KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)

(Established Under Section 3 of UGC Act, 1956)

Coimbatore – 641 021.

SYLLABUS

DEPARTMENT OF BIOTECHNOLOGY

STAFF NAME: Dr. K. SUNDARAM

SUBJECT NAME: CHEMISTRY-I SUB.CODE:19BCU103

SEMESTER: I CLASS: I B.Sc (BIOCHEMISTRY)

19BCU103 CHEMISTRY-I 4H 4C

Instruction Hours/week :L: 4 T:0 P:0 Marks: Internal:40 External: 60 Total:100

Course Objectives

The student should know

1. The molecular orbital theory, preparation and properties of inorganic compounds.
2. Theory of covalent bond, polar effects and stereochemistry of organic compounds.
3. About important industrial chemicals like silicones, fuel gases and fertilizers and their impact on environment.
4. Elements of photochemistry, chemical kinetics and chromatography.
5. About the dyes, chemotherapy and vitamins.

Course Outcome

The student understand

1. The molecular orbital theory, preparation and properties of inorganic compounds.
2. Theory of covalent bond, polar effects and stereochemistry of organic compounds.
3. About important industrial chemicals like silicones, fuel gases and fertilizers and their impact on environment.
4. Elements of photochemistry, chemical kinetics and chromatography.
5. About the dyes, chemotherapy and vitamins.

UNIT-I

Chemical Bonding: Molecular orbital theory-linear combination of atomic orbitals-bonding and antibonding molecular orbitals-energy level diagram-bond order- M.O. configuration of H_2, N_2 and F_2 molecules. Diborane: Preparation, properties and structure. $NaBH_4$: Preparation and uses. Borazole: Preparation and properties. Interhalogen compounds: ICl, BrF_3, IF_5 - preparation, properties, uses and structure. Basic properties of iodine. Compounds of sulphur: Sodium hydrosulphite- preparation, properties, uses and structure. Per acids of sulphur: Preparation, properties, uses and structure.

UNIT- II

Covalent Bond and Stereoisomerism: Covalent Bond: Orbital overlap, hybridization and geometry of CH_4, C_2H_4 and C_2H_2. Polar effects: Inductive effect-electromeric effect-mesomeric effect- steric effect- hyperconjugation. **Stereoisomerism:** Elements of symmetry-polarised light and optical activity-isomerism in tartaric acid-racemisation-resolution- geometrical isomerism of maleic and fumaric acids-keto-enol tautomerism of acetoacetic esters.

UNIT-III

Industrial Chemistry: Silicones: Synthesis, properties and uses. Fuels gases: Natural gas-water gas-semi water gas-carbureted water gas-producer gas- oil gas (Manufacturing details not required).Fertilizers: NPK fertilizer-ammonium sulphate-urea-superphosphate of lime-triple superphosphate- potassium nitrate-ammonium nitrate. Pollution: Water, air and soil pollution-sources and remedies-acid rain-ozone hole-greenhouse effect.

UNIT-IV

Elements of Photochemistry, Chemical Kinetics and Chromatography: Elements of Photochemistry: Photochemical laws-Beer Lambert’s law-Grotthuss-Draper law-Stark-Einstein law (statement only). **Chemical Kinetics:** Rate-order-molecularity-pseudo first order reactions-zero order reactions-determination of order of reaction-measurement of order and rates of reactions-effect of temperature on reaction rate-energy of activation. **Chromatography:** Principles and applications of Column, Paper and Thin Layer Chromatography.

UNIT- V

Dyes, Chemotherapy and Vitamins: Dyes: Terms used chromophore, auxochrome, bathachromic shift and hypsochromic shift- classification of dyes– based on chemical structure and application-one example each for azo, triphenylmethane, vat and mordant dyes- preparation.

Chemotherapy: Preparation, uses and mechanism of action sulpha drugs- preparation and uses of prontosil, sulphadiazine and sulphafurazole-structure and uses of pencillins and Chloromycetin. **Vitamins:** Diseases caused by the deficiency of vitamins A, B_1, B_2, C and D-sources of these vitamins.

Text Books:

1. Thangamani, A. (2019). *Text Book on Allied Chemistry* (1st Edition). Coimbatore: Karpagam Publication.
2. Puri, B.R., Sharma, L. R., & Kalia, K. C. (2017). *Principles of Inorganic Chemistry* (33rd Edition). Jalandar: Vishal Publishing Company.

3. Bahl, A., & Bahl, B.S. (2015). *A Textbook of Organic Chemistry* (21st Revised Edition). New Delhi: S.Chand & Company Pvt. Ltd.
4. Puri, B. R., Sharma, L. R. & Pathania, M. S. (2014). *Elements of Physical Chemistry* (46th Edition). Jalandhar: Vishal Publishing Company.

Reference Book:

1. Gopalan, R., & Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University)
(Established Under Section 3 of UGC Act, 1956)
Coimbatore – 641 021.

LECTURE PLAN
DEPARTMENT OF CHEMISTRY

STAFF NAME: Dr. K. SUNDARAM
SUBJECT NAME: CHEMISTRY-I SUB.CODE:19BCU103
SEMESTER: I CLASS: I-B.Sc (BIOCHEMISTRY)

S.No.	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
		UNIT-I	
1	1	**Chemical Bonding:** Molecular orbital theory-linear combination of atomic orbitals- bonding and antibonding molecular orbitals-energy level diagram-bond order.	T1:1-5 R1:1-4
2	1	Molecular orbital configuration of H_2, N_2 and F_2 molecules.	T1:5-10 R1:4-6
3	1	Diborane- preparation, properties and structure. Sodium borohydride ($NaBH_4$)-preparation and uses.	T1:10-15 R1:13-16 & 18-19
4	1	Borazole-preparation and properties.	T1:15-16 R1:19-21
5		Interhalogen compounds-ICl-preparation, properties, uses and structure.	T1:17-18 R1:22-23
6	1	BrF_3 and IF_5- preparation, properties, uses and structure.	T1:19-21 R1:23-25
7	1	Basic properties of iodine. Compounds of sulphur-sodium hydrosulphite-preparation, properties, uses and structure.	T1:23-26 R1:28-29
8	1	Per acids of sulphur-preparation, properties, uses and structure.	T1:26-29 R1:29-31
9	1	Recapitulation and discussion of important questions.	
	Total No of Hours Planned For Unit I=09		
		UNIT-II	
1	1	**Covalent Bond and Stereoisomerism:** **Covalent Bond:** Orbital overlap, hybridization	T1:30-33 R1:122-126

		and geometry of methane (CH_4), ethylene (C_2H_4) and acetylene (C_2H_2) molecules.	
2	1	Polar effects-Inductive effect-consequences of Inductive effect-basic nature of amines.	T1:34-39 R1:133-137
3	1	Electromeric effect-definition and examples. Mesomeric (resonance) effect- definition- effects of resonance and examples.	T1:39-43 R1:137-140
4	1	Hyperconjugation effect-consequences of Hyperconjugation and examples.	T1:45-47 R1:140-141
5	1	Steric effect- Introduction and examples.	T1:43-45 R1:141-143
6	1	**Stereoisomerism:** Elements of symmetry-polarised light and optical activity	T1:47-51 R1:74-77 & 81-83
7	1	Isomerism in tartaric acid-racemisation-resolution.	T1:52-55 R1:84-86
8	1	Geometric isomerism of maleic and fumaric acids. Keto-enol tautomerism of acetoacetic esters.	T1:56-63 R1:78-80
9	1	Recapitulation and discussion of important questions.	
	Total No of Hours Planned For Unit II=09		
		UNIT-III	
1	1	**Industrial Chemistry:** Silicones-synthesis, properties and uses.	T1:64-67
2	1	Fuel gases- Introduction-requisites of good fuel-different types of fuels. Natural gas and water gas-preparations, compositions and uses.	T1:67-69 R1:61-63
3	1	Semi water gas, carbureted water gas, oil gas and producer gas- preparations, compositions and uses.	T1:69-71 R1:62-64
4	1	Fertilizers-Introduction-requisites of good fertilizer. NPK fertilizer-ammonium sulphate and urea-preparation, compositions and uses.	T1:72-74 R1:64-65
5	1	Superphosphate of lime and triple superphosphate-preparation and compositions. Potassium nitrate and ammonium nitrate-synthesis.	T1:74-76 R1: 65-66
6	1	Pollution-definition-classification. Water and air pollution-sources and remedies.	T1:76-79
7	1	Soil pollution- sources and remedies.	T1:79

8	1	Acid rain-ozone hole and greenhouse effect.	T1:80-81
9	1	Recapitulation and discussion of important questions.	
	Total No of Hours Planned For Unit III=09		
		UNIT-IV	
1	1	**Elements of Photochemistry, Chemical Kinetics and Chromatography:** **Elements of Photochemistry:** Photochemical laws-Beer Lambert's law- Grotthuss-Draper law and Stark-Einstein law.	T1:82-87 R2:789-792
2	1	**Chemical Kinetics:** Introduction-law of mass action.	T1:88 R1:222-225
3	1	Rate -definition-unit. Order of reaction-definition-examples for first and second order reactions-molecularity of a reaction.	T1:89-91 R1:226-230
4	1	Pseudo first order reactions-zero order reactions. Determination of order of reaction-measurement of order and rates of reactions.	T1:91-95 R1:230-231 & 234-235
5	1	Effect of temperature on reaction rate-temperature coefficient.	T1:95-97 R1:235
6	1	Energy of activation-Arrhenius theory.	T1:97-101 R1:236-237
7	1	**Chromatography:** Introduction. Column chromatography-principles and applications.	T1:102-103 R1:239-240
8	1	Paper and Thin layer chromatography-principles and applications. Thin layer chromatography-advantages. Ion-exchange chromatography-uses.	T1:103-106 R1:239-240
9	1	Recapitulation and discussion of important questions.	
	Total No of Hours Planned For Unit IV=09		
		UNIT-V	
1	1	**Dyes, Chemotherapy and Vitamins:** **Dyes:** Introduction-conditions- definition of chromophore, auxochrome, bathachromic shift and hypsochromic shift.	T1:107-109 R1:92-93
2	1	Classification of dyes- based on chemical structure and application.	T1:109-111 R1:93
3	1	Classification of dyes- based on application.	T1:112

			R1:93
4	1	One example each for azo, triphenylmethane, vat and mordant dyes-preparation.	T1:113-114 R1:94-96
5	1	**Chemotherapy:** Preparation, uses and mechanism of action of sulpha drugs.	T1:114-116 R1:107-108, 110
6	1	Preparation and uses of prontosil, sulphadiazine and sulphafurazole.	T1:117-118 R1:108-109
7	1	**Antibiotics**-structure and uses of pencillins and chloromycetin.	T1:118-121 R1:111-112
8		**Vitamins:** Classification. Diseases caused by the deficiency of vitamins A, B_1, B_2, C and D- sources of theses vitamins.	T1:123-130 R1:112-117
9	1	Recapitulation and discussion of important questions.	
10	1	Discussion of previous ESE question papers.	
11	1	Discussion of previous ESE question papers.	
12	1	Discussion of previous ESE question papers.	
	Total No of Hours Planned for unit V=12		
Total Planned Hours	**48**		

Text Book:

1. Thangamani, A. (2019). *Text Book on Allied Chemistry* (I Edition). Coimbatore: Karpagam Publication.

Reference Books:

1. Gopalan, R., and Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.
2. Puri, B. R., Sharma, L. R., and Pathania, M. S. (2014). *Elements of Physical Chemistry* (46th Edition). Jalandhar: Vishal Publishing Company.

UNIT-I

SYLLABUS

Chemical Bonding: Molecular orbital theory-linear combination of atomic orbitals-bonding and antibonding molecular orbitals-energy level diagram-bond order- M.O. configuration of H_2, N_2 and F_2 molecules. Diborane: Preparation, properties and structure. $NaBH_4$: Preparation and uses. Borazole: Preparation and properties. Interhalogen compounds: ICl, BrF_3, IF_5 - preparation, properties, uses and structure. Basic properties of iodine. Compounds of sulphur: Sodium hydrosulphite- preparation, properties, uses and structure. Per acids of sulphur: Preparation, properties, uses and structure.

CHAPTER-1

MOLECULAR ORBITAL THEORY

(M.O.Theory)

The molecular orbital theory was developed by Hund and Millikan and later by Lennard Jones and Coulson. This theory is modern and more rational. This theory is more popular than Valence Bond Theory (V.B.Theory) because it is able to explain certain experimental facts which were not explained by V.B.Theory.

M.O.Theory is also based on quantum mechanics, but its approach to bond formation is quite different from V.B. approach. In V.B. theory, when atoms are combined to form molecules, only the outermost atomic orbitals of the combining atoms lose their identity and all the remaining inner atomic orbitals of the combining atoms remain undisturbed. The nucleus of each atom is also localised in the atom itself even when the atoms are chemically bonded. But in M.O. theory, when atoms are combined to form molecule, all the atomic orbitals in the outer shell or valence shell of the participating atoms are disturbed and lose their individual identity. These valence shell atomic orbitals are mixed up to form a new set of orbitals known as *molecular orbitals*. The nuclei of the participating atoms which were originally surrounded by their respective atomic orbitals are now surrounded by newly formed molecular orbitals. Thus, the molecular orbitals are **polycentric** in nature. Some important basic concepts of M.O. theory are explained below.

1) Linear Combination of Atomic Orbitals (LCAO)

The formation of M.O. from atomic orbitals is governed by quantum mechanical principles. According to this, every atomic orbital is associated with a **wave function** given as ψ (Psi). This can be explained by considering the simplest diatomic molecule, hydrogen (H_2). H_2 is made up of two hydrogen atoms – H_A and H_B and their atomic orbitals are given by wave function, ψ_A and ψ_B respectively.

According to M.O. theory, the wave function of the atomic orbitals are combined in a linear fashion (i.e. either added or subtracted) so as to obtain a new wave function for the molecular orbital.

The method of obtaining a wave function for the molecular orbital from the wave function of atomic orbitals is known as linear combination of atomic orbitals (LCAO) method.

2) Bonding and Anti-bonding molecular orbitals

According to LCAO method, the number of molecular orbitals that are obtained will be equal to the number of atomic orbitals that are combined. In the case of hydrogen molecule, we obtain only two molecular orbitals-

(i) The first molecular orbital is obtained by adding the wave function of the two atomic orbitals and is known as *bonding molecular orbital* (BMO) and is represented as σ_{1s}

$$\Psi = \Psi_A + \Psi_B \;\ldots\ldots\ldots..(1)$$

(ii) The second molecular orbital is obtained by subtracting the wave functions of the two atomic orbitals and is known as *anti-bonding molecular orbital* (ABMO). This is represented as σ^*_{1s}:

$$\Psi^* = \Psi_A - \Psi_B \;\ldots\ldots.. (2)$$

It is to be noted that in the bonding (σ_{1s}) orbitals, the electron charge is concentrated in the region between two nuclei. This increases the electrostatic attraction and holds the nuclei together.

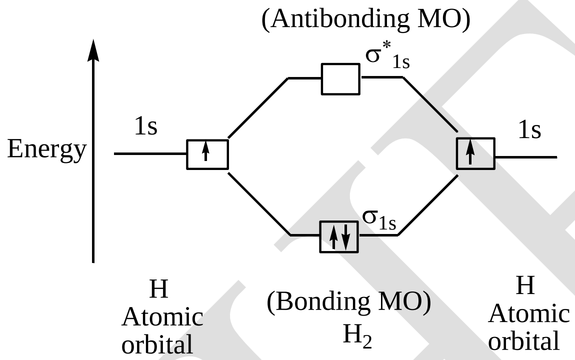
On the other hand, in an anti-bonding (σ^*_{1s}) orbitals, the electron charge is drifted from the region between the nuclei. This increases the electrostatic repulsion between the nuclei.

The differences between Bonding molecular orbitals and Antibonding molecular orbitals are given in the following table:

No.	**Bonding Molecular orbitals**	**Anti-bonding molecular orbitals**
1.	A bonding molecular orbital is formed by the combination of electron waves of the same sign.	An Anti-bonding molecular orbital is formed by the combination of electron waves of the opposite sign.
2.	It is formed by the addition overlap of atomic orbitals. $\Psi = \Psi_A + \Psi_B$	It is formed by the subtraction overlap of atomic orbitals. $\Psi^* = \Psi_A - \Psi_B$
3.	It possesses lower energy than the atomic orbitals from which it is formed.	It possesses higher energy than the atomic orbitals from which it is formed.
4.	The electron density in between the nuclei is high.	The electron density in between the nuclei is low.
5.	As the attraction between the nuclei is high, a bond between the atoms is formed.	As the repulsion between the nuclei is high, a bond is not formed between the atoms.
6.	It stabilises the molecule.	It destabilizes the molecule.

