl₂ H₂(g)+Cl₂(g) $\xrightarrow{h\nu}$ 2HCl(g)
- 2. Decomposition of N₂O on hot platinum surface

$$N_2O(g) \Longrightarrow N_2(g) + \frac{1}{2}O_2(g)$$

3. Iodination of acetone in acid medium is zero order with respect to iodine.

 $\mathrm{CH_3COCH_3} \ + \ \mathrm{I_2} \xrightarrow{\mathrm{H^+}} \mathrm{ICH_2COCH_3} \ + \ \mathrm{HI}$

 $Rate = k [CH_3COCH_3] [H^+]$

General rate equation for a nth order reaction involving one reactant [A].

 $A \longrightarrow \text{product}$ Rate law $\frac{-d[A]}{dt} = k[A]^n$ Consider the case in which $n \neq 1$, integration of above equation between $[A_0]$ and [A] at time t = 0 and t = trespectively gives $\frac{1}{[A]^{n-1}} - \frac{1}{[A_0]^{n-1}} = (n-1)kt$

7.6 Half life period of a reaction:

The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant i.e., it does not depend on the initial concentration.

The rate constant for a first order reaction is given by

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

at $t = t_{\frac{1}{2}}$; $[A] = \frac{[A_0]}{2}$
$$k = \frac{2.303}{t_{\frac{1}{2}}} \log \frac{[A_0]}{[A_0]_2}$$

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

$$k = \frac{2.303 \times 0.3010}{t_{\frac{1}{2}}} = \frac{0.6932}{t_{\frac{1}{2}}}$$

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

Let us calculate the half life period for a zero order reaction.

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

at $t = t_{\frac{1}{2}}$; $[A] = \frac{[A_0]}{2}$
 $k = \frac{[A_0] - \frac{[A_0]}{2}}{t_{\frac{1}{2}}}$
 $k = \frac{[A_0]}{2t_{\frac{1}{2}}}$
 $t_{\frac{1}{2}} = \frac{[A_0]}{2t}$

Hence, in contrast to the half life of a first order reaction, the half life of a zero order reaction is directly proportional to the initial concentration of the reactant.

More to know

Half life for an n^{th} order reaction involving reactant A and $n \neq 1$

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

Example 4

(i) A first order reaction takes 8 hours for 90% completion. Calculate the time required for 80% completion. (log 5 = 0.6989 ; log10 = 1)

Solution:

For a first order reaction,

$$k = \frac{2.303}{t} \log\left(\frac{[A_0]}{[A]}\right) \qquad \dots (1)$$

Let $[A_0] = 100M$

When

 $t = t_{90\%}$; [A]=10M (given that $t_{90\%}$ =8hours) $t = t_{80\%}$; [A]=20M

$$k = \frac{2.303}{t_{80\%}} \log\left(\frac{100}{20}\right)$$
$$t_{80\%} = \frac{2.303}{k} \log(5) - (2)$$

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Find the value of k using the given data

$$k = \frac{2.303}{t_{90\%}} \log\left(\frac{100}{10}\right)$$
$$k = \frac{2.303}{8 \text{ hours}} \log 10$$
$$k = \frac{2.303}{8 \text{ hours}} (1)$$

Substitute the value of k in equation (2)

$$t_{80\%} = \frac{2.303}{2.303/8 \text{ hours}} \log(5)$$
$$t_{80\%} = 8 \text{hours } x \ 0.6989$$
$$t_{80\%} = 5.59 \text{hours}$$

Example 5

(ii) The half life of a first order reaction $x \longrightarrow products$ is $6.932 \times 10^4 s$ at 500K . W h a t percentage of x would be decomposed on heating at 500K for 100 min. ($e^{0.06} = 1.06$)

Solution:

Given $t_{\frac{1}{2}} = 0.6932 \times 10^4 s$ To solve: when t=100 min,

$$\frac{[A_0]-[A]}{[A_0]} \ge 100 = ?$$

We know that
For a first order reaction, $t_{\frac{1}{2}} = \frac{0.6932}{k}$
 $k = \frac{0.6932}{6.932 \ge 10^4}$
 $k = 10^{-5} \text{ s}^{-1}$

 $k = \left(\frac{1}{t}\right) \ln \left(\frac{[A_0]}{[A]}\right)$ $10^{-5} s^{-1} \ge 100 \ge 60 = \ln \left(\frac{[A_0]}{[A]}\right)$ $0.06 = \ln \left(\frac{[A_0]}{[A]}\right)$ $\frac{[A_0]}{[A]} = e^{0.06}$ $\frac{[A_0]}{[A]} = 1.06$ $\therefore \frac{[A_0] \cdot [A]}{[A_0]} \ge 100 \%$ $= \left(1 \cdot \frac{[A]}{[A_0]}\right) \ge 100 \%$ $= \left(1 \cdot \frac{1}{1.06}\right) \ge 100 \%$ = 5.6 %Example 6

Show that in case of first order reaction, the time required for 99.9% completion is nearly ten times the time required for half completion of the reaction.

Let

$$A_{0} = 100;$$

when t = t_{99.9%}; [A] = (100-99.9) = 0.1
$$k = \frac{2.303}{t} \log\left(\frac{[A_{0}]}{[A]}\right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log\left(\frac{100}{0.1}\right)$$

$$t_{99.9\%} = \frac{2.303}{k} \log 1000$$

$$t_{99.9\%} = \frac{2.303}{k} (3)$$

$$t_{99.9\%} = \frac{6.909}{k}$$
$$t_{99.9\%} \simeq 10 \text{ x} \frac{0.69}{k}$$
$$t_{99.9\%} \simeq 10 \text{ t}_{\frac{1}{2}}$$

Evaluate yourself:

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- (1) In a first order reaction $A \longrightarrow products$ 60% of the given sample of A decomposes in 40 min. what is the half life of the reaction?
- (2) The rate constant for a first order reaction is $2.3 \times 10^4 s^{-1}$ If the initial concentration of the reactant is 0.01M. What concentration will remain after 1 hour?
- (3) Hydrolysis of an ester in an aqueous solution was studied by titrating the liberated carboxylic acid against sodium hydroxide solution. The concentrations of the ester at different time intervals are given below.

Time (min)	0	30	60	90
Ester concentration mol L^{-1}	0.85	0.80	0.754	0.71

Show that, the reaction follows first order kinetics.

7.7 Collision theory:

Collision Theory was proposed independently by Max Trautz in 1916 and William Lewis in 1918. This theory is based on the kinetic theory of gases. According to this theory, chemical reactions occur as a result of collisions between the reacting molecules. Let us understand this theory by considering the following reaction.

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

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Fig 7.5 progress of the reaction

If we consider that, 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 \propto 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 $\propto [A_2][B_2]$ Collision rate = Z [A₂][B₂]

Where, Z is a constant.

The collision rate in gases can be calculated from kinetic theory of gases. For a gas at room temperature (298K) and 1 atm pressure, each molecule undergoes approximately 10^9 collisions per second, i.e., 1 collision in 10^{-9} second. 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. 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) is given by the following expression

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

To understand the magnitude of collision factor (f), Let us calculate the collision factor (f) for a reaction having activation energy of 100 kJ mol^{-1} at 300K.

$$f = e^{-\left(\frac{100 \times 10^3 \text{ J mol}^{-1}}{8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 K}\right)$$
$$f = e^{-40} \approx 4 \times 10^{-18}$$

Thus, out of 10¹⁸ collisions only four collisions are sufficiently energetic to convert reactants to products. This fraction of collisions is further reduced due to

Proper allignment В Effective collission В Products В Reactants В improper allignment А A В В В Reactants ineffective collision Reactants

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 figure 7.6 illustrates the importance of proper alignment of molecules which leads to reaction.

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

 \Rightarrow Rate = p x f x collision rate

i.e., Rate =
$$p \ge e^{\frac{-E_a}{RT}} \ge Z [A_2][B_2] ...(1)$$

As per the rate law,

Rate = k $[A_2] [B_2]$...(2)

Where k is the rate constant

On comparing equation (1) and (2), the rate constant k is '

7.8 Arrhenius equation – The effect of temperature on reaction rate

Generally, the rate of a reaction increase with increasing temperature. However, there are very few exceptions. The magnitude of this increase in rate is different for different reactions. As a rough rule, for many reactions near room temperature, reaction rate tends to double when the temperature is increased by 10° C.

Activity

Let us understand the effect of temperature on reaction rate by doing this activity.

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- i. Take two test tubes, label them as A and B
- ii. Take 5 ml of cold water in A, add a drop of phenolphthalein indicator and then add Magnesium granules.
- iii. Repeat the above with 5 ml of hot water in test tube B.