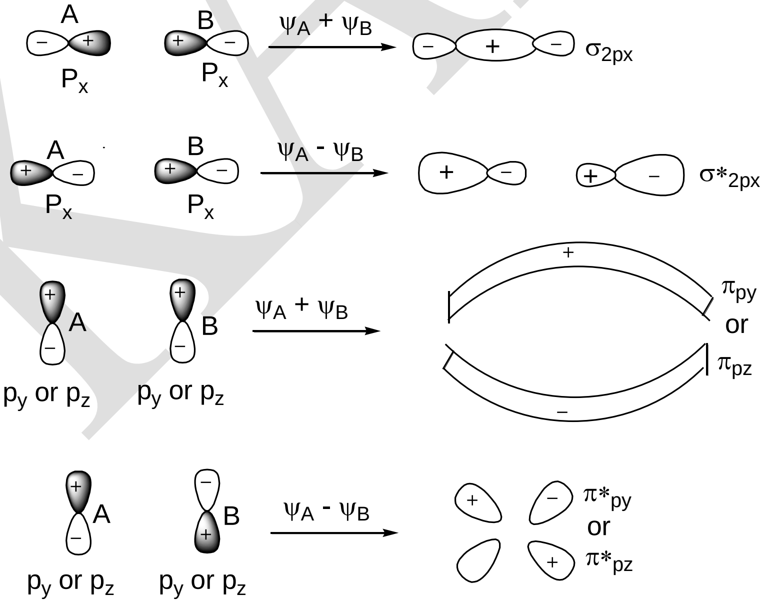
3) Energy level diagram

Based on energy consideration, the bonding orbital (due to attraction) has lesser energy and anti-bonding orbital (due to repulsion) has more energy than the individual atomic orbitals from which they are obtained as shown in the figure:



4) Formation of molecular orbitals from p-orbitals

Like s orbital, P_x, p_y and p_z atomic orbitals also combine linearly to form molecular orbitals as shown below.



As seen from the figures, it is evident that p_x atomic orbitals overlap to give sigma bonding (σ_{2px}) and sigma anti-bonding (σ^*_{2px}) orbitals. But, p_y or p_z atomic orbitals overlap in sideways to give only pi-bonding (π_{2py} or π_{2pz}) and pi anti-bonding (π^*_{2py} or π^*_{2pz}) orbitals.

(5) Sequence of energy of various molecular orbitals

The energies of various molecular orbitals are determined from spectroscopic methods. Based on this, the sequence of energy of various molecular orbitals is as follows:

$$\sigma_{1s} < \sigma^*_{1s} < \sigma_{2s} < \sigma^*_{2s} < \sigma_{2px} < \pi_{2py} = \pi_{2pz} < \pi^*_{2py} = \pi^*_{2pz} < \sigma^*_{2px}$$

(6) Distribution of electrons in various, molecular orbitals

The electrons are now distributed in the above molecular orbitals following *Aufbau principle, Pauli Exclusion Principle and Hund's rule* of maximum multiplicity. These are explained below:

The electrons are now placed in the various molecular orbitals in the increasing order of energy (Aufbau principle) – the molecular orbital with lowest energy is filled first. Each molecular orbital can accommodate only a maximum number of two electrons (Pauli principle) and these two electrons must have opposite spin (Hund's principle).

(7) Bond Order

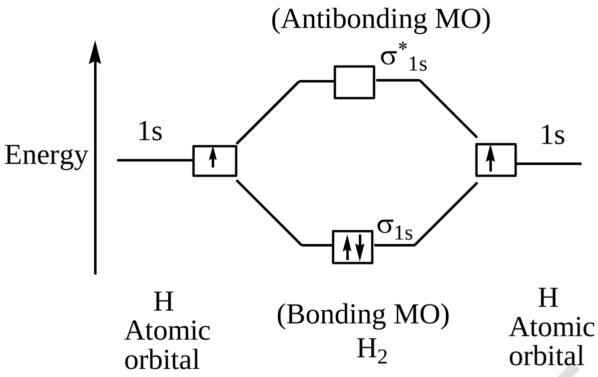
The actual number of bonds present in the molecule is known as bond order and is calculated using the formula:

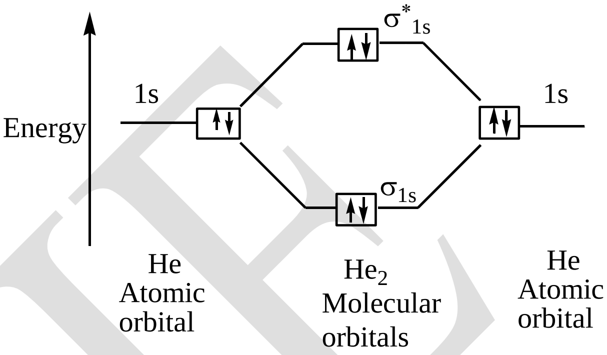
$$\text{Bond order} = \frac{\text{No. of electrons in bonding orbitals - No. of electrons in the antibonding orbitals}}{2}$$

APPLICATION OF M.O THEROY

a) **Hydrogen molecule, H_2**

Hydrogen molecule is made by two hydrogen atoms. It contains two electrons and two molecular orbitals namely σ_{1s} and σ^*_{1s}. Both the electrons of the molecule will occupy the low energy σ_{1s} orbital and σ^*_{1s} orbital is vacant as in the figure.





Thus, the electronic configuration of hydrogen molecule is:

$$2H\,(1s^1) \longrightarrow H_2\,(\sigma_{1s})^2$$

The bond order is (2-0) / 2 =1. There is a strong sigma bond between two hydrogen atoms with bond energy 432 kJ/mol. The molecule is *diamagnetic*.

b) Helium molecule He_2

The atomic number of helium is 2 and its electronic configuration is $1s^2$. Hence, a diatomic helium molecule will contain four electrons. Among them, two electrons enter the bonding σ_{1s} orbital and the remaining two electrons enter the antibonding σ^*_{1s}.

The electronic configuration of helium (He_2) molecule is:

$$2He\,(1s^2) \longrightarrow He_2\,[(\sigma_{1s})^2, (\sigma^*_{1s})^2]$$

Two electrons in the bonding orbitals stabilise the molecule while two electrons in the antibonding orbital will destabilise the molecule making the bond order zero, (2-2) / 2 = 0. Hence, He_2 does not exist. *Helium will exist only as monoatomic species*.

c) Nitrogen molecule, N_2

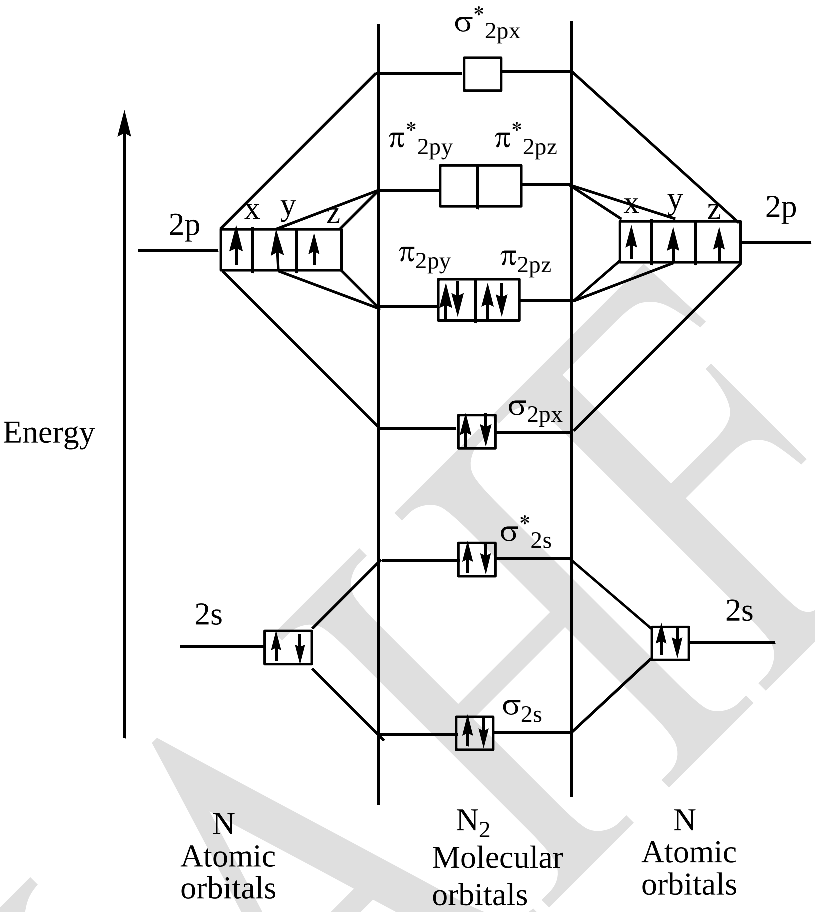
The atomic number of nitrogen is 7 and its electronic configuration is $1s^2$, $2s^2$, $2px^1$, $2py^1$, $2pz^1$. The outer shell or valence atomic orbitals (2s and 2p) in each nitrogen atom combine to form the following eight molecular orbitals:

Overlap of -

(i)	2s and 2s gives	σ_{2s} and σ^*_{2s} M.O.
(ii)	$2p_x$ and $2p_x$ gives	σ_{2px} and σ^*_{2px} M.O.
(iii)	$2p_y$ and $2p_y$ gives	π_{2py} and π^*_{2py} M.O.
(iv)	$2p_z$ and $2p_z$ gives	π_{2pz} and π^*_{2pz} M.O.

Each nitrogen atom has five electrons in the valence shell. Hence, in nitrogen molecule (N_2), there are ten electrons. These electrons are to be accommodated in the above eight molecular orbitals. Four electrons will enter low energy, σ_{2s} and σ^*_{2s} M.Os. The remaining six electrons will enter the σ_{2px}, π_{2py} and π_{2pz} M.Os. which are lying at the next higher energy level as in the energy level diagram. The electronic configuration of nitrogen molecule is:

$$2N(1s^2\,2s^2\,2p^3) \longrightarrow N_2\,[KK\,(\sigma_{2s})^2\,(\sigma^*_{2s})^2\,(\sigma_{2px})^2\,(\pi_{2py})^2\,(\pi_{2pz})^2]$$



Here, KK represents completely filled inner shells which do not take part in the molecular orbitals formation.

The bond order of the molecule is, (8-2) / 2 = 3. Out of this, one is a sigma bond and the remaining two are pi-bonds.

Out of ten electrons, eight electrons occupy the bonding orbitals.This makes the nitrogen molecule a highly stable molecule with high bond energy of 942 kJ/mol.

Nitrogen molecule is experimentally found to be diamagnetic. This is due to the absence of odd electrons in any one of the molecular orbitals, i.e., all electrons are paired.

d) Oxygen Molecule, O_2

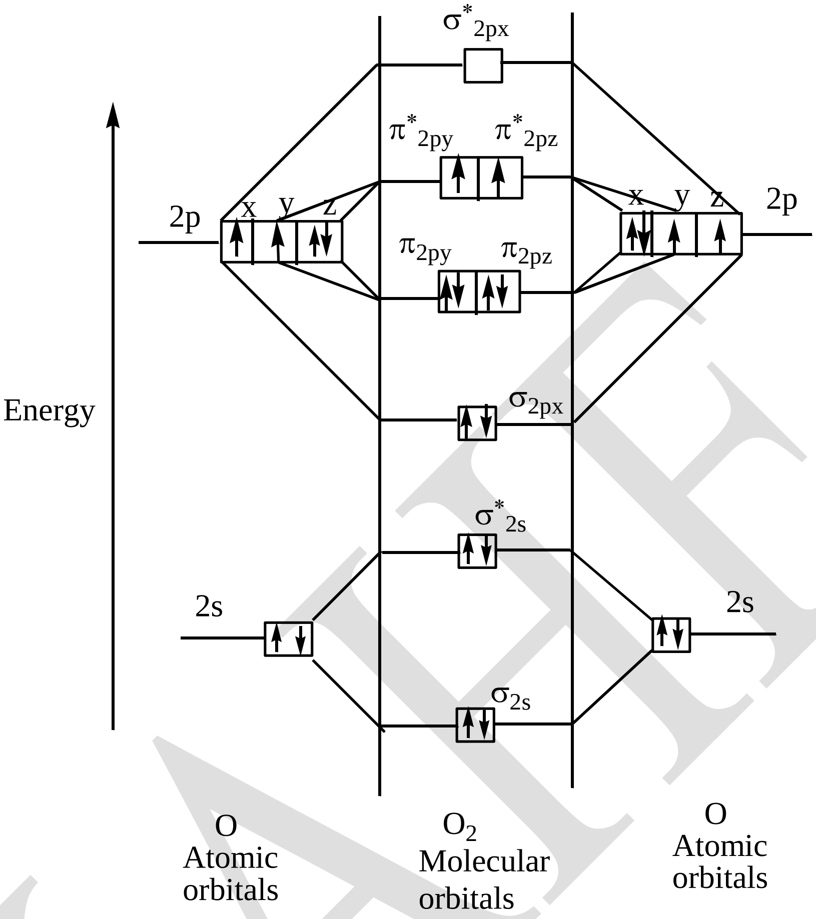
The atomic number of oxygen is eight and its electronic configuration is $1s^2\ 2s^2\ 2p_x^{\ 2}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$. The outer, valence shell atomic orbitals (i.e., 2s and 2p) in each oxygen atom combine to form a total of eight molecular orbitals.

Each oxygen atom has six valence electrons. Hence, in oxygen molecule (O_2), twelve electrons are to be accommodated in the eight molecular orbitals that are formed. Four electrons will enter σ_{2s} and σ^*_{2s} molecular orbitals. Six electrons will enter σ_{2px}, π_{2py} and π_{2pz} molecular orbitals. The remaining two electrons will occupy π^*_{2py} and π^*_{2pz} i.e., **one electron will go to each of the antibonding orbitals,** as these orbitals are of same energy, to give two unpaired electrons. The distribution of electrons in various molecular orbitals is given in the figure. The electronic configuration of O_2 molecule is:

$$2O\ (1s^2\ 2s^2\ 2p^4) \longrightarrow O_2\ [KK\ (\sigma_{2s})^2, (\sigma^*_{2s})^2\ (\sigma_{2px})^2\ (\pi_{2py})^2\ (\pi_{2pz})^2\ (\pi^*_{2py})^1\ (\pi^*_{2pz})^1]$$

The bond order is (8 - 4) / 2 = 2. The two oxygen atoms are bonded by a double bond .This double bond consists of one sigma bond and one pi bond. The formation of these bonds is explained as follows:

Two electrons in the σ_{2s} and two electrons in the σ^*_{2s} cancel each other. Two electrons in the σ_{2px} will form a sigma bond. Out of four electrons in the pi bonding orbitals, two electrons are cancelled by the two electrons in the pi anti-bonding orbitals. Hence, two pi-electrons form a pi bond.



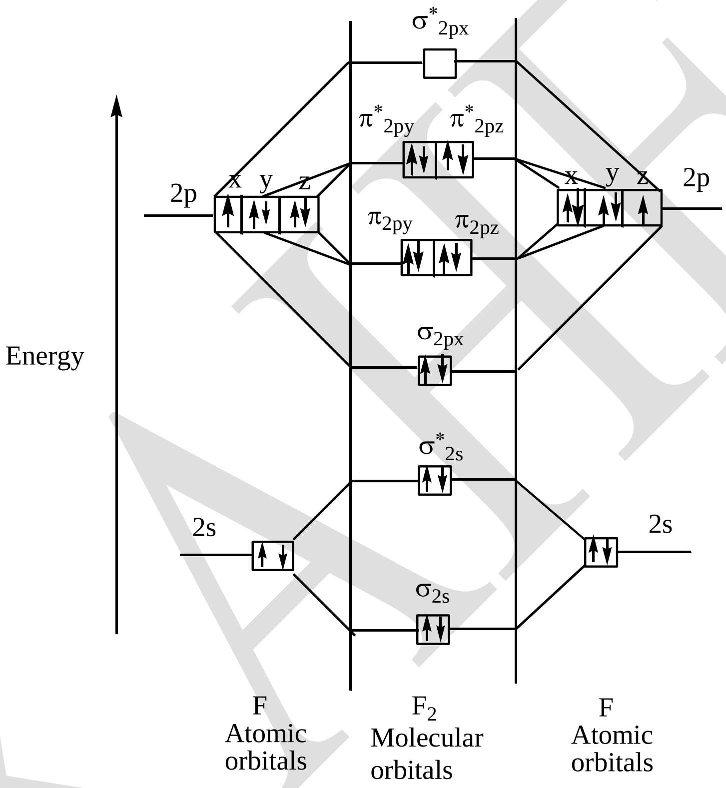
Comparison of the molecular orbitals of oxygen molecule with nitrogen molecule reveals that oxygen has more number of anti-bonding (4) electrons than nitrogen molecule (2). Hence, oxygen is less stable than nitrogen with low bond energy of 494 kJ/mol.

Various experiments show that oxygen molecule is paramagnetic having one or more odd electrons and M.O theory, clearly indicates the presence of two unpaired electrons as $(\pi^*_{2py})^1$ and $(\pi^*_{2pz})^1$.

e) Fluorine molecule, F_2

The atomic number of fluorine is nine and its electronic configuration is ($1s^2\ 2s^2\ 2px^1\ 2py^2\ 2pz^2$). The valence shell atomic orbitals (2s and 2p) in each fluorine atom combine to form a total of eight molecular orbitals.

Each fluorine atom has seven valence electrons. Hence, in fluorine molecule (F_2), fourteen electrons are to be accommodated in the eight molecular orbitals. Four electrons will enter, σ_{2s} and σ^*_{2s} M.Os. Six electrons will enter σ_{2px}, π_{2py} and π_{2pz} orbitals. The remaining four electrons will occupy π^*_{2py} and π^*_{2pz} orbitals. The distribution of electrons in various M.Os is given in the figure.



The electronic configuration of fluorine molecule is:

$$2F\ (1s^2\ 2s^2\ 2p^5) \longrightarrow F_2\ [KK\ (\sigma_{2s})^2, (\sigma^*_{2s})^2\ (\sigma_{2px})^2\ (\pi_{2py})^2\ (\pi_{2pz})^2\ (\pi^*_{2py})^2\ (\pi^*_{2pz})^2\ ]$$

The bond order is (8-6) / 2 = 1 and this single bond is a sigma bond. As all the bonding electrons are cancelled by the corresponding antibonding electrons except the two electrons present in σ_{2px} orbital, a sigma bond is formed between two fluorine atoms. Fluorine molecule has more numbers of anti-bonding electrons (6) than in nitrogen (2) and in oxygen (4) molecules.

Hence, fluorine is less stable than nitrogen and oxygen, with low bond energy of 155 kJ/mol. It is evident from the molecular orbitals that fluorine molecule is *diamagnetic*.

DIBORANE

Sir H. Davy first reported the existence of a hydride of boron but the systematic study of the subject was due to Alfred Stock who prepared a mixture of the following boron hydrides (also called *boranes*)

B_2H_6	- Diborane	B_4H_{10}	-Tetraborane
B_5H_9	- Pentaborane-9	B_5H_{11}	- Pentaborane-11
B_6H_{10}	- Hexabrorane	$B_{10}H_{14}$	-Decaborane

The general formula of the boranes is B_nH_{n+4} and B_nH_{n+6}, the simplest boron hydrides, BH_3 is not known. Diborane (B_2H_6) is the simplest of the hydrides of boron.

Preparation

Diborane can be prepared using the following methods-

(i) By treating lithium hydride with boron trifluride.

$$6LiH + 8BF_3 \longrightarrow 6\ LiBF_4 + B_2H_6$$

(ii) By passing silent electric discharge through a mixture of hydrogen and boron trichlorode.

$$2\ BCl_3 + 6\ H_2 \longrightarrow B_2H_6 + 6\ HCl$$

(iii) Reducing boron tricholoride with lithium aluminium hydride ($LiAlH_4$).

$$4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

(iv) By heating tetraborane in a sealed glass tube at about 373 K, when a mixture containing B_2H_6 and traces of B_5H_9 and B_6H_{10} is produced.

(v) By the reaction of sodium borohydride with anhydrous sulphuric acid or phosphoric acid.

$$2NaBH_4 + H_2SO_4 \longrightarrow B_2H_6 + Na_2SO_4 + 2H_2$$

(vi) By the hydrogenation of boron trioxide at high pressure in the presence of aluminum and aluminum chloride.

$$B_2O_3 + 2Al + 3H_2 \longrightarrow B_2H_6 + Al_2O_3$$

Properties

(1) Diborane is a gas and is stable at low temperatures.

(2) When heated, it changes into a number of other boranes.

$$B_2H_6 \longrightarrow B_4H_{10}\ ,\ B_5H_9\ ,\ B_5H_{11}\ ,\ B_6H_{10}\ \text{etc.}$$

(3) On combustion, it releases large amount of energy.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O;\ \Delta H = -2000\ \text{k.J.}$$

(4) It is readily decomposed by water into boric acid and hydrogen.

$$B_2H_6 + 6H_2O \longrightarrow 2H_3BO_3 + 6H_2$$

(5) Reaction with methyl alcohol gives methyl borate:

$$B_2H_6 + 6CH_3OH \longrightarrow 2B(OCH_3)_3 + 6H_2$$

(6) It dissolves in strong alkali giving metaborates and hydrogen.

$$B_2H_6 + 2KOH + 2H_2O \longrightarrow 2KBO_2 + 6H_2$$

(7) It reacts with dry hydrogen chloride in presence of aluminium chloride forming chlorodiborane.

$$B_2H_6 + HCl \longrightarrow B_2H_5Cl + H_2$$

In the same manner, it reacts with HBr and HI.

(8) It reacts with chlorine at 298 K forming boron trichloride:

$$B_2H_6 + 6Cl_2 \longrightarrow 2BCl_3 + 6HCl$$

(9) It combines with hydrides of alkali metals to form complex hydride:

$$B_2H_6 + 2NaH \longrightarrow 2NaBH_4$$

(10) Diborane reacts with ammonia and the product depends upon the temperature of the experiment as given below:

(i) *At low temperature (153 K)*

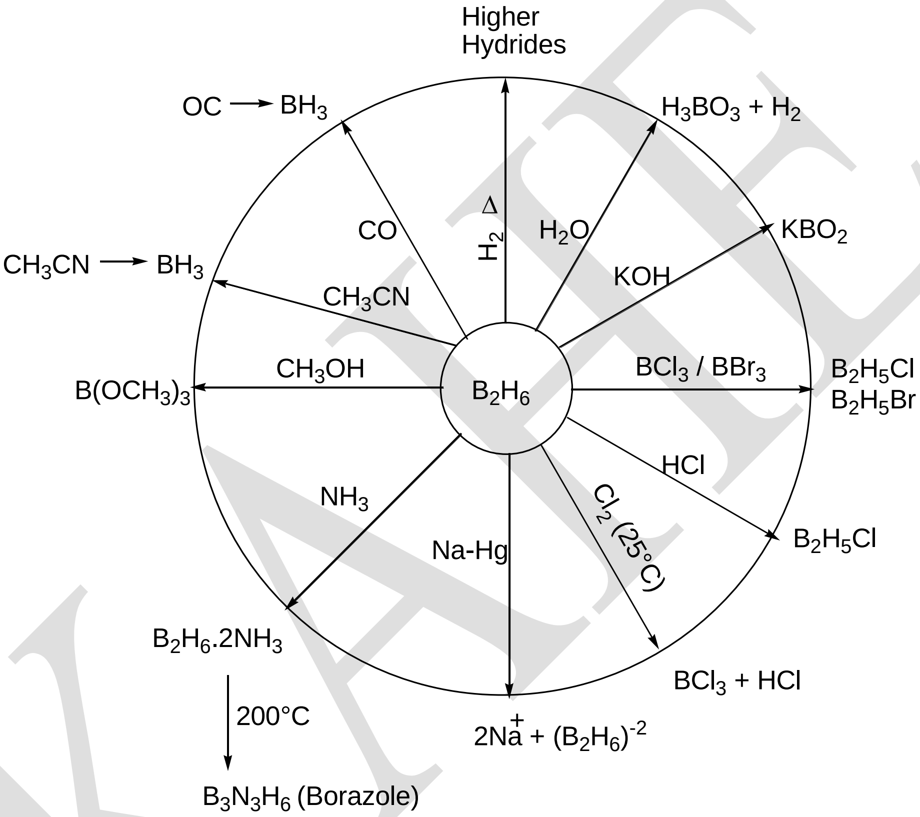
$$B_2H_6 + 2NH_3 \longrightarrow B_2H_6.2NH_3$$

(ii) *At high temperature (473 K)*

$$3B_2H_6 + 6NH_3 \longrightarrow 2B_3N_3H_6 + 12H_2$$

$$\text{(or) } 3B_2H_6 \cdot 2NH_3 \longrightarrow 2B_3N_3H_6 + 12H_2$$

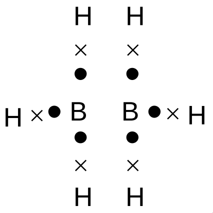
Some important reactions of diborane are summarized in the following figure.



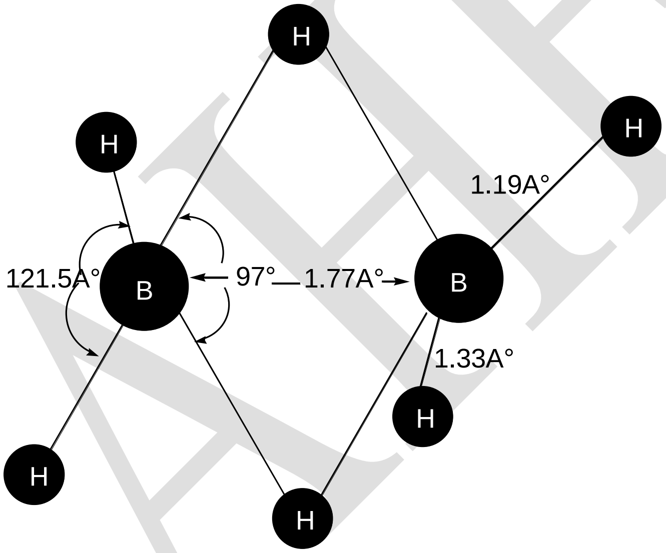
STRUCTURE OF DIBORANE

Diborane (in fact, all boranes) is of great interest from the point of view of their electronic structure. B_2H_6 serves as an interesting example of *electron deficient compound*.

(i) Boron (atomic number 5 with electronic configuration, in the excited state, as $1s^2 2s^1 2px^1 2py^1$ has three electrons for sharing. Hence, it can link to three hydrogen atoms. While doing so, there are no electrons left to form a bond between two boron atoms as shown in the figure.



(ii) Electron diffraction and infrared experimental results indicate that B_2H_6 possesses the following structure.

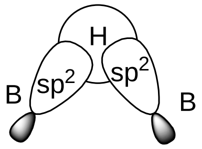


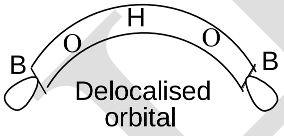
B_2H_6 molecule contains two co-planar BH_2 groups and the remaining two H atoms lie above and below the plane linking the BH_2 groups and prevent rotation between the two boron atoms.

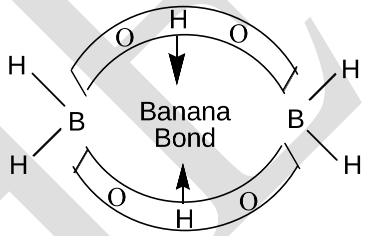
Four hydrogen atoms, two attached to boron on the left and two on the right, are called *terminal hydrogens*. The remaining two hydrogens which link the two BH_2 group are known as the *bridging atoms*. The two boron atoms and the four terminal hydrogen atoms lie in the same plane while the two bridging hydrogen atoms, one above and the other below, lie in a plane perpendicular to this plane.

Nature of bonds in hydrogen bridges

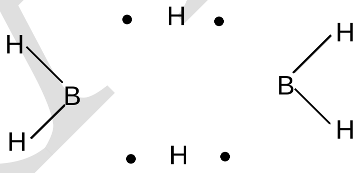
The nature of bond in the hydrogen bridges is now well established. These bonds are quite unique indeed. The two bridges involve four electrons (one electron from each boron atom and one from each hydrogen atom) and are thus abnormal bonds. An sp^2 hybridized orbital from each boron atom overlaps with the 1s orbital of the hydrogen giving a delocalized orbital containing one pair of electrons and covering all the three nuclei of each B.H.B. set and makes up one of bridges. Diborane molecule contains two such bonds.







This type of bond is called *3-centre, 2-electron bond.* Since, one electron pair is shared between three atoms instead of two, the strength of the bond in only one half of the strength of a normal 2-centre, 2-electron bond. The structure of diborane in a simpler form may be represented as in the following figure.



SODIUM BOROHYDRIDE, $NaBH_4$

Sodium borohydride is an example of complex borohydride and contains the complex ion, BH_4^-.

Preparation

(1) Sodium borohydride is obtained by treating sodium hydride with methyl borate in tetrahydrofuran solvent.

$$4NaH + B(OCH_3)_3 \longrightarrow NaBH_4 + 3CH_3ONa$$

(2) Sodium hydride reacts with diborane to form $NaBH_4$.

$$2NaH + B_2H_6 \longrightarrow 2NaBH_4$$

Uses

(1) It is used as a handy source of diborane:

$$2NaBH_4 + 2HCl \longrightarrow 2NaCl + 2H_2 + B_2H_6$$

(2) It is used in the preparation of lithium borohydride.

$$NaBH_4 + LiCl \longrightarrow LiBH_4 + NaCl$$

(3) It is used as a strong reducing agent in organic as well as inorganic chemistry.

BORAZOLE, BORAZINE, $B_3N_3H_6$

Preparation:

(1) Borazole can be prepared by heating ammonium chloride and boron trichloride mixture and reducing the product obtained with sodium borohydride at 425 K in presence of chlorobenzene :

$$3NH_4Cl + 3BCl_3 \longrightarrow (B_3N_3H_3Cl_3) \xrightarrow{NaBH_4} B_3N_3H_6$$

(2) Diborane reacts with ammonia at 473 K to form borazole :

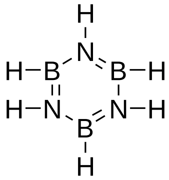
$$3B_2H_6 + 6NH_3 \longrightarrow 2B_3N_3H_6 + 12H_2$$

Properties:

Borazole is a colourless liquid with aromatic smell and solvent properties.

Borazole has a planar structure like benzene. It resembles benzene is some physical and chemical properties. Hence, borazole is called as *'inorganic benzene'*. But, borazole is not aromatic in character.

In benzene, the C = C bonds are non-polar and the nucleus is very resistant to addition reactions. But, borazole nucleus is fairly reactive due to the polarity of bonds. Borazole readily adds three molecules of H_2O, CH_3OH and HCl in which the more negative group generally attaches to the boron atom.



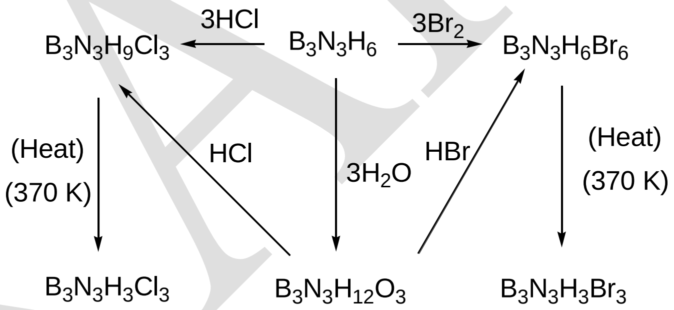
When borazole vapour is heated to 713 K, few hydrogen atoms are eliminated so as to form naphthalene or biphenyl analogue compounds.

Borazole is more susceptible to hydrolysis. It is hydrolysed on boiling with water.

$$B_3N_3H_6 + 9H_2O \longrightarrow 3H_3BO_3 + 3NH_3 + 3H_2$$

On boiling with alkali solution, the borazole ring is ruptured.

Few important reactions of borazole are given below:



INTERHALOGEN COMPOUNDS

The binary covalent compounds formed by halogens amongest themselves are known as interhalogen compounds. They have the general formula, AX_n where A is a large halogen atoms and X is a smaller halogen atom. The value of n is 1, 3, 5 and 7. Some examples are given in the table.

S.No	Type	Example
1.	AX	ClF, BrF, BrCl, ICl, IBr
2.	AX_3	ClF_3, BrF_3, IF_3, ICl_3
3.	AX_5	ClF_5, BrF_5, IF_5
4.	AX_7	IF_7

(i) In naming the compounds, the less electronegative elements are mentioned first.

(ii) All interhalogen compounds are diamagnetic, since n is odd.

(iii) Iodine alone forms all type of inter-halogen compounds mainly due to its big size and electropositive nature.

(iv) It is found that the greater the difference in the electronegativity values of the two halogens, the stronger is the bond between them.

We shall discuss few interhalogen compounds in detail.

IODINE MONOCHLORIDE, (ICl)

Preparation

a) This is prepared by adding iodine to liquid chlorine. The mixture is kept at 308 K for 24 hours to ensure complete reaction.

$$I_2 + Cl_2 \longrightarrow 2\,ICl$$

b) It is also formed by heating iodine with potassium chlorate.

$$KClO_3 + I_2 \longrightarrow KIO_3 + ICl$$

Properties

It is a dark red liquid but solidifies on standing at 290-300 K.

It exists in two forms- stable and metastable form.

It is readily hydrolyzed forming hypoiodite and iodate ions.

$$Cl^- + OI^- \xleftarrow{H_2O} ICl \xrightarrow{H_2O} Cl^- + IO_3^-$$

When current is passed through ICl, iodine is liberated at the cathode and chlorine at the anode.