- iv. Observe the two test tubes.
- v. The observation shows that the solution in test tube B changes to pink colour and there is no such colour change in test tube A. That is, hot water reacts with magnesium according to the following reaction and there is no such reaction in cold water.

$$Mg + 2H_2O \longrightarrow Mg^{2+} + 2OH^- + H_2 \uparrow$$

vi. The resultant solution is basic and it is indicated by phenolphthalein.

A large number of reactions are known which do not take place at room temperature but occur readily at higher temperatures. Example: Reaction between H_2 and O_2 to form H_2O takes place only when an electric spark is passed.

Arrhenius suggested that the rates of most reactions vary with temperature in such a way that the rate constant is directly proportional to $e^{-\left(\frac{E_a}{RT}\right)}$ and he proposed a relation between the rate constant and temperature.

$$k = Ae^{-\left(\frac{E_a}{RT}\right)}$$

Where A the frequency factor,

R the gas constant,

 $(\mathbf{0})$

 \boldsymbol{E}_{a} the activation energy of the reaction and,

T the absolute temperature (in K)

The frequency factor (A) is related to the frequency of collisions (number of collisions per second) between the reactant molecules. The factor A does not vary significantly with temperature and hence it may be taken as a constant.

 E_a is the activation energy of the reaction, which Arrhenius considered as the minimum energy that a molecule must have to posses to react.

Taking logarithm on both side of the equation (1)

$$\ln k = \ln A + \ln e^{-\left(\frac{E_a}{RT}\right)}$$

$$\ln k = \ln A - \left(\frac{E_a}{RT}\right) \qquad (\therefore \ln e = 1)$$

$$\ln k = \ln A - \left(\frac{E_a}{R}\right) \left(\frac{1}{T}\right) \qquad \dots (2)$$

$$y = c + m x$$

The above equation is of the form of a straight line y = mx + c.

A plot of $\ln k \operatorname{Vs} \frac{1}{T}$ gives a straight line with a negative slope $-\frac{E_a}{R}$. If the rate constant for a reaction at two different temperatures is known, we can calculate the activation energy as follows.

At temperature $\mathbf{T}=\mathbf{T}_{\!\!1}$; the rate constant $\mathbf{k}=\mathbf{k}_{\!\!1}$

$$\ln k_1 = \ln A \cdot \left(\frac{E_a}{RT_1}\right) \qquad \dots (3)$$

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....(1)

At temperature
$$T = T_2$$
; the rate constant $k = k_2$

$$\ln k_2 = \ln A \cdot \left(\frac{E_a}{RT_2}\right) \qquad \dots (4)$$

$$label{eq:constraint} \begin{array}{l} (4) -(3) \\ \ln k_2 - \ln k_1 &= -\left(\frac{E_a}{RT_2}\right) + \left(\frac{E_a}{RT_1}\right) \\ \ln \left(\frac{k_2}{k_1}\right) &= \frac{E_a}{R} \left(\frac{1}{T_1} - \frac{1}{T_2}\right) \\ 2.303 \log \left(\frac{k_2}{k_1}\right) &= \frac{E_a}{R} \left(\frac{T_2 - T_1}{T_1 T_2}\right) \\ \log \left(\frac{k_2}{k_1}\right) &= \frac{E_a}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2}\right) \\ \ln k_2 - \ln k_1 &= -\left(\frac{E_a}{RT_2}\right) + \left(\frac{E_a}{RT_1}\right) \end{array}$$

This equation can be used to calculate E_a from rate constants k_1 and k_2 at temperatures T_1 and T_2

Example 7

The rate constant of a reaction at 400 and 200K are 0.04 and 0.02 s⁻¹ respectively. Calculate the value of activation energy.