Alkali metal chlorides like KCl dissolve in it.

$$KCl + ICl \longrightarrow K^+ [ICl_2]^-$$

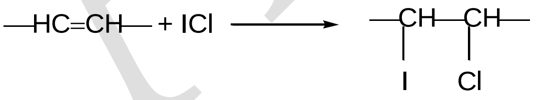
It is used to iodinate organic compounds. Chlorination may also occur depending on the condition.

$$\text{Chlorination} \xleftarrow[\text{Vapour}]{\text{ICl}} \text{Salicylic Acid} \xrightarrow[\text{nitrobenzene}]{\text{ICl in}} \text{Iodination}$$

Uses

(1) Liquid ICl is used as an ionizing solvent.

(2) It finds use as *Wij's reagent* in the estimation of iodine value of fats and oils.

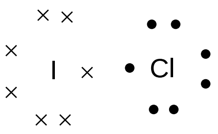


$$—HC{=}CH— + ICl \longrightarrow —\underset{I}{CH}—\underset{Cl}{CH}—$$

(3) It is used to iodinate organic compounds.

Structure

It has the following linear structure:



BROMINE TRIFLUORIDE, BrF_3

Preparation

a) It is prepared by mixing bromine vapour and fluorine in a stream of nitrogen:

$$Br_2 + 3F_2 \longrightarrow 2BrF_3$$

b) It is also formed by the action of ClF_3 on bromine at 283 K:

$$ClF_3 + Br_2 \longrightarrow BrF_3 + BrCl$$

Properties

It is a colourless liquid (b.p. 400 K). It has got high electrical conductivity.

It undergoes auto-ionisation as –

$$2BrF_3 \rightleftharpoons BrF_2^+ + BrF_4^-$$

It reacts with metals and metallic oxides forming salts containing BrF_2^+ and BrF_4^- groups. For example,

$$[BrF_2]^+ [SbF_2]^- ; [BrF_2]^+ [AuF_4]^-$$

$$[BrF_2]_2^{+2} [SnF_6]^{-2} \text{ and } K^+ [BrF_4]^-$$

It coverts may metal oxides and chlorides into fluorides as it is a good fluorinating agent:

$$6M + 2BrF_3 \longrightarrow 6MF + Br_2$$

$$3MCl + BrF_3 \longrightarrow 3MF + BrCl_3$$

It is decomposed violently by water giving bromine, oxygen, bromic acid ($HBrO_3$) and hydrofluoric acid:

$$3BrF_3 + 5H_2O \longrightarrow O_2 + Br_2 + HBrO_3 + 9HF$$

It displaces oxygen from oxides like SiO_2, CuO etc.

$$3SiO_2 + 4BrF_3 \longrightarrow 3SiF_4 + 2Br_2 + 3O_2$$

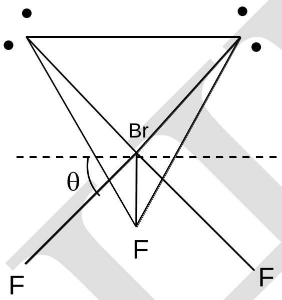
Uses

(1) BrF_3 is used as a solvent.

(2) It is a good fluorinating agent.

Structure

In bromine trifluoride molecule, ten electrons are present in the valency shell of the bromine atom. Out of these, two pairs are lone pairs. The expected geometry is trigonal bipyramidal. But due to the presence of the two lone pairs, the shape is distorted. To avoid repulsion, the bonding pairs contract and it has a *bent T shape*. It makes use of sp^3d-hybridization.



IODINE PENTAFLUORIDE, IF_5

Preparation

a) It is prepared by passing fluorine (diluted with nitrogen) over iodine in a heated quartz tube :

$$I_2 + 5F_2 \longrightarrow 2IF_5$$

b) It is formed by the action of fluorine on I_2O_5:

$$2I_2O_5 + 10F_2 \longrightarrow 4IF_5 + 5O_2$$

c) It can also obtained by heating I_2 with silver fluoride :

$$I_2 + 10AgF \longrightarrow 2IF_5 + 10Ag$$

Properties

It is a colourless liquid (b.p. 330 K). It is a good conductor of electricity as it undergoes self ionization as

$$2IF_5 \longrightarrow IF_4^+ + IF_6^-$$

It reacts with water to form iodic and hydrofluoric acids:

$$2IF_5 + 5H_2O \longrightarrow 10HF + I_2O_5$$

$$I_2O_5 + H_2O \longrightarrow 2HIO_3$$

When heated to about 773 K it decomposes to iodine and iodine heptafluoride.

$$7IF_5 \longrightarrow 5IF_7 + I_2$$

Boiling iodine pentafluoride dissolves potassium fluoride to give, $K^+[IF_6]^-$.

Metals like silver, mercury, iron and copper are slowly attacked by IF_5. With chlorine it gives chlorine trifluoride.

$$4Cl_2 + 3IF_5 \longrightarrow 5ClF_3 + 3ICl$$

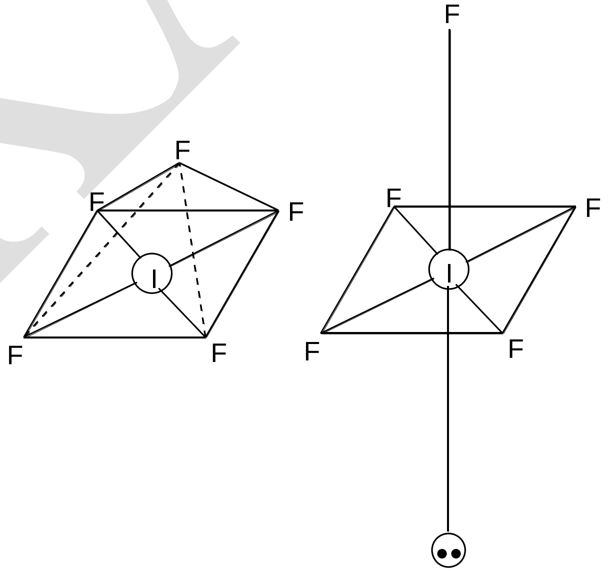
The alkali metals, sulphur, bromine react when heated.

Uses

IF_5 is used as an ionizing solvent.

Structure

There are six pairs of electrons around the central atom, iodine. Of these one is a lone pair. Therefore, the expected geometry of octahedron is slightly distorted and the molecule has a square pyramidal structure.



Chemistry of iodine heptafluoride, IF_7

Preparation

(i) It can be prepared by passing fluorine over IF_3 or IF_5 at 300°C.

$$IF_3 + 2F_2 \xrightarrow{300°C} IF_7$$
$$IF_5 + F_2 \xrightarrow{300°C} IF_7$$

(ii) It can be prepared from the following reaction.

$$PbI_2 + 8F_2 \longrightarrow PbF_2 + 2IF_7$$

(iii) It can also be prepared by passing excess fluorine over gaseous iodine at 300°C.

$$I_2 + 7F_2 \longrightarrow 2IF_7$$

Properties

It is a colourless gas with m.p. 6.5°C. It is diamagnetic in nature.

IF_7 is a stronger fluorinating agent than IF_5. It reacts with most elements in cold or on warming including glass or silica at 100°C.

$$SiO_2 + 2IF_7 \longrightarrow SiF_4 + 2IOF_5$$

Vapours of IF_7 undergo smooth hydrolysis to HIO_4 and HF.

$$IF_7 + 4H_2O \longrightarrow HIO_4 + 7HF$$

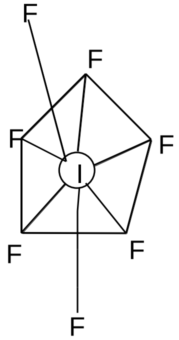
An oxoflouride (IOF_5) is formed with less amount of water at room temperature.

$$IF_7 + H_2O \longrightarrow 2HF + IOF_5$$

It react with most metal (except the platinum group), non metals including Cl_2 and I_2, water (to give periodate and fluoride ions), many inorganic compounds and a verity of organic materials.

It explodes when heated with hydrogen.

Two of seven fluorine atoms present in IF_7 can easily be removed.



Uses

It is used as a fluorinating agent.

Basic property of iodine

Metallic or basic properties of elements increase on descending a group. For example, in group IVA, VA and VIA, the first elements namely C, N and O are nonmetals while the heavier element in these groups –Pb, Bi and Po are metals. In the same manner, coming towards the lower end of the halogen group, iodine possesses considerable electro positive character. As a result, iodine forms many compounds (simple or complex) in which it is supposed to exist as I^+ and I^{3+}.

Few compounds of I^+ *are –*

ICl, ICN, HIO, $I(py)_2NO_3$, $I(py)_2ClO_4$, $I(py)\ CH_3COO$, $I(py)C_6H_5COO$, I_2SO_4, INO_3

Few compounds of I^{3+} *are –*

ICl_3, IPO_4, $I\ (NO_3)_3$, $(IO)_2\ SO_4$, $I(CH_3COO)_3$

Evidences for I^+

(i) Molten ICl conducts electricity and on electrolysis only iodine is liberated at the cathode. It is presumed that ICl ionises as

$$ICl \longrightarrow I^+ + Cl^-$$

$$\text{or, } 2ICl \longrightarrow I^+ + ICl_2^-$$

Molten ICN behaves similarly during electrolysis.

(ii) When a solution of iodine monochloride in an inert solvent is passed through a column of cationic ion exchange resin, some iodine is retained on the resin. This provides another proof for the existence of I^+.

(iii) A number of stable coordination compounds of monopositive iodine (with pyridine) are prepared.

Evidences for I^{3+}

(i) Electrolysis of ICl_3 in the molten state liberated Cl_2 and I_2 at both the electrodes. This is due to the following ionization

$$2ICl_3 \longrightarrow ICl_2^+ + ICl_4^-$$

(ii) When molten iodine acetate is electrolysed using silver electrodes, one equivalent of silver iodine is formed at the cathode for every 3 faradays of electricity passed. This observation shows that the compound ionises as:

$$I(CH_3COO)_3 \longrightarrow I^{3+} + 3CH_3COO^-$$

Sodium hydrosulphite, $Na_2 S_2 O_4$

Preparation

a) The salt is formed by reducing sodium bisulphite saturated with sulphur dioxide with zinc dust. Thin prisms of $Na_2 S_2 O_4 .2H_2O$ are obtained.

$$2NaHSO_3 + Zn + SO_2 \longrightarrow ZnSO_3 + Na_2S_2O_4 + H_2O$$

b) It is also obtained by the action of sulphur dioxide diluted with hydrogen over sodium hydride.

$$2NaH + 2SO_2 \longrightarrow Na_2S_2O_4 + H_2$$

c) Electrolytic reduction of sodium sulphite also yields the salt.

Properties

It decomposes on heating:

$$2Na_2S_2O_4 \xrightarrow{\Delta} Na_2S_2O_3 + SO_2 + Na_2SO_3$$

The salt is stable in the solid state. But in aqueous solution, it decomposes slowly. In the presence of acids, the decomposition is very rapid.

A solution of the salt on acidification with sulphuric acid or phosphoric acid gives a red coloured solution but the colour fades away very soon. This may be stabilised by the addition of SO_2. The red colour may be due to the presence of free acid, $H_2 S_2 O_4$.

Solution of the salt disproportionates to bisulphite and thiosulphate:

$$2S_2O_4^{2-} + H_2O \longrightarrow 2HSO_3^- + S_2O_3^{2-}$$

Sodium dithionite is a powerful reducing agent. It bleaches indigo or vat dyes.

$$Na_2S_2O_4 + 2H_2O \longrightarrow 2NaHSO_3 + 2[H]$$

Oxidizing agent like iodine, iodate and permanganate are reduced by this salt.

It reduces ferric sulphate to ferrous sulphate in acidic medium:

$$Fe_2(SO_4)_3 + Na_2S_2O_4 + H_2SO_4 \longrightarrow 2NaHSO_4 + 2FeSO_4 + 2SO_2$$

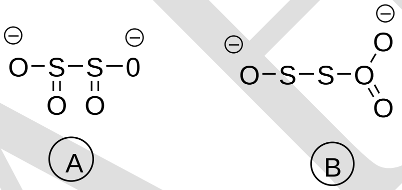
Uses

(1) It is employed as a reducing agent for the conversion of indigo to thio indigo.
(2) It is used in bleaching fabrics.
(3) It is used to absorb oxygen in gas analysis.

Structure

The dithionate ion is given the following structure (A):

The S-S bond length is abnormal and sulphur-oxygen bonds show considerable double bond character. The another possible structure is (B):



PER ACIDS OF SULPHUR

Two per acids of sulphur are known. They are-

(i) Permono sulphuric acid or *Caro's acid,* H_2SO_5 and
(ii) Perdi sulphuric acid or *Marshall's acid*, $H_2S_2O_8$.

Caro's Acid

Preparation

a) The acid prepared by the action of hot concentrated sulphuric acid over potassium perdisulphate at low temperature. It is allowed to stand for an hour and the mixture is poured over ice:

$$K_2S_2O_8 + H_2SO_4 \longrightarrow K_2SO_4 + H_2S_2O_8$$

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

b) The acid may also be obtained by the action of hydrogen peroxide on calculated quantity of chlorosulphonic acid Cl-SO_2-OH

$$H\text{-}O\text{-}O\text{-}H + Cl—SO_2—OH \longrightarrow H_2SO_5 + HCl$$

c) In aqueous solution, perdisulphuric acid is slowly hydrolyzed to give H_2SO_5:

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

Properties

The anhydrous acid is a white crystalline solid (m.p.45°C). Fairly stable but loses oxygen. It has strong oxidizing properties-

a) It liberates Cl_2 and I_2 from their respective halides immediately *(distinction from Marshall's acid)*

$$2KI + H_2SO_5 \longrightarrow I_2 + K_2SO_4 + H_2O$$

b) It oxidises aniline to nitrobenzene, sulphur dioxide to sulphur trioxide and ferrous salts to ferric salts:

$$C_6H_5NH_2 \xrightarrow{H_2SO_5} C_6H_5NO_2$$

$$SO_2 + H_2SO_5 \longrightarrow H_2SO_4 + SO_3$$

$$2FeSO_4 + H_2SO_5 \longrightarrow Fe_2(SO_4)_3 + H_2O$$

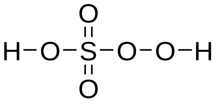
c) With H_2O_2 it evolves oxygen**:**

$$H_2SO_5 + H_2O_2 \longrightarrow H_2SO_4 + H_2O + O_2$$

No solid salts of this acid are known.

Structure

It is shown to possess the following structure:



$$H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-O-H$$

Marshall's Acid

Preparation

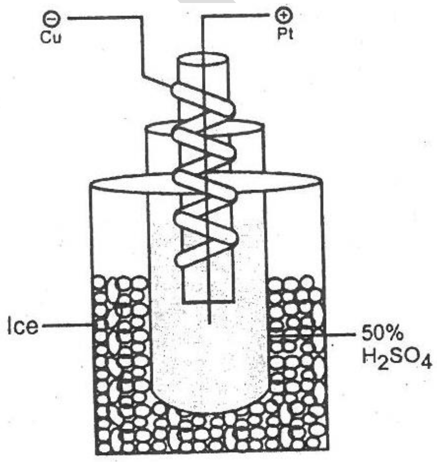
a) The anhydrous acid is obtained by adding one volume of H_2O_2 to two volume of chlorosulphonic acid.

$$\mathrm{H{-}O{-}SO_2{-}Cl + H{-}O{-}O{-}H + Cl{-}SO_2{-}O{-}H \longrightarrow}$$

$$\mathrm{2HCl + H{-}O{-}SO_2{-}O{-}O{-}SO_2{-}O{-}H}$$

This is known as *d Ans and Friedrich's method.*

b) It may also be prepared by electrolysing a 50-60% conc.H_2SO_4 at low temperature. Concentrated sulphuric acid is taken in a test tube. A copper coil dipped in the acid acts as cathode. The anode is a fine platinum wire inside a glass tube. The apparatus is kept in an ice bath. When a current of about one ampere is passed, hydrogen appears at the cathode and a solution of the acid is obtained at the anode. Dilute hydrochloric acid is added to catalyze the reaction.



The possible mechanism is:

$$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$$

At cathode: $H^+ + e^- \longrightarrow H; \quad 2H \longrightarrow H_2$

At anode: $2HSO_4^- \longrightarrow H_2S_2O_8 + 2e^-$

Properties

It is a crystalline solid. Fairly stable at ordinary temperature.

a) On warming it loses oxygen:

$$2H_2S_2O_8 \longrightarrow 2H_2SO_4 + 2SO_3 + O_2$$

b) In aqueous solution it is slowly hydrolysed into sulphuric acid and permono sulphuric acid:

$$H_2S_2O_8 + H_2O \longrightarrow H_2SO_4 + H_2SO_5$$

c) The acid and its salts are powerful oxidising agents. They oxidise ferrous salts to ferric salts, Mn(II) salts to Mn(VII) and chromic salts to dichromates:

$$2FeSO_4 + H_2S_2O_8 \longrightarrow Fe_2(SO_4)_3 + H_2SO_4$$

d) It liberates iodine from potassium iodide but slowly *(distinction from Caro's acid).*

$$2KI + H_2S_2O_8 \longrightarrow K_2SO_4 + H_2SO_4 + I_2$$

e) Many metals dissolved in potassium perdisulphate:

$$K_2S_2O_8 + Zn \longrightarrow K_2SO_4 + ZnSO_4$$

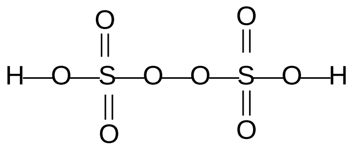
Uses

(1) Perdisulphates are used in the commercial preparation of H_2O_2.

(2) In dyeing industry $H_2S_2O_8$ is used as an oxidising agent.

Structure

It is shown to possess the following structure:



$$H-O-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-O-O-\overset{O}{\overset{\|}{\underset{\underset{O}{\|}}{S}}}-O-H$$

Difference between Caro's acid and Marshall's acid

S.No	Reaction	H_2SO_5	$H_2S_2O_8$
1.	With acidified Potassium iodide	liberates iodine readily	liberates iodine slowly
2.	With aniline	forms nitrobenzene	froms aniline black

Text Book:

1. Thangamani, A. (2019). *Text Book on Allied Chemistry* (I Edition). Coimbatore: Karpagam Publication.

Reference Book:

1. Gopalan, R., and Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. Define chromophore with examples.
2. What are the diseases caused by the deficiency of vitamin A, and B_1?
3. How to prepare methyl orange azo dyes.
4. Define auxochrome with examples.
5. Write the preparation of methyl orange dye.
6. What is meant by sulpha drugs?
7. Define bathochromic shift with examples.
8. Write the preparation of Malachite green dye.
9. Write the preparation of sulphadiazine.

10. Define hypsochromic shift with examples.
11. How is sulphanilamide prepared from benzene?
12. How is prontosil prepared?
13. Name few sulpa drugs with their structure.
14. Explain classification of dyes according to application.
15. Write the structure of methyl orange, chrysoidine and para red and mention the chromophore and auxochrome in it.

PART-C (Each Question Carry Six Marks)

1. Explain the classification of dyes with examples.
2. Discuss the preparation and mechanism of action of sulpha drugs.
3. (i) What are the requisites of a dye.
   (ii) How are dyes classified?
4. (i) What is an antibiotic? Give examples.
   (ii) Write a note on penicillin.
5. (i) Write note on prontosil.
   (ii) Explain atleast one preparation of triphenylmethane dyes, azo dyes, vat dyes and mordant dyes.
6. (i) What are vitamins.
   (ii) How are vitamins classified? Give examples.
7. (i) How is sulphafurazole synthesized .
   (ii) Write the structure formula of some sulpha drugs and the diseases they cure.
8. Write the following for (a) retinol (b) dehydroretinol (c) thiamine (d) riboflavin (e) ascorbic acid
   (i) molecular formula (ii) daily requirement (iii) deficiency diseases (iv) sources.
9. Write a note on (i) pencillin (ii) chloromycetin.
10. Write the structure, sources, and diseases caused by the deficiency of the following-
   (i) vitamin A (ii) vitamin B_1 (iii) vitamin B_2 (iv) vitamin C.

KARPAGAM ACADEMY OF HIGHER EDUCATION

(*Deemed to be University*)
(*Established Under Section 3 of UGC Act, 1956*)
Pollachi Main Road, Eachanari Post, Coimbatore–641 021.

DEPARTMENT OF CHEMISTRY

UNIT-I

CHEMICAL BONDING

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. Molecular orbital theory was developed by

a) Hund and Mullikan b) Sir.H. Davy c) Sidgwick d) Werner

2. Valence shell atomic orbitals are mixed up to form a new set of orbitals known as

a) atomic orbitals **b) molecular orbitals** c) mixed orbitals d) special orbitals

3. Molecular orbital theory is based on

a) quantum mechanics b) classical mechanics c) non-classical mechanics

d) molecular mechanics

4. Bonding molecular orbital is represented as

a) $\Psi = \Psi_A + \Psi_B$ b) $\Psi^* = \Psi_A - \Psi_B$ c) $\Psi^* = \Psi_A + \Psi_B$ d) $\Psi = \Psi_A < \Psi_B$

5. The bonding molecular orbitals the electron density in between the nuclei is

a) high b) low c) same d) medium

6. The bonding molecular orbitals is formed by the addition overlap of

a) atomic orbitals b) molecular orbitals c) valence orbitals d) inner orbitals

7. The electrons would prefer to occupy the orbitals singly rather than getting paired according to

a) the Pauli Exclusion Principle **b) the Hunds rule** c) Fajans rule d) the octet rule

8. Identify the correct statement:

a) N_2 has a bond order 3 b) N_2 is paramagnetic c) F_2 is more stable than N_2

d) F_2 is more stable than O_2

9. Bond order of the molecule is 3, out of this

a) one sigma bond b) two pi-bond c) one sigma bond and one pi-bond

d) one sigma bond and two pi-bond

10. Which of the following is the correct statement? The fluorine molecule is

a) heteronuclear diatomic b) paramagnetic c) polar in nature **d) diamagnetic**

11. The electrons are now placed in the various molecular orbitals in the increasing order of energy according to

a) Aufbau Principle b) Pauli Principle c) Hunds rule d) Fajans rule

12. The bond energy of F_2 molecule is low due to

a) less non-bonding electrons **b) more anti-bonding electrons**

c) less anti-bonding electrons d) more bonding electrons

13. The maximum number of electrons that could be accommodated in a molecular orbital is

a) the Pauli Exclusion Principle b) the Hunds rule c) Fajans rule d) the Aufbau Principle

14. The actual number of bonds present in the molecule is known as

a) bond length **b) bond order** c) bond angle d) torsion angle

15. $\Psi^* = \Psi_A - \Psi_B$ is represented as

a) bonding molecular orbital **b) anti-bonding molecular orbital**

c) non-bonding molecular orbital d) covalent molecular orbital

16. Bond order of hydrogen molecule is

a) 4 b) 6 c) 2 **d) 1**

17. Bond energy of hydrogen molecule is

a) 532 kJ/mol b) 632 kJ/mol c) 434 kJ/mol **d) 432 kJ/mol**

18. H_2 molecule is

a) paramagnetic **b) diamagnetic** c) ferromagnetic d) anti-ferromagnetic

19. Hydrogen molecule is simplest

a) monoatomic molecule b) polyatomic molecules **c) diatomic molecule**

d) triatomic molecules

20. The bond order of fluorine molecule is

a) 3 b) 2 c) 4 **d) 1**

21. The nitrogen molecule has a bond energy of

a) 155 kJ/mol b) 432 kJ/mol **c) 942 kJ/mol** d) 941 kJ/mol

22. Nitrogen molecule has

a) one σ bond and 2π bonds b) 2σ bond and 1π bonds c) 3σ bonds d) 3π bonds

23. How many electrons in the valence shell of nitrogen atom?

a) 6 **b) 5** c) 4 d) 3

24. Permonosulphuric acid is known as

a) caro's acid b) marshall's acid c) boric acid d) peracid

25. Diborane is the simplest hydrides of

a) boric acid **b) boron** c) methyl borate d) meta borate

26. Bond order of N_2 molecule is

a) 2 **b) 3** c) 4 d) 5

27. The fluorine molecule has a bond energy of

a) 942 kJ/mol b) 941 kJ/mol **c) 155 kJ/mol** d) 432 kJ/mol

28. Diborane is an

a) electron rich compound **b) electron deficient compound**

c) electron precise compound d) ionic hydride

29. Diborane reacts with methyl alcohol to gives

a) methyl borate b) metaborates c) ethyl borate d) chlorodiborane

30. Borazine is known as

a) inorganic aniline b) inorganic phenol c) inorganic toluene **d) inorganic benzene**

31. Structure of ICl is

a) bent **b) linear** c) T shape d) square pyramidal

32. Nitrogen molecule is

a) paramagnetic **b) diamagnetic** c) anti-ferromagnetic d) ferromagnetic

33. The molecular formula for borazole is

a) B_2H_6 b) B_4H_{10} c) $B_3N_3H_9$ **d) $B_3N_3H_6$**

34. The oxidation state of iodine in $I(CH_3COO)_3$ is

a) 3 b) 1 c) 2 d) 4

35. How many electrons occupy in bonding molecular orbitals of nitrogen molecules?

a) 8 b) 4 c) 6 d) 10

36. Diborane has

a) 2-centre 3-electrons bond b) 2-centre 2-electrons bond **c) 3-centre 2-electrons bond**

d) 3-centre 3-electrons bond

37. Iodine monochloride is used to

a) fluorinating agent **b) iodinate organic compounds**

c) brominating agent d) nitrating agent

38. Interhalogen compounds are

a) diamagnetic b) paramagnetic c) ferromagnetic d) anti-ferromagnetic

39. Sodium borohydride is an example of

a) complex borohydride b) simple borohydride

c) mixed borohydride d) neutral borohydride

40. Structure of borazine is similar to that of

a) phenol b) biphenyl **c) benzene** d) naphthalene

41. Iodine monochloride is used as

a) Tollens reagent b) Fehlings reagent c) Schiff reagent **d) Wijs reagent**

42. BrF_3 has

a) trigonal shape **b) bent T shape** c) planar shape d) tetragonal shape

43. The hybridization of BrF_3 is

a) sp^2 b) sp^3 **c) sp^3d** d) sp^3d^2

44. Sodium hydrosulphite is used in

a) oxidizing agent **b) bleaching fabrics** c) redox reaction d) preparation of H_2O_2

45. Perdi sulphuric acid is known as

a) marshall’s acid b) caro’s acid c) boric acid d) phosphoric acid

46. The antibonding molecular orbitals the electron density in between the nuclei is

a) low b) same c) high d) medium

47. Caro’s acid has the molecular formula

a) H_2SO_4 **b) H_2SO_5** c) $H_2S_2O_8$ d) $H_2S_2O_3$

48. The oxidation state of sulphur in marshall’s acid is

a) 7 b) 2 **c) 6** d) 4

49. $Na_2S_2O_4$ is known as

a) sodium dithionite b) sodium tetrathionate c) sodium persulphate d) sodium thiosulphate

50. Borazine has

a) trigonal structure **b) planar structure** c) tetragonal structure

d) square planar structure

51. Which one of the following is example for AX_3?

a) ClF_3 b) FBr_3 c) FCl_3 d) ClI_3

52. Diborane reacts with dry hydrogen chloride in presence of aluminium chloride forming

a) boron trichloride b) borazine **c) chlorodiborane** d) borazole

53. BrF_3 is used as

a) a brominating agent **b) a fluorinating agent** c) a Lewis base d) a reducing agent

54. Wijs solution contains

a) ICl b) IBr c) IF_3 d) IF_5

55. The oxidation state of iodine in ICl is

a) 0 b) 2 **c) 1** d) 3

56. The oxidation state of sulphur in caro's acid is

a) 6 b) 8 c) 2 d) 4

57. The molecular formula for marshall's acid is

a) H_2SO_5 **b) $H_2S_2O_8$** c) $H_2S_2O_7$ d) $H_2S_2O_3$

58. Sodium dithionite is a

a) strong reducing agent b) strong oxidizing agent c) weak reducing agent

d) weak oxidizing agent

59. The molecule of IF_5 has a

a) octahedron **b) square pyramidal** c) bent T shape d) tetrahedral

60. IF_5 is used as an

a) iodinating agent b) fluorinating agent **c) ionizing solvent** d) brominating agent

UNIT-II

SYLLABUS

Covalent Bond and Stereoisomerism: Covalent Bond: Orbital overlap, hybridization and geometry of CH_4, C_2H_4 and C_2H_2. Polar effects: Inductive effect-electromeric effect-mesomeric effect- steric effect- hyperconjugation.

Stereoisomerism: Elements of symmetry-polarised light and optical activity-isomerism in tartaric acid-racemisation- resolution- geometrical isomerism of maleic and fumaric acids-keto-enol tautomerism of acetoacetic esters.

CHAPTER-1

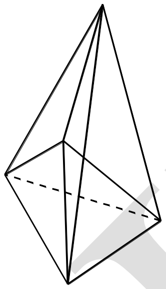
COVALENT BOND

The atomic number of carbon is six and its electronic configuration is $1s^2$, $2s^2$, $2p_x^1$, $2p_y^1$. Since only unpaired electrons are involved in bonding, it appears that the carbon is *divalent*. This bivalency is observed in very few compounds of carbon. But actually carbon exhibits *tetravalency*. This can be achieved by promoting one electron from 2s orbital to empty $2p_z$ orbital of the same carbon. The carbon atom now is said to be in the *excited* state as some energy is required for this process.

	1s	**2s**	**$2p_x$**	**$2p_y$**	**$2p_z$**
Carbon in ground state	↑↓	↑↓	↑	↑	
Carbon in excited state	↑↓	↑	↑	↑	↑

It is obvious that the four unpaired electrons are of two type- s electron and p electrons. Hence, the strength of bond formed by them should have been different. Because the energy of 2s orbital is less than that of 2p orbitals, the carbon atom is expected to form one bond (using the spherical 2s orbital) of different strength than the other three (using three dumb-bell shaped 2p orbitals). The reality is however different, since in methane it was found that the all the four C-H bonds are of equal strength.

Hence it is assumed that these four orbitals 2s, $2p_x$, $2p_y$ and $2p_z$ *mix* up or *deform* to yield four new identical and symmetrically disposed orbitals of exactly equal strength. This process is called *hybridisation* and these orbitals are oriented towards the four corners of a *regular tetrahedron* and subtend an angle of $109^o28'$.



Since the hybridization has taken place by combining one s and three p orbitals, it is called sp^3 *hybridisation or tetrahedral hybridisation.* If the hybridized orbital overlaps along the internuclear axis. i.e., overlapping is *head to head, a* σ (sigma) bond is formed.

Thus, in methane each of the four hybridised orbitals of carbon overlaps with 1s orbital of the hydrogen to yield four sigma bonds.

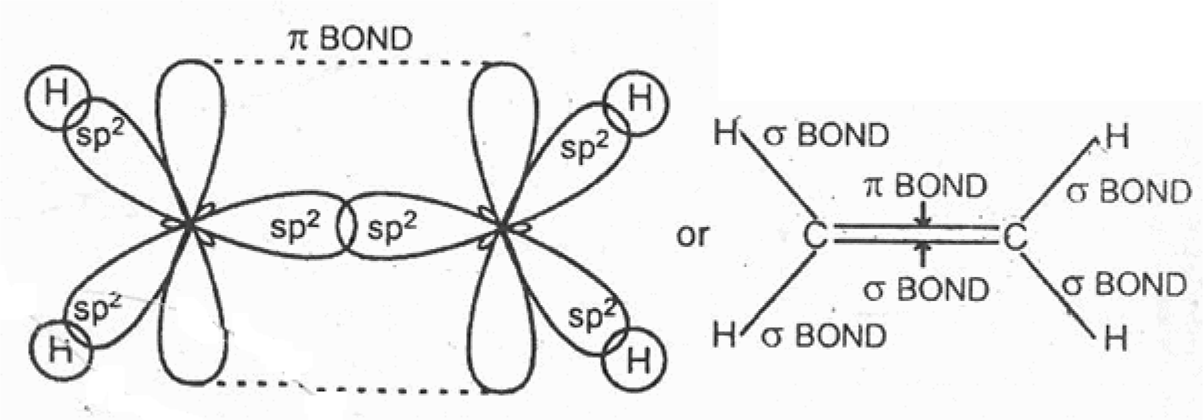
The next homologue, ethane is also formed by sp^3 hybridisation and has seven sigma bonds as all the hybridised orbital overlap along the internuclear axes. Similarly other alkanes and compounds containing a saturated carbon atom can be drawn using sp^3 hybrid orbitals.

The structure of ethylene (ethene) and acetylene (ethyne) can be explained satisfactorily on the basis of hybridisation.

Ethylene (and other alkenes)

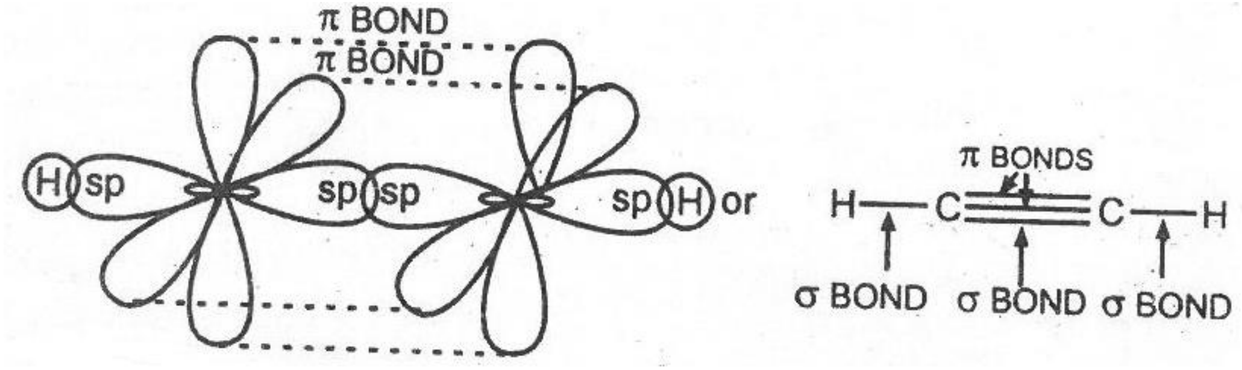
In ethylene to form the required number of bonds, each carbon contributes one s and two p orbitals hybridised to give three sp^2 *hybridised* orbitals. The three hybrid orbitals lie in the same plane and make an angle of 120^o between each other. The two carbon atoms form a σ bond by the overlap of an sp^2 orbital with other sp^2 orbital. The other two sp^2 hybrid orbitals of each carbon atom form two sigma bonds with two hydrogen atoms thus giving five σ bonds in all.