Solution

According to Arrhenius equation

$$\log\left(\frac{k_2}{k_1}\right) = \frac{E_a}{2.303R} \left(\frac{T_2 - T_1}{T_1 T_2}\right)$$
$$T_2 = 400K \quad ; \quad k_2 = 0.04 \text{ s}^{-1}$$
$$T_1 = 200K \quad ; \quad k_1 = 0.02 \text{ s}^{-1}$$
$$\log\left(\frac{0.04 \text{ s}^{-1}}{0.02 \text{ s}^{-1}}\right) = \frac{E_a}{2.303 \text{ x } 8.314 \text{ JK}^{-1} \text{mol}^{-1}} \left(\frac{400\text{K} - 200\text{K}}{200\text{K} \text{ x } 400\text{K}}\right)$$

$$\log(2) = \frac{E_{a}}{2.303 \text{ x } 8.314 \text{ JK}^{-1} \text{mol}^{-1}} \left(\frac{1}{400 \text{ K}}\right)$$

 $E_a = \log(2) \times 2.303 \times 8.314 \text{ JK}^{-1} \text{mol}^{-1} \times 400 \text{K}$ $E_a = 2305 \text{ J mol}^{-1}$

Example 8

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Rate constant k of a reaction varies with temperature T according to the following Arrhenius equation

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

Where E_a is the activation energy. When a graph is plotted for $\log k Vs \frac{1}{T}$ a straight line with a slope of -4000K is obtained. Calculate the activation energy

Solution

$$\log k = \log A - \frac{E_{a}}{2.303R} \left(\frac{1}{T}\right)$$

$$y = c + mx$$

$$m = -\frac{E_{a}}{2.303R}$$

$$E_{a} = -2.303 \text{ R } m$$

$$E_{a} = -2.303 \text{ x } 8.314 \text{ J K}^{-1} \text{ mol}^{-1} \text{ x } (-4000K)$$

$$E_{a} = 76,589 \text{ J mol}^{-1}$$

$$E_{a} = 76.589 \text{ kJ mol}^{-1}$$

Evaluate yourself

For a first order reaction the rate constant at 500K is 8 X $10^{-4} s^{-1}$. Calculate the frequency factor, if the energy of activation for the reaction is 190 kJ mol⁻¹.

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7.9 Factors affecting the reaction rate:

The rate of a reaction is affected by the following factors.

- 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

7.9.1 Nature and state of the reactant:

We know that a 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.

Let us compare the following two reactions that you carried out in volumetric analysis.

- 1). Redox reaction between ferrous ammonium sulphate (FAS) and KMnO₄
- 2). Redox reaction between oxalic acid and $KMnO_4$

The oxidation of oxalate ion by $KMnO_4$ is relatively slow compared to the reaction between $KMnO_4$ and Fe^{2+} . In fact heating is required for the reaction between $KMnO_4$ and Oxalate ion and is carried out at around $60^{\circ}C$.

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.

Let us consider another example that you carried out in inorganic qualitative analysis of lead salts. If you mix the aqueous solution of colorless potassium iodide with the colorless solution of lead nitrate, precipitation of yellow lead iodide take place instantaneously, whereas if you mix the solid lead nitrate with solid potassium iodide, yellow coloration will appear slowly.

7.9.2 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.

Activity

- 1. Take three conical flasks and label them as A, B, and C.
- 2. using a burette, add 10, 20 and 40 ml of 0.1M sodium thiosulphate solution to the flask A, B and C respectively. And then add 40, 30 and 10 ml of distilled water to the respective flasks so that the volume of solution in each flask is 50ml.

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3. Add 10 ml of 1M HCl to the conical flask A. Start the stop watch when half of the HCl has been added. Shake the contents carefully and place it on the tile with a cross mark as shown in the figure. Observe the conical flask from top and stop the stops watch when the cross mark just becomes invisible. Note the time.

Flask	Volume of $Na_2S_2O_3$	Volume of water	Strength of $Na_2S_2O_3$	Time taken (t)
А	10	40	0.02	
В	20	30	0.04	
С	40	10	0.08	

4. Repeat the experiment with the contents on B and C. Record the observation.

Draw a graph between $\frac{1}{t}$ Vs concentration of sodium thiosulphate. A graph like the following one is obtained.

 $\frac{1}{t}$ is a direct measure of rate of reaction and therefore, the increase in the concentration of reactants i.e Na₂S₂O₃, increases the rate.

7.9.3 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. For example, powdered calcium carbonate reacts much faster with dilute HCl than with the same mass of CaCO₃ as marble

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Activity

A Known mass of marble chips are taken in a flask and a known volume of dilute HCl is added to the content, a stop clock is started when half the volume of HCl is added. The mass is noted at regular intervals until the reaction is complete. Same experiment is repeated with the same mass of powdered marble chips and the observations are recorded.

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Reaction

 $CaCO_3(s) + 2HCl(aq) \longrightarrow CaCl_2(aq) + H_2O(l) + CO_2(g)$

Since, carbon dioxide escapes during reaction, the mass of the flask gets lighter as the reaction proceeds. So, by measuring the flask, we can follow the rate of the reaction. A plot of loss in mass Vs time is drawn and it looks like the one as shown below.

For the powdered marble chips, the reaction is completed in less time. i.e., rate of a reaction increases when the surface area of a solid reactant is increased.

7.9.4 Effect of presence of catalyst:

So far we have learnt, that rate of reaction can be increased to certain extent by increasing the concentration, temperature and surface area of the reactant. However significant changes in the reaction can be brought out by the addition of a substance called 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 at the end of the reaction. In the presence of a catalyst, the energy of activation is lowered and hence, number of greater molecules can cross the energy barrier and change over to products, thereby increasing the rate of the reaction.

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Activity

Take two test tubes and label them as A and B. Add 7 ml of 0.1N oxalic acid solution, 5 ml of 0.1N KMnO₄ solution and 5 ml of 2N dilute H_2SO_4 in both the test tubes. The colour of the solution is pink in both the test tubes.

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Now add few crystals of manganese sulphate to the content in test tube A. the pink colour fades up and disappears. In this case, $MnSO_4$ acts as a catalyst and increases the rate of oxidation of $C_2O_4^{2^-}$ by MnO_4^{-}

Chemical kinetics in pharmaceuticals

Chemical kinetics has many applications in the field of pharmaceuticals. It is used to study the lifetimes and bioavailability of drugs within the body and this branch of study is called **pharmacokinetics** Doctors usually prescribe drugs to be taken at different times of the day. i.e.some drugs are to be taken twice a day, while others

are taken three times a day, or just once a day. Pharmacokinetic studies is used to determine the prescription (dosage and frequency). For example, Paracetamol is a well known anti-pyretic and analgesic that is prescribed in cases of fever and body pain. Pharmacokinetic studies showed that Paracetamol has a half-life of 2.5 hours within the body i.e.the plasma concentration of a drug is halved after 2.5 hrs. After 10 hours (4 half-lives)only 6.25 % of drug remains. Based on such studies the dosage and frequency will be decided. In case of paracetamol, it is usually prescribed to take once in 6 hours depending upon the conditions.

Summary

- Chemical kinetics is the study of the rate and the mechanism of chemical reactions, proceeding under given conditions of temperature, pressure, concentration etc.
- The change in the concentration of the species involved in a chemical reaction per unit time gives the rate of a reaction.
- The rate of the reaction, at a particular instant during the reaction is called the instantaneous rate. The shorter the time period, we choose, the closer we approach to the instantaneous rate,
- The rate represents the speed at which the reactants are converted into products at any instant.
- The rate constant is a proportionality constant and It is equal to the rate of reaction, when the concentration of each of the reactants is unity.
- Molecularity of a reaction is the total number of reactant species that are involved in an elementary step.
- The half life of a reaction is defined as the time required for the reactant concentration to reach one half its initial value. For a first order reaction, the half life is a constant

i.e., it does not depend on the initial concentration.

- According to collision theory, chemical reactions occur as a result of collisions between the reacting molecules.
- Generally, the rate of a reaction increase with increasing temperature. However, there are very few exceptions. The magnitude of this increase in rate is different for different reactions. As a rough rule, for many reactions near room temperature, reaction rate tends to double when the temperature is increased by 10°C.
- According to Arrhenius, activation energy of the reaction is the minimum energy that a molecule must have to posses to react.
- The rate of a reaction is affected by the following factors.
 - 1. Nature and state of the reactant
- 4. Temperature of the reaction

5. Presence of a catalyst

- 2. Concentration of the reactant
- 3. Surface area of the reactant

EVALUATION

- 1. For a first order reaction $A \longrightarrow B$ the rate constant is $x \min^{-1}$. If the initial concentration of A is 0.01M, the concentration of A after one hour is given by the expression.
 - a) 0.01 e^{-x} b) $1 \times 10^{-2} (1 e^{-60x})$
 - c) $(1 \times 10^{-2})e^{-60x}$ d) none of these
- A zero order reaction X → Product, with an initial concentration 0.02M has a half life of 10 min. if one starts with concentration 0.04M, then the half life is
 - a) 10 s b) 5 min c) 20 min
 - d) cannot be predicted using the given information
- 3. Among the following graphs showing variation of rate constant with temperature (T) for a reaction, the one that exhibits Arrhenius behavior over the entire temperature range is