There remains on each carbon atom one unhybridised p orbital perpendicular to the plane of C-H and C-C bond after the formation of σ bonds. The second type of bond between carbon atoms is formed by the *sideways overlap* of these p-orbitals resulting in the formation of pi (π) bond and is shown in the figure.



The electron cloud of this bond is unsymmetrical and concentrates above and below the plane of the sigma bond. Thus, the double bond in ethylene (and in other alkenes) is made up of one sigma and one pi bonds.

By a similar reasoning in acetylene each carbon atom makes use of two sp-hybrid orbitals in the formation of σ- bonds. i.e., one sigma bond with the hydrogen and other sigma bond with the neighbouring carbon. The state of hybridisation is *‘diagonal’* and the angle between the two sp-hybrid orbitals is 180^{o}. This leaves two unhybridised p-orbitals mutually perpendicular to each other and also perpendicular to the hybrid axis. Each pair of this p- orbital’s now overlap in sideways to form two pi-bonds. Thus, the triple bond in acetylene is actually made up of one sigma bond and two pi-bonds. The situation is represented as below.

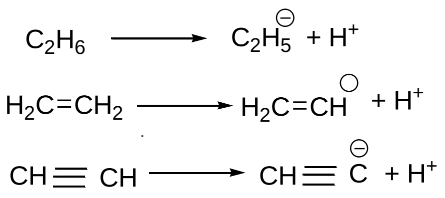


The table summarises the physical constants of aliphatic hydrocarbons.

Molecule	State of hybridization and shape	No. bonds		C-C bond length, Å	Bond energy kJ mole^{-1}	Bond angle	s/p value
		σ	π				
Methane	sp^{3,} tetrahedron	4	0	-	-	109 ° 28'	1:3
Ethane	sp^{3,} tetrahedron	7	0	1.54	347.5	109 ° 28'	1:3
Ethylene	sp^{2}, triangle	5	1	1.33	598.7	120°	1:2
Acetylene	sp, linear	3	2	1.20	812.3	180 °	1:1

Acidic nature of acetylene

The basic requirement for any species to be an acid is that it must release the proton readily and the anion formed should be stable. Let us compare the acidities of ethane, ethylene and acetylene.



$$C_2H_6 \longrightarrow C_2\overset{\ominus}{H_5} + H^+$$

$$H_2C{=}CH_2 \longrightarrow H_2C{=}\overset{\bigcirc}{CH} + H^+$$

$$CH{\equiv}CH \longrightarrow CH{\equiv}\overset{\ominus}{C} + H^+$$

Obviously the unshared pair of electrons of $C_2H_5^{:-}$, $CH_2=CH^{:-}$ and $CH\equiv C^{:-}$ reside in an sp^3, sp^2 and sp orbital respectively. As seen from the table as we proceed along the hydrocarbon series, s-character of the hybrid orbital increases and the p-character decreases.

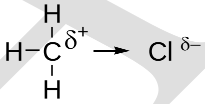
An electron occupying an s-orbital is very close to the nucleus and is held firmly, whereas the electron in a p-orbital is away from the nucleus and is held less tightly. Hence the unshared pair of electrons in acetylide ion, $CH\equiv C^{:-}$ is held more firmly than that in $C_2H_5^{:-}$ and will not be available for protonation. Thus, acetylene is most acidic and ethane least so.

POLAR EFFECTS

1) INDUCTIVE EFFECT

If a covalent bond is formed by two atoms differing much in electronegativity, then the bond is said to be *polarised*. The electron pair shifts towards the more electronegative atom resulting in the origin of fractional charges on the atoms.

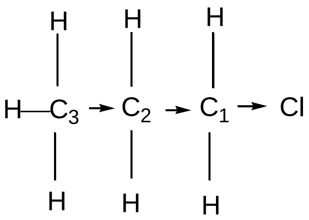
Consider methyl chloride,



$\mathrm{H_3C^{\delta+} \rightarrow Cl^{\delta-}}$

In this molecule, chlorine atom is more electronegative than the carbon atom. Due to this, chlorine pulls the electron pair and acquires a small negative charge.

Let us consider, 1-chloropropane-



$\mathrm{H_3C_3 \rightarrow H_2C_2 \rightarrow H_2C_1 \rightarrow Cl}$

As C_1 is positively charged, it attracts towards itself the electron pair shared between C_1 and C_2. This causes C_2 to acquire a small positive charge but the charge is smaller than the charge on C_1. This *type of electron displacement occurring in saturated compound along a carbon chain is termed, inductive effect.*

It is a permanent effect and decreases rapidly as the distance from the electronegative atom increases. It is represented by → the arrow head pointing towards the more electronegative atom. This effect operates in the case of σ-*electrons only.*

For measurements of relative inductive effect, atoms or groups having greater electron affinity than hydrogen are said to have –I effect. Similarly, atoms or groups having lesser electron affinity than hydrogen are said to have +I effect. Some of the atoms and groups arranged in the increasing order of inductive effect are given as -

Group having – I effect

$\text{H—},\ C_6H_5\text{—},\ \text{OH},\ \text{—}OCH_3,\ \text{—I},\ \text{—Br},\ \text{—Cl},\ \text{—F}$

Group having +I effect

$\text{H—},\ \text{—D},\ \text{—}CH_3,\ \text{—}CH_2R,\ \text{—}CHR_2,\ \text{—}CR_3,\ \text{—}COO^-$

Consequences of Inductive Effect

Relative strength of various aliphatic monocarboxylic acids can be explained with the help of inductive effect.

Consider a simple aliphatic monocarboxylic acid, AH. It undergoes dissociation in water to a smaller extent to form its ions A^- and H^+ in the following way:

$$AH + H_2O \rightleftharpoons H_3O^+ + A^-$$

The equilibrium constant or the acid dissociation constant, K_a is given as,

$$K_a = \frac{[A^-][H^+]}{[AH]}$$

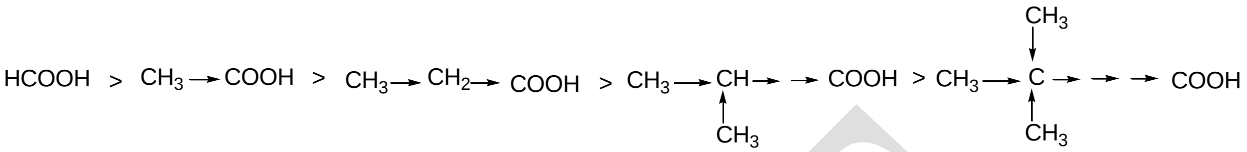
$$\text{and} \quad pK_a = -\log K_a$$

Thus, the K_a or pK_a values amply throw light on the strength of monocarboxylic acids. Evidently, from the definition of pK_a value, *the lower the* pK_a *value, greater is the acid strength.* The pK_a values of few aliphatic acids are reported in the table.

S.No	NAME	FORMULA	pK_a
1.	Formic acid	HCOOH	3.75
2.	Acetic acid	CH_3COOH	4.76
3.	Propionic acid	CH_3CH_2COOH	4.87
4.	Isobutyric acid	$(CH_3)_2$ CH COOH	4.92
5.	Trimethyl acetic acid	$(CH_3)_3$ CCOOH	5.02
6.	Chloroacetic acid	$ClCH_2COOH$	2.85
7.	Dichloroacetic acid	$Cl_2CHCOOH$	1.25
8.	Trichloroacetic acid	Cl_3 C COOH	0.66
9.	Trifluoroacetic acid	F_3 C COOH	0.23
10.	Bromoacetic acid	$BrCH_2$ COOH	2.95
11.	Iodoacetic acid	ICH_2COOH	3.15
12.	α- chlorobutyric acid	CH_3 $CH_2CH(Cl)COOH$	2.85
13.	β- chlorobutyric acid	$CH_3CH(Cl)CH_2COOH$	4.05
14.	γ- chlorobutyric acid	$ClCH_2CH_2CH_2COOH$	4.52

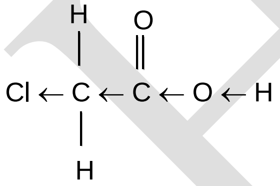
(1) The pK_a values reported in the table clearly show that formic acid is roughly ten times stronger than acetic acid. This is mainly due to the +I effect of methyl group than that of hydrogen. Since the methyl group is electron repelling, it increases the electron density on the carbon of the carboxyl group of acetic acid thereby holding the proton more strongly.

(2) From the table it is also evident that as the number of methyl groups on the α-carbon atom of the acetic acid increases, the acid strength is gradually decreasing. The order of acid strengths is given below:



$$HCOOH > CH_3 \rightarrow COOH > CH_3 \rightarrow CH_2 \rightarrow COOH > CH_3 \rightarrow \underset{\overset{\uparrow}{CH_3}}{CH} \rightarrow \rightarrow COOH > CH_3 \rightarrow \overset{\overset{CH_3}{\downarrow}}{\underset{\overset{\uparrow}{CH_3}}{C}} \rightarrow \rightarrow \rightarrow COOH$$

(3) On the other hand, if we compare the acid strengths of acetic acid and chloroacetic acid, we find that chloroacetic acid is much stronger. Since chlorine atoms has –I effect the electron density of the carbon carrying chlorine is decreased which helps to release the proton readily:



$$Cl \leftarrow \overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}} \leftarrow \overset{\overset{O}{\|}}{C} \leftarrow O \leftarrow H$$

(4) Dichloroacetic acid and trichloro acetic acid are even stronger than monochloro acetic acid because more the number of chlorine atoms on the carbon atom, the greater is the inductive effect.

(5) Because of the large –I effect of three fluorine atoms, the electron density at the α-carbon atom is much lower. Thus, the trifluoro acetic acid is the strongest organic acid known!

(6) The increasing order of the –I effect of the halogen given earlier is further supported form the pK_a value of various halogen substituted carboxylic acids:

$$ClCH_2COOH > BrCH_2COOH > ICH_2COOH$$

2.85 2.95 3.15

(7) As seen from the table, among the isomeric chlorobutyric acids, the position of the chlorine atom in the carboxylic acids determines the acid strength. This is in close harmony with the fact that the inductive effect diminishes rapidly with distance. In other

words, *the farther the chlorine atom from the carboxyl group, the weaker is the acid.* Thus, α-chlorobutyric acid is the strongest among the isomeric acids.

DISCUSSION ON THE BASIC NATURE OF AMINES

All amines are basic. They are stronger bases than ammonia. This is due to the presence of unshared electron pair on the nitrogen atom which accepts proton. The relative basic strengths of amines, however, are based on the readiness with which the lone pair of electrons is available for coordination with a proton.

(1) It would appear that as the number of alkyl group increases, the availability of the lone pair of electrons on nitrogen will be more. This is due to the electron repelling nature (+I effect) of the alkyl groups. On that basis, the order of base strength expected will be:

$$\underset{3^o}{R_3N} > \underset{2^o}{R_2NH} > \underset{1^o}{RNH_2} > NH_3$$

But the actual order, based on the pK_b values reported in table is:

$$R_2NH > RNH_2 > R_3N > NH_3$$

This is due to the *steric hindrance* of the bulky alkyl group which does not allow the lone pair to be readily available for donation to a proton in tertiary amines.

S.No.	Amines	Formula	pK_b
1.	Ammonia	NH_3	4.73
2.	Methyl amine	CH_3NH_2	3.38
3.	Dimethyl amine	$(CH_3)_2NH$	3.32
4.	Trimethyl amine	$(CH_3)_3N$	4.20
5.	Ethyl amine	$C_2H_5NH_2$	3.37
6.	Diethyl amine	$(C_2H_5)_2NH$	3.07
7.	Triethyl amine	$(C_2H_5)_3N$	3.13
8.	Aniline	$C_6H_5NH_2$	9.42

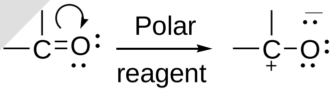
9.	*p*-nitroaniline	*p*- NO_2- C_6H_4-NH_2	12.98
10.	*p*-chloroaniline	*p*- Cl- C_6H_4-NH_2	10.02
11.	*o*-nitroaniline	*o*- NO_2- C_6H_4-NH_2	14.29
12.	*o*-chloroaniline	*o*- Cl- C_6H_4-NH_2	11.36
13.	*p*-methylaniline	*p*- CH_3- C_6H_4-NH_2	8.88
14.	*p*-aminoaniline	*p*- NH_2- C_6H_4-NH_2	7.92

(2) Aniline is weaker base than any aliphatic primary amines due to the electron releasing behavior of the aromatic ring. When the attracting groups such as nitro, chloro are present in the aniline molecule, they reduce further the basic nature of aniline (See Table) since they are stabilised by resonance also.

On the other hand, when -CH_3 or –NH_2 group is present, it increases the electron density on the amino group of aniline, thereby they are stronger bases than aniline.

2) ELECTROMERIC EFFECT

A multiple bond consists of σ and π bonds. Due to the nature of π bonding, the electrons involved in such a combination are loosely held and easily polarisable. Hence, when a compound having double or triple bond is approached by a charged reagent, due to electrostatic attraction, the electrons of the bond are completely polarised or displaced towards one of the constituent atom. Thus,

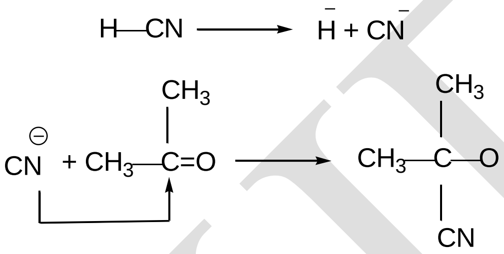


The atom that now acquires the electron pair becomes negatively charged while the other atom gets a positive charge.

The effect, involving the complete transfer of a shared pair of electron in one of the atom joined by a double or triple bond at the requirement of attacking reagent, is known as electromeric effect.

It is a temporary effect and brought into play instantaneously at the demand of the attacking reagent. However, as soon as the attacking reagent is removed, original electronic condition is restored.

An example of the electromeric effect is the reaction of acetone with HCN to form acetone cyanohydrin. When CN^- approaches the acetone molecule, there is a charge separation in this molecule and then CN^- ion attacks at the positive site:



The electromeric effect is indicated by E and represented by a curved arrow showing the direction of shifting of electron pair. In cases where inductive and electromeric effects operate simultaneously, usually the electromeric effect predominates. Electromeric effect is very useful in explaining the mechanism of the most of the ionic organic reactions.

3) RESONANCE (MESOMERIC) EFFECT

When several structures may be assumed to contribute to the true structure of a molecule but none of them can be said to represent it uniquely, then the molecule is referred to as a *resonance hybrid* and the phenomenon is termed as *resonance.*

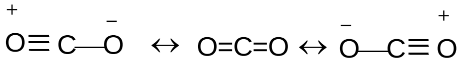
It is somewhat abstract, but it can be better understood if we consider the structure of a simple molecule carbon dioxide.

$$O = C = O$$

(I)

The above structure dose not account for all observed properties although it can explain many. The C-O bond length in CO_2 molecule is 1.15 Å whereas it is expected to be 1.22 Å on the basis of the above structure.

Again, the heat of formation of carbon dioxide is 1592 kJ mol^{-1}. Whereas on the basis of the above structure it is expected to be approximately 1466 kJ mol^{-1}. These discrepancies can be explained only if we assume the following resonance hybrid for carbon dioxide:



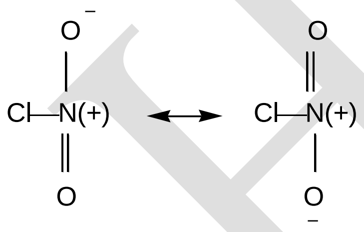
$$\overset{+}{O}\equiv C-\overset{-}{O} \leftrightarrow O=C=O \leftrightarrow \overset{-}{O}-C\equiv \overset{+}{O}$$

The different in energy i.e., 126 kJ/mol is regarded as *resonance energy*.