4. For a first order reaction A → product with initial concentration x mol L⁻¹, has a half life period of 2.5 hours. For the same reaction with initial concentration \$\left(\frac{x}{2}\right)\$ mol L⁻¹ the half life is a) (2.5×2) hours

b)
$$\left(\frac{2.5}{2}\right)$$
 hours

c) 2.5 hours

- d) Without knowing the rate constant, t_{1/2} cannot be determined from the given data
- 5. For the reaction, $2NH_3 \longrightarrow N_2 + 3H_2$, if $\frac{-d[NH_3]}{dt} = k_1[NH_3]$, $\frac{d[N_2]}{dt} = k_2[NH_3]$, $\frac{d[H_2]}{dt} = k_3[NH_3]$

then the relation between k_1, k_2 and k_3 is

- a) $k_1 = k_2 = k_3$ b) $k_1 = 3 k_2 = 2 k_3$
- c) 1.5 $k_1 = 3 k_2 = k_3$
- d) $2k_1 = k_2 = 3 k_3$
- 6. The decomposition of phosphine (PH₃) on tungsten at low pressure is a first order reaction. It is because the (NEET)
 - 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
- 7. For a reaction Rate = $k[acetone]^{\frac{3}{2}}$ then unit of rate constant and rate of reaction respectively is

a)
$$(\operatorname{mol} L^{-1} s^{-1}), (\operatorname{mol}^{-\frac{1}{2}} L^{\frac{1}{2}} s^{-1})$$

b) $(\operatorname{mol}^{-\frac{1}{2}} L^{\frac{1}{2}} s^{-1}), (\operatorname{mol} L^{-1} s^{-1})$

c) $(mol^{\frac{1}{2}} L^{\frac{1}{2}} s^{-1}), (mol L^{-1}s^{-1})$ d) $(mol L s^{-1}), (mol^{\frac{1}{2}} L^{\frac{1}{2}}s)$

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- 8. The addition of a catalyst during a chemical reaction alters which of the following quantities? (NEET)
 - a) Enthalpy b)Activation energy
 - c) Entropy d) Internal energy
- 9. Consider the following statements :
 - (i) increase in concentration of the reactant increases the rate of a zero order reaction.
 - (ii) rate constant k is equal to collision frequency A if $E_a = 0$
 - (iii) rate constant k is equal to collision frequency A if $E_a = \infty$
 - (iv) a plot of $\ln(k)$ vs T is a straight line.
 - (v) a plot of $\ln(k)vs\left(\frac{1}{T}\right)$ is a straight line with a positive slope.

Correct statements are

- a) (ii) only b) (ii) and (iv)
- c) (ii) and (v) d) (i), (ii) and (v)
- 10. In a reversible reaction, the enthalpy change and the activation energy in the forward direction are respectively -x kJ mol⁻¹ and y kJ mol⁻¹. Therefore, the energy of activation in the backward direction is
 - a) (y-x)kJ mol⁻¹ b) (x+y)J mol⁻¹
 - c) (x-y)kJ mol⁻¹
 - d) $(x+y) \times 10^3$ J mol⁻¹

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- 11. What is the activation energy for a reaction if its rate doubles when the temperature is raised from 200K to 400K? (R = 8.314 JK⁻¹mol⁻¹)
 - a) 234.65 kJ mol⁻¹
 - b) 434.65 kJ mol⁻¹
 - c) 2.305 kJ mol⁻¹
 - d) 334.65 J mol⁻¹
- 12. \triangle \rightarrow \rightarrow \bigcirc ; This reaction follows first order kinetics. The rate constant at particular temperature is 2.303 × 10⁻² hour⁻¹. The initial concentration of cyclopropane is 0.25 M. What will be the concentration of cyclopropane after 1806 minutes? (log 2 = 0.3010)

a) 0.125M b) 0.215M

c) 0.25×2.303 M d) 0.05 M

13. For a first order reaction, the rate constant is 6.909 min⁻¹.the time taken for 75% conversion in minutes is

a)
$$\left(\frac{3}{2}\right)\log 2$$

b) $\left(\frac{2}{3}\right)\log 2$
c) $\left(\frac{3}{2}\right)\log\left(\frac{3}{4}\right)$
d) $\left(\frac{2}{3}\right)\log\left(\frac{4}{3}\right)$