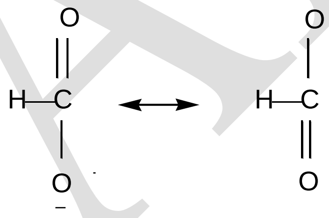
Few other examples –

(1) Benzene (resonance energy, 150.6 kJ/mol)

(2) Nitryl chloride, NO_2Cl



(3) Formate ion, $HCOO^-$



(4) Naphthalene, $C_{10}H_8$ (resonance energy, 255.2 kJ/mol)

(5) Anthracene, $C_{14}H_{10}$ (resonance energy, 351.2 kJ/mol)

Conditions for resonance

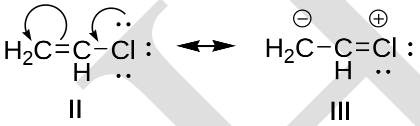
1) The arrangement of the atoms must be identical.
2) The energy content of all the canonical forms must be nearly the same.
3) Each canonical form must have same number of unpaired electrons.

Effect of resonance

The phenomenon resonance has marked effects on the physical and chemical properties of compounds. We shall discuss few of them in this section.

(i) Dipole moment

The phenomenon resonance can account for the polar character of certain molecules. For instance, the existence of a certain amount of polarity and the lower value of dipole moment (1.44 D) in vinyl chloride can only be explained by resonance:

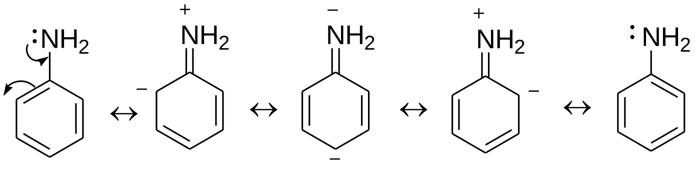


In order to account for the low dipole moment, the lower C-Cl bond distance (1.72 Å) than that in ethyl chloride (1.78 Å) and for its inertness towards nucleophiles structure III contributes significantly to the resonance hybrid structure of vinyl chloride.

(ii) Basic property of aniline

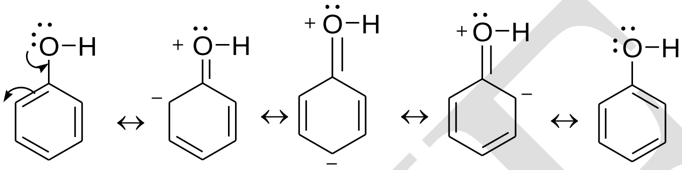
Aniline is a weaker base ($pK_b = 9.42$) than the primary aliphatic amines, because aryl group is electron withdrawing and decreases the electron availability at the nitrogen atom. Moreover the lone pair of electrons on the nitrogen atom is involved in resonance (which is not possible in aliphatic amines).

Hence, electron pair is lesser available for protonation. The small positive charge on the nitrogen atom tends to repel a proton.

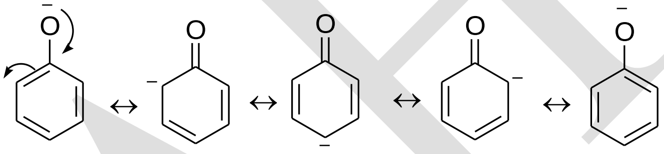


(iii)Acidic nature of phenol

Aliphatic alcohols are neutral whereas phenol is an acid (pKa =10). The oxygen atom of the –OH group in phenol, due to resonance, acquires a positive charge and so proton is released easily. This type of resonance is not possible in alcohols.



Moreover, when phenol ionises, the phenoxide ion is also stabilised by resonance.



(iv)Stability of free radicals

The following relative order of stability of free radicals is explained by resonance.

$(C_6H_5)_3C\bullet > (C_6H_5)_2CH\bullet > C_6H_5CH_2\bullet > CH_3\bullet$

3° 2° 1°

The tertiary free radical is the most stable because the odd electron can delocalise over the central carbon atom and totally ten resonance hybrids stabilise the triphenyl methyl, $(C_6H_5)_3C^{\bullet}$ free radical. The corresponding numbers of resonance hybrids for secondary and primary free radicals are seven and four respectively. Hence, they are less stable.

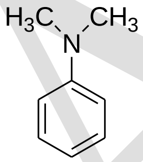
4) STERIC EFFECT

Since a proton occupies a very small volume, its *overcrowding effects or steric effects* are not of much significance in proton transfer reactions. However, when protons are replaced by bulky groups they cause steric hindrance. This may indirectly influence the nature by interfering in resonance stabilisation. This will retard the rate of the reaction and may alter the mechanism of the reaction as well. Because all atoms of a delocalised system must be in one plane, any steric factor that prevents atom from assuming coplanarity reduces resonance and therefore destabilises the whole system.

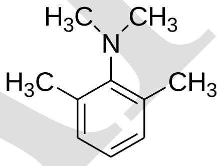
There are few reactions in which the rate of the reaction is enhanced by steric factor and are said to *steric accelerated* reactions.

The properties of ortho compounds usually differ from those of the corresponding meta- and para-isomers. These effects are known as *ortho effect*. Few instances are discussed below –

N, N-dimethylaniline (**1**) undergoes coupling with benzenediazonium chloride whereas 2, 6-dimethyl-N, N-dimethylaniline (**2**) does not couple under these conditions.

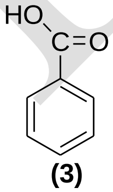


(1)

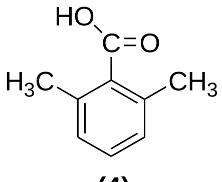


(2)

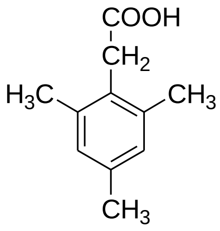
Benzoic acid (**3**) forms methyl ester with methanol and hydrogen chloride but under the same conditions di-ortho substituted benzoic acid (**4**) fails to form ester. But mesityl acetic acid (**5**) forms ester since the carboxylic group is far away from the bulky methyl groups.



(3)

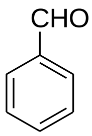


(4)

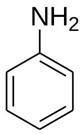


(5)

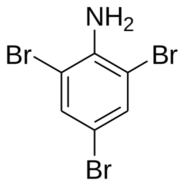
Benzaldehyde (**6**) reacts aniline (**7**) to form an anil or Schiff's base but not with sym-tribromoaniline (**8**).



(6)



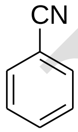
(7)



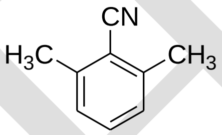
(8)

It has been found that triethylamine, $(C_2H_5)_3N$ is a weaker base (pK_b=3.13) than diethylamine, $(C_2H_5)_2NH$ (pK_b = 3.07) although it should have been otherwise on the basis of inductive effect alone. This apparent anomaly is due to steric hindrance caused by ethyl group.

Upon hydrolysis, phenylcyanide (**9**) gives benzoic acid but 2,6- dimethylphenylcyanide (**10**) hardly yields corresponding 2,6-dimethyl benzoic acid under identical conditions.



(9)



(10)

Steric hindrance increases the base strength of aromatic amines. Thus, N, N-dimethyl-o-toluidine is a stronger base (pK_b =8.1) than the N, N- dimethyl aniline (pK_b =8.85).

5) HYPERCONJUGATION

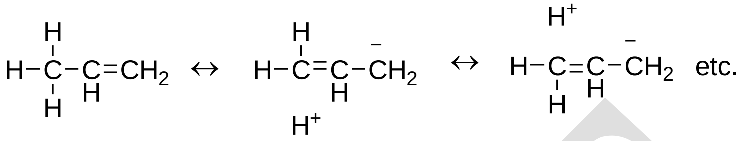
The relative magnitude of inductive effect of alkyl group normally expected to follow the order:

$$\underset{3^\circ}{R_3C—} > \underset{2^\circ}{R_2CH—} > \underset{1^\circ}{RCH_2—} > CH_3$$

When, however the alkyl groups are attached to an unsaturated system, e.g, a double bond or a benzene nucleus, this order is found to be disturbed. **Baker** and **Nathan** studied the actual rates of reaction of p- alkylbenzyl bromide and observed the opposite order –

$$\underset{1^\circ}{CH_3—} > CH_3CH_2— > \underset{2^\circ}{(CH_3)_2CH—} > \underset{3^\circ}{(CH_3)_3C—}$$

The stabilising influence of methyl group has been explained in terms of delocalisation of electron brought about by overlapping between a p-orbital and a s-orbital of alkyl group. The hyperconjugative forms of propene are as shown below -



(I) **(II)** **(III)**

Hyperconjugation is thus **no bond resonance.** Its effect is to increases the ionic character of the C-H bond and partial delocalisation of its electrons.

Consequence of Hyperconjugation

(a) Heats of Hydrogenation

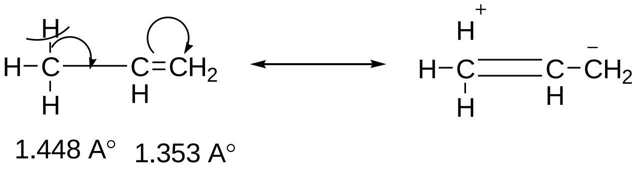
In compounds have similar structures, the lesser the heat of hydrogenation, the more stable is the compound. Thus, the heat of hydrogenation of

Pent -2- ene, CH_3^*-CH=CH- CH_2^*- CH_3 and

Pent -1-ene, CH_2=CH - CH_2^*- CH_2- CH_3 are 135.2 and 125.6 kJ/mol respectively. The difference (135.2 -125.6 = 9.6 kJ/mol) is attributed to greater stability of pent-2-ene than pent–1-ene through hyperconjugation since the former will have six no bond resonance structures and the latter will have only three (the hydrogen atoms involved in hyperconjugation are indicated by asterisk).

(b) Bond length

Hyperconjugation affects bond lengths like resonance since during the process, the double bond in question acquires some single bond character and vice versa. For example, the C-C bond length in propene is 1.488 Å in contrast to 1.543 Å and the C= C bond is 1.353 Å as compared to 1.33 Å in ethylene.



(c) Dipole moment

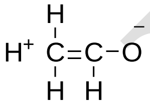
The dipole moment value of –

Formaldehyde, HCHO (2.27 D)

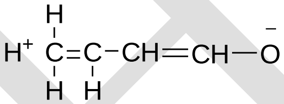
Acetaldehyde, CH_3CHO (2.72 D) and

Crotonaldehyde, CH_3-CH =CH – CHO (3.68 D)

amply indicate the importance of hyperconjugation in these molecules, since the process causes the development of charges. The much larger dipole moment of crotonaldehyde can be attributed to the greater separation of charges in the ionic forms as the dipole moment depends on the distance (*μ* = e x d).



(μ = 2.72 D)



(μ = 3.68 D)

CHAPTER-2

STEREOISOMERISM

This is a type of isomerism exhibited by compounds with identical structural and molecular formula but have different spatial arrangement of the component atoms. There are two kinds of stereo isomerism- *Optical isomerism* and *Geometrical isomerism.*

Optical isomers have two structures that are not identical and also are mirror images of one another. They rotate the plane polarised light and mirror images are not *superimposable* such as our hands and a pair of shoes.

Elements of symmetry

It has been found that in order to exhibit optical activity, a compound must be **chiral.** A chiral molecule may be defined as one that is not super-imposable on its mirror reflection. However, the presence of asymmetric carbon atoms or chiral may not make a compound necessarily optically active. What is essential is the asymmetry of the molecule as a whole. In order to examine the presence or absence of symmetry elements in a molecule, it becomes important to know them.

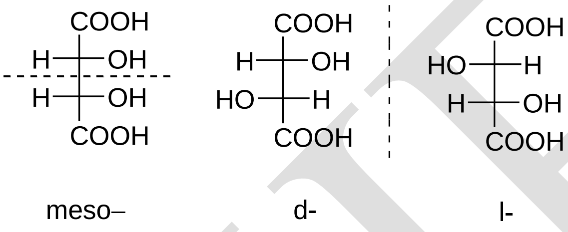
Symmetry elements are the following -

i) Plane of symmetry
ii) Centre of symmetry
iii) Roto reflection symmetry or alternating axis of symmetry.

The molecules, which possess any one of these symmetry elements are known as *symmetric* and they can superimpose and they cannot rotate the plane polarized light, i.e., they cannot be optical isomers.

Plane of symmetry: It is denoted by σ. A plane of symmetry (also called a mirror plane) is an imaginary plane which cuts the molecule into two parts, so that each part is the mirror image of the other.

The molecules possessing such a plane are always inactive and are said to be inactive due to internal compensation **e.g.** meso tartaric acid.



tartaric acids

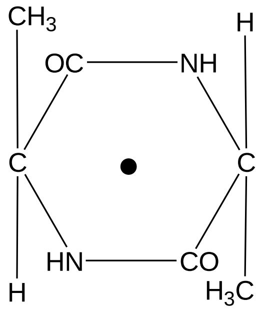
But the d-and l- forms of these compound will no have plane of symmetry and they will be optically active.

Centre of symmetry or inversion centre

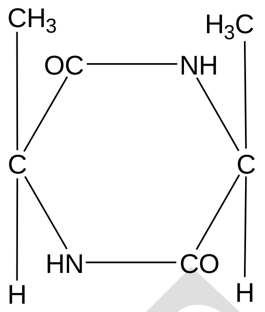
It is denoted by *i*. A centre of symmetry is an imaginary point in the molecule such that, if a line is drawn from any group of the molecule to this point and then extended to an equal distance beyond the point, it meets the mirror image of the original group.

Centre of symmetry is prevalent in cyclic compounds. e.g. Dimethyl diketopiperazines.

Please note that trans compound has the centre of symmetry and cis compound dose not have the centre of symmetry and cis compound is optically active.



trans



cis

Alternating axis of symmetry or Rotation reflection axis

A species is said to possess an improper rotation axis of order n, if rotation of the species about the axis by $2\pi/n$ or ($360^o/n$) followed by reflection through a plane perpendicular to axis produces a structure indistinguishable from the original. The improper rotation is denoted by symbol S_n. Only a few compounds are optically inactive due to this element of symmetry.

Example: i) 1,2,3,4- tetramethyl cyclobutane
ii) Spiro compounds.

Polarized light and optical activity

Light has wave-particle duality. According to wave theory, an ordinary light is able to vibrate in all planes perpendicular to its line of propagation. But if a ray of monochromatic light is allowed to pass through a *nicol prism*, the transmitted ray is found to vibrate in only one plane. This phenomenon is called *polarization* and the beam of light is said to be plane polarised. The nicol prism is known as *polarizer*.

If this plane polarized light is passed through a solution of certain substances like lactic acid, tartaric acid etc., it was observed that the plane polarized light is rotated through a certain angle, called the *angle of rotation.* Substances which rotate the plane polarized light are called as *optically active substances* and the phenomenon is called as *optical activity*. Isomers which exhibit this property are called *optical isomer, optical antipodes or enantiomer (Gr, enantio* = opposite, *morphos* = forms). Substances which rotate the plane polarized light to the right (in the clockwise direction) are called *dextro rotatory* and is symbolized by either d or (+). The enantiomer that rotates the plane polarized light to the left is *laevo rotatory* (in the anticlockwise direction) and is symbolized by *l* or (-).

In order to determine the angle of rotation of the plane polarised light, a *polarimeter* or *polariscope* is used. The angle of rotation is found to vary with the following.

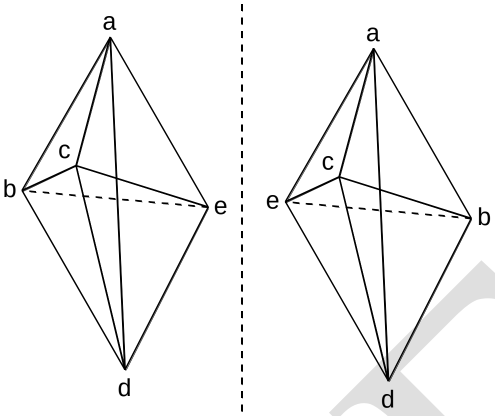
(a) The temperature
(b) Nature of the solvent
(c) Nature of the compound
(d) Wavelength of the light used
(e) The concentration of the solution
(f) Length of the column of the solution.

The rotatory power is expressed in terms of *specific rotation* and is defined as the *angle of rotation (α) produced by one decimeter length of solution having one gram of the substance per ml.* If the measurement is made at temperature T K sodium light then,

$$[\alpha]_D^{T\,K} = 100\,\theta / l\,C$$

Where, θ is the observed angle of rotation,
l is the length in decimeters and
C is the concentration in grams of substance present in 100 ml. of the solution.

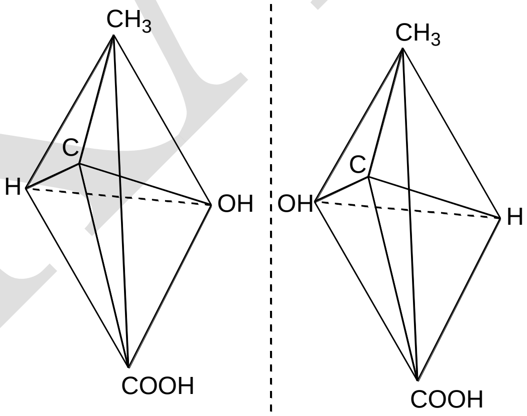
The optical isomerism was explained in the following manner by Van’t Hoff and Le Bell. Carbon has valency of four in all organic compounds and the four valances are directed in the three dimensional space towards the corners of a regular tetrahedron, the carbon atom being at its centre. The cause of optical activity is the presence of four non-identical atoms or groups around a single carbon atom in the molecule. Therefore, for a compound, C_{abde}, two different arrangements may exist as in the figure.