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

a)
$$\left(\frac{\log 2}{k}\right)$$
 b) $\left(\frac{0.693}{(0.1) k}\right)$
c) $\left(\frac{\ln 2}{k}\right)$ d) none of these

15. Predict the rate law of the following reaction based on the data given below

 $2A + B \longrightarrow C + 3D$

Reaction	[A]	[B]	Initial rate
number	(min)	(min)	(M s ⁻¹)
1	0.1	0.1	x
2	0.2	0.1	2 <i>x</i>
3	0.1	0.2	4 <i>x</i>
4	0.2	0.2	8 <i>x</i>

a) rate =
$$k[A]^{2}[B]$$
 b) rate = $k[A][B]^{2}$

c) rate =
$$k[A][B]$$

d) rate =
$$k[A]^{\frac{1}{2}}[B]^{\frac{3}{2}}$$

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

Reason: rate constant also doubles

- 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.
- 17. The rate constant of a reaction is $5.8 \times 10^{-2} \text{ s}^{-1}$. The order of the reaction is
 - a) First order b) zero order
 - c) Second order d) Third order
- 18. For the reaction $N_2O_5(g) \longrightarrow 2NO_2(g) + \frac{1}{2}O_2(g)$, the value of rate of disappearance of N_2O_5 is given as $6.5 \times 10^{-2} \text{ mol } L^{-1}s^{-1}$. The rate of formation of NO₂ and O₂ is given

respectively as

- a) $(3.25 \times 10^{-2} \text{ mol } L^{+}s^{-1})$ and $(1.3 \times 10^{-2} \text{ mol } L^{+}s^{-1})$
- b) $(1.3 \times 10^{-2} \text{ mol } L^{-4} s^{-4})$ and $(3.25 \times 10^{-2} \text{ mol } L^{-4} s^{-4})$
- c) $(1.3 \times 10^{-1} \text{ mol } L^{-1} s^{-1})$ and $(3.25 \times 10^{-2} \text{ mol } L^{-1} s^{-1})$
- d) None of these
- 19. During the decomposition of H_2O_2 to give dioxygen, 48 g O_2 is formed per minute at certain point of time. The rate of formation of water at this point is
 - a) 0.75 mol min⁻¹
 - b) 1.5 mol min⁻¹
 - c) 2.25 mol min⁻¹
 - d) 3.0 mol min⁻¹
- 20. If the initial concentration of the reactant is doubled, the time for half reaction is also doubled. Then the order of the reaction is

a) Zero	b) one
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- c) Fraction d) none
- 21. In a homogeneous reaction $A \longrightarrow B + C + D$, the initial pressure was P₀ and after time t it was P. expression for rate constant in terms of P₀, P and t will be

a)
$$k = \left(\frac{2.303}{t}\right) \log\left(\frac{2P_0}{3P_0 - P}\right)$$

b)
$$k = \left(\frac{2.303}{t}\right) \log\left(\frac{2P_0}{P_0 - P}\right)$$

c)
$$k = \left(\frac{2.303}{t}\right) \log\left(\frac{3P_0 - P}{2P_0}\right)$$

d) k =
$$\left(\frac{2.303}{t}\right)\log\left(\frac{2P_0}{3P_0-2P}\right)$$

- 22. If 75% 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
- 23. The half life period of a radioactive element is 140 days. After 560 days , 1 g of element will be reduced to

a)
$$\left(\frac{1}{2}\right)g$$

b) $\left(\frac{1}{4}\right)g$
c) $\left(\frac{1}{8}\right)g$
d) $\left(\frac{1}{16}\right)g$

- 24. The correct difference between first and second order reactions is that (NEET)
 - a) A first order reaction can be catalysed; a second order reaction cannot be catalysed.
 - b) The half life of a first order reaction does not depend on $[A_0]$; the half life of a second order reaction does depend on $[A_0]$.
 - c) The rate of a first order reaction does not depend on reactant concentrations; the rate of a second order reaction does depend on reactant concentrations.
 - d) The rate of a first order reaction does depend on reactant concentrations; the rate of a second order reaction does not depend on reactant concentrations.
- 25. After 2 hours, a radioactive substance becomes $\left(\frac{1}{16}\right)^{\text{th}}$ of original amount.

Then the half life (in min) is

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

Answer the following questions:

- 1. Define average rate and instantaneous rate.
- 2. Define rate law and rate constant.
- 3. Derive integrated rate law for a zero order reaction $A \longrightarrow product$.
- 4. Define half life of a reaction. Show that for a first order reaction half life is independent of initial concentration.
- 5. What is an elementary reaction? Give the differences between order and molecularity of a reaction.
- 6. Explain the rate determining step with an example.
- 7. Describe the graphical representation of first order reaction.
- 8. 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 Br₂.
- 9. Explain the effect of catalyst on reaction rate with an example.
- 10. The rate law for a reaction of A, B and C hasbeen found to be rate = $k[A]^2[B][L]^{\frac{3}{2}}$. How would the rate of reaction change when
 - (i) Concentration of [L] is quadrupled
 - (ii) Concentration of both [A] and [B] are doubled
 - (iii) Concentration of [A] is halved

- (iv) Concentration of [A] is reduced to $\begin{pmatrix} 1/3 \end{pmatrix}$ and concentration of [L] is quadrupled.
- 11. The rate of formation of a dimer in a second order reaction is $7.5 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{s}^{-1}$ at 0.05 mol L⁻¹ monomer concentration. Calculate the rate constant.
- 12. For a reaction $x + y + z \longrightarrow$ products the rate law is given by rate = $k[x]^{\frac{3}{2}}[y]^{\frac{1}{2}}$ what is the overall order of the reaction and what is the order of the reaction with respect to z.
- 13. Explain briefly the collision theory of bimolecular reactions.
- 14. Write Arrhenius equation and explains the terms involved.
- 15. The decomposition of Cl_2O_7 at 500K in the gas phase to Cl_2 and O_2 is a first order reaction. After 1 minute at 500K, the pressure of Cl_2O_7 falls from 0.08 to 0.04 atm. Calculate the rate constant in s⁻¹.
- 16. Give two exapmles for zero order reaction
- 17. Explain pseudo first order reaction with an example.
- 18. Identify the order for the following reactions
- (i) Rusting of Iron
- (ii) Radioactive disintegration of $_{92}U^{238}$
- (iii) $2A + 3B \longrightarrow \text{products}$; $\text{rate} = k[A]^{\frac{1}{2}}[B]^2$
- 19. A gas phase reaction has energy of activation 200 kJ mol⁻¹. If the frequency factor of the reaction is $1.6 \times 10^{13} s^{-1}$. Calculate the rate constant at 600 K. $(e^{-40.09} = 3.8 \times 10^{-18})$

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[x] (M)	[y] (M)	rate (M s ⁻¹)
0.2	0.02	0.15
0.4	0.02	0.30
0.4	0.08	1.20

20. For the reaction $2x + y \longrightarrow L$ find the rate law from the following data.

- 21. How do concentrations of the reactant influence the rate of reaction?
- 22. How do nature of the reactant influence rate of reaction.
- 23. The rate constant for a first order reaction is 1.54×10^{-3} s⁻¹. Calculate its half life time.
- 24. The half life of the homogeneous gaseous reaction $SO_2Cl_2 \rightarrow SO_2 + Cl_2$ which obeys first order kinetics is 8.0 minutes. How long will it take for the concentration of SO_2Cl_2 to be reduced to 1% of the initial value?
- 25. The time for half change in a first order decomposition of a substance A is 60 seconds. Calculate the rate constant. How much of A will be left after 180 seconds?
- 26. A zero order reaction is 20% complete in 20 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?
- 27. The activation energy of a reaction is 22.5 k Cal mol⁻¹ and the value of rate constant at 40°C is 1.8×10^{-5} s⁻¹. Calculate the frequency factor, A.

28. Benzene diazonium chloride in aqueous solution decomposes according to the equation $C_6H_5N_2Cl \longrightarrow C_6H_5Cl + N_2$. Starting with an initial concentration of 10 g L⁻¹, the volume of N₂ gas obtained at 50 °C at different intervals of time was found to be as under:

t (min):	6	12	18	24	30	∞
Vol. of N ₂	19.3	32.6	41.3	46.5	50.4	58.3
(ml):						

Show that the above reaction follows the first order kinetics. What is the value of the rate constant?

29. 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 $KMnO_4$ solution required for titrating the same volume of the reaction mixture.

30. A first order reaction is 40% complete in 50 minutes. Calculate the value of the rate constant. In what time will the reaction be 80% complete?

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