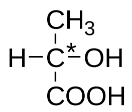
It is evident that these are non-superimposable but mirror images of each other. They cannot be divided into two equal halves. The carbon atom is linked with four different atoms or groups and such carbon atom is known as *asymmetric carbon* atom. These two isomers are optically active and their rotatory power is equal but opposite in direction.

Isomerism in Lactic Acid

As discussed earlier that the necessary condition for a molecule to be optically active is its non-superimposability on its mirror image and the presence of an asymmetric carbon atom. Thus, the molecule lactic acid, $CH_3CH(OH)$ COOH can be represented in three dimension as two optically active forms as below:



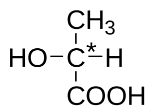
or, this can be represented by *projection formula* as given below:



$H-\overset{CH_3}{\underset{COOH}{C^*}}-OH$

d or (+) lactic acid

$[\alpha]_D = +2.2°$



$HO-\overset{CH_3}{\underset{COOH}{C^*}}-H$

l or (-) lactic acid

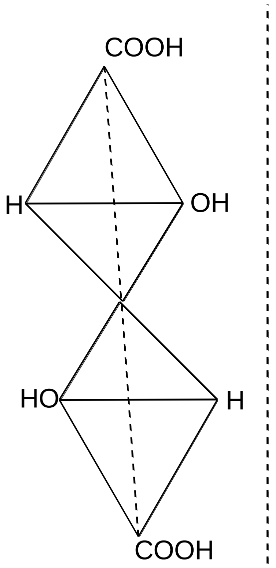
$[\alpha]_D = -2.2°$

These two forms are related as object and mirror image and one cannot be superimposed on the other. One of these two forms represented the dextro-lactic acid and the other is laevo-lactic acid. The mixture containing equimolecular quantities of d and l-lactic acids is optically inactive in solution due to *external compensation.* This is called *racemic mixture (racemic modification), dl*-mixture or (±) lactic acid.

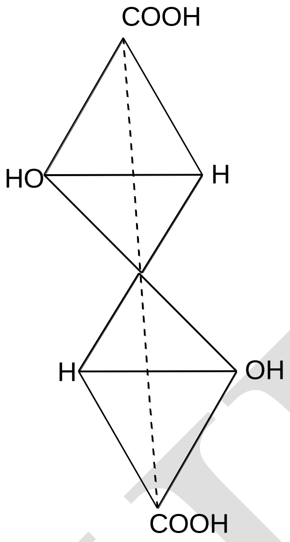
It is to be noted that the enatiomer are identical in their physical properties like m.p. (299 K), specific gravity (1.24) etc. They differ only in the direction of rotation of the plane polarised light but the numerical value of rotation (2.2^o) will be equal. All the three types of lactic acids (d, *l* and d*l*-) adopt the same kind of chemical reactions and their reaction rates are also identical.

Isomerism in tartaric acid

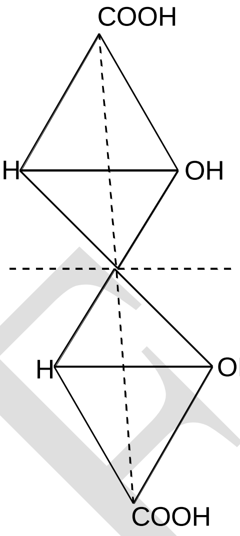
Tartaric acid, $HOOC-(CHOH)_2-COOH$, contains two asymmetric carbon atoms (marked by*) each linked to the same four different group, namely, -OH, -H, -COOH and –CH(OH) COOH. Compounds of this type can exist in three different spatial arrangements. The tetrahedral models of the different forms of tartaric acid are shown below:



(+) or d

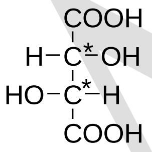


(-) or l



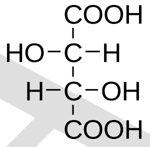
meso

They may also be represented by the following projectional formula:



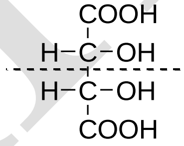
$$\begin{array}{c} COOH \\ H-\overset{*}{C}-OH \\ HO-\overset{*}{C}-H \\ COOH \end{array}$$

(+) acid



$$\begin{array}{c} COOH \\ HO-C-H \\ H-C-OH \\ COOH \end{array}$$

(-) acid



$$\begin{array}{c} COOH \\ H-C-OH \\ \hdashline H-C-OH \\ COOH \end{array}$$

meso acid

d or (+) *tartaric acid:* This acid rotates the plane polarized light to the right since it contains two dextro-rotatory carbon atoms. It has no plane of symmetry. This is obtained from natural source. e.g. grapes.

l or (-) *tartaric acid:* This is the mirror image of the above. It rotates the plane polarized light to the left since it contains two laevo-rotatory carbon atoms. This also has no plane of symmetry. It dose not occur in nature and is prepared by resolving the racemic acid.

Meso-tartaric acid: It is composed of one dextro-rotatory carbon atom and one laevo-rotatory carbon atom. One half of the molecule is the mirror image of the other half in this form. Meso-tartaric acid is denoted as i-tartaric acid. Though it contains two asymmetric carbon atoms, it is optically inactive. Since the rotation of the two carbon atoms are equal but opposite in direction, they are cancelled out. Thus, they are *internally* compensated. The physical properties of this acid are entirely different from those of d- and *l* acids. Unlike racemic tartaric acid, it cannot be resolved into (+) and (-) tartaric acids. It has a plane of symmetry and does not occur in nature.

Racemic tartaric acid: It is 50-50 mixture of d and l tartaric acids and hence is optically inactive. It can, however be resolved into active constituents. This inactiveness is due to external compensation.

Diastereo isomers: There are four different tartaric acids – d-tartaric acid, *l*-tartaric acid, meso-tartaric acid and racemic or d*l*- tartaric acid. Only the first two are optically active. Meso-tartaric acid is not enantiomorphic with d or *l* tartaric acid but is said to be a *diastereo isomer* of these two compounds. They are optical isomers but not mirror images. They differ much in physical properties (see table). They are chemically similar but their rates of reaction with other optically active compounds are different.

Various physical properties of the (Tartaric acid) isomers are reported in the following table.

S.No	**Name**	**$[\alpha]_D$**	**Specific gravity**	**Solubility**	**Crystalline form**	**M.p. (K)**
1.	Dextro	+12	1.76	139	Prism	443
2.	Laevo	-12	1.76	139	Prism	443
3.	Meso	0	1.66	125	Plates	413
4.	Racemic	0	1.69	20.6	rhombic	479

RACEMISATION

The process of producing a racemic modification starting with one of the pure enantiomers is termed racemisation.

For racemisation (i) heat (ii) light (iii) acid (iv) base are used. Depending on the nature of the reactants one or more of these are used.

(i) **Thermal recemisation:** This is carried out by applying heat.
Ex : o-substitued biphenyls, amyl alcohol.

(ii) **Treating with reagents:** When the enantiomers are treated with suitable reagents, racemisation occurs. Examples -

a) When laevo lactic acid is treated with dilute sodium hydroxide, racemic lactic acid is obtained.
Mandelic acid also behaves in the same way.

b) When mandelic acid is reacted with hydrobromic acid, racemic mandelic acid is formed.

RESOLUTION

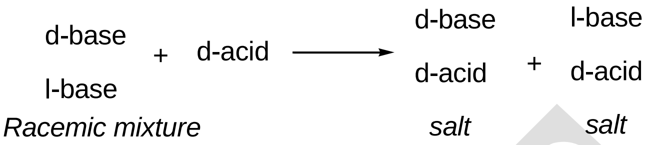
The separation of a racemic mixture into its enantiomers (d and l-components) is termed resolution. Since the optical isomers have identical physical properties, their separation is difficult. However, the following methods have been used for resolution.

(a) **Mechanical separation:** This method is only of historical interest and depends upon classifying them on the basis of their crystalline structure. When two isomers or their salts from well defined crystals showing hemihedral faces, they can be separated by simple hand picking.

(b) **Biochemical separation:** Certain lower organisms such as moulds, fungi or bacteria when allowed to grow in a solution of racemic mixture, destroy one of the optical isomers at a much faster rate than the other due to *selective assimilation.* When one of the components is not needed, then this method may be adopted.

(c) **Selective adsorption:** Optically active substances may be selectively adsorbed by certain optically active adsorbents. For example, camphor was resolved using dextro-lactose as an adsorbent.

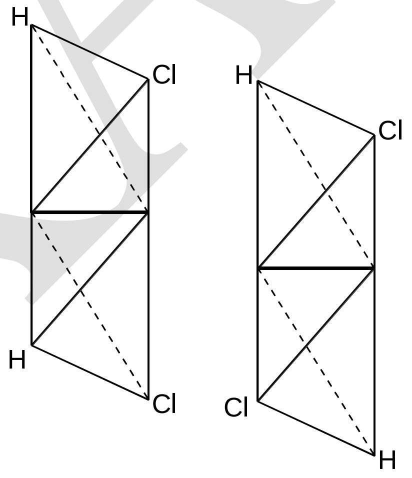
(d) Salt formation method: This is the best of all methods of resolution. Suppose the racemic mixture is a base, then it is treated with an optically active acid, resulting in the formation of a salt with both the components:



Thus, they can be separated by fractional crystallization as the two salts differ in their solubility. Bases used for this purpose are – quinine, brucine, chinchonine and morphine. The acids commonly employed are- tartaric acid and camphor sulphonic acid.

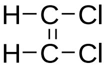
GEOMETRICAL ISOMERISM

Let us consider ethylene. The two carbon atoms are sp^2-hybridised. The unhybridised p-orbitals overlap with each other to form a π-bond. The molecule is thus locked up and free rotation is restricted. If the hydrogen atoms are substituted by different groups, two different spatial arrangements are possible. One from cannot be transformed into the other. For example, dichloroethylene, $C_2H_2Cl_2$ can exist in the two forms.



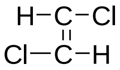
Cis Trans

These two forms are different, because they differ in their spatial arrangement of the different groups. All the four groups attached to the carbon atoms lie in the same plane. The molecule has a plane of symmetry and hence is optically inactive. Even if all the four groups are different the molecule will not be asymmetric. This type of isomerism is called geometrical isomerism. The above two forms of dichloroethylene may be



$$\begin{array}{c} H-C-Cl \\ \| \\ H-C-Cl \end{array}$$

I, cis-

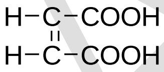


$$\begin{array}{c} H-C-Cl \\ \| \\ Cl-C-H \end{array}$$

II, trans-

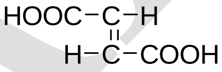
In structure I, the two chlorine atoms lie on the same side of the double bond. This type of configuration is known as *cis- configuration* (Gr. cis = same side). The two chlorine atoms are on the opposite sides of the double bond in the II structure and is known as *trans-form* (Gr. trans = across). Thus, this isomerism is also known as *cis-trans* isomerism.

A well known example for geometrical isomerism is that existing between maleic acid and fumaric acid. Both are unsaturated dicarboxylic acids with the formula, $C_4H_4O_4$. The cis-acid is called maleic acid and fumaric acid is the trans-form.



$$\begin{array}{c} H-C-COOH \\ \| \\ H-C-COOH \end{array}$$

maleic acid



$$\begin{array}{c} HOOC-C-H \\ \| \\ H-C-COOH \end{array}$$

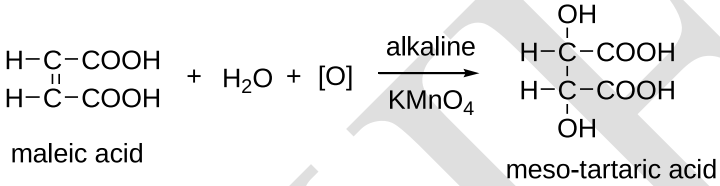
fumaric acid

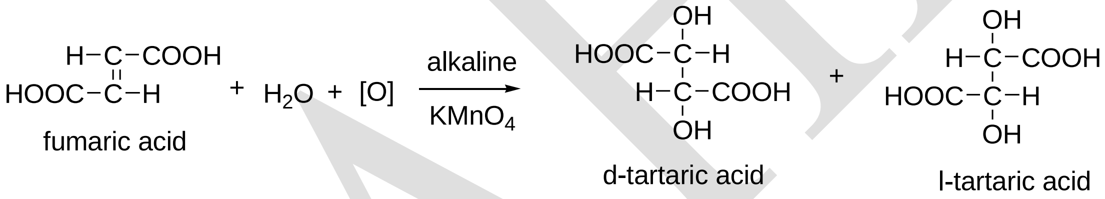
The geometrical isomers have differences in their physical properties. Although they show similarity in chemical reactions, their reactivity differs to a considerable extent. These variations in properties and reactivity enable us to identify the isomers.

a) The trans-isomers are found to have greater stability than the cis-form. This has been confirmed from the heat of combustion values.
b) The melting point of a trans-isomer is always found to have a higher value.
c) The two isomers differ in solubility also.
d) The dipole moment for a trans-compound must be zero since the two dipoles act in exactly opposite directions.

e) The difference in chemical reactivity can be explained taking fumaric and maleic acids. Since, the two carboxylic groups are on the same side, maleic acid readily forms an anhydride whereas fumaric acid forms an anhydride only at very high temperature.

f) Maleic acid gives meso-tartaric acid when oxidised with alkaline potassium permanganate. On the otherhand, fumaric acid gives a racemic mixture of tartaric acid.





Some important physical properties are summerised in the following Table.

S.No	**Property**	**Maleic acid (cis-)**	**Fumaric acid (trans-)**
1)	Melting point	403 K	560 K
2)	Sp.gravity	1.59	1.67
3)	Solubility per 100 g. water	60.0	0.6
4)	Heat of combustion	1370 kJ	134 kJ
5)	pKa_1	1.9	3.5
6)	pKa_2	3.0	4.5
7)	Formation of anhydride	forms readily	forms on heating
8)	Dipole moment (D)	non-zero	zero

Inter-conversion of fumaric and maleic acids

a) On heating at 423 K for a long time, maleic acid changes into fumaric acid.

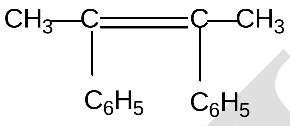
b) An equilibrium mixture of fumaric acid and maleic acid is obtained on exposing fumaric acid in ultra violet in presence of little bromine for some time.

Few other examples for cis- trans isomerism are

a) Cinnamic acid, C_6H_5-CH =CH-COOH

b) Crotonic acid CH_3-CH =CH-COOH

c) 2,3-diphenyl-but-2-ene,



$$\underset{C_6H_5}{\overset{}{CH_3-C}}=\underset{C_6H_5}{C}-CH_3$$

TAUTOMERISM

Study of chemical behaviour of compounds like acetone, acetylacetone, acetonylacetone etc., revealed that these compounds possess some of the properties of unsaturated alcohols (*enol)*. To explain this, it was suggested that these compounds change into alcoholic structure and consequently show the properties of an alcohol. For instance, acetone was believed to exist in two different forms:

$$H_3C-\overset{O}{\overset{\|}{C}}-CH_3 \quad \text{and} \quad H_2C=\overset{OH}{\overset{|}{C}}-CH_3$$

These two compounds spontaneously changes from one to other. This is due to a 1,3 shift of a proton.

The phenomenon by which a compound changes from one isomeric modification to the other due to the presence of a mobile hydrogen atom is called tautomerism.

The phenomenon tautomerism was studied in detail only after the discovery of acetoacetic ester. This ester was first discovered by Geuther in 1863. He prepared this compound by the action of sodium on ethyl acetate.

CH_3-C(OH) =CH-$COOC_2H_5$

(Ethyl ester of β-hydroxycrotonic acid)

Two years later Frankland-Duppa also prepared the same compound by the action of sodium on ethyl acetate and proposed the formula.

CH_3-CO-CH_2-$COOC_2H_5$ *(β-ketobutyric ester)*

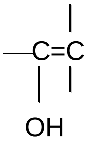
Opinion was divided among the scientists, one school favouring the Geuther's formula and the other upholding the frankland-Duppa formula. Both the views were supported by experimental evidences.

Evidences in favour of Geuther formula (reactions of an unsaturated alcohol)

a) When the ester is treated with sodium, it liberates hydrogen and forms the sodio derivative. This shows that an alcoholic group is present.

b) Acetoacetic ester decolorises bromine water indicating the presence of a carbon-carbon double bond.

c) It gives violet colour with neutral ferric chloride.

Thus, *enol*,  $-\underset{OH}{\underset{|}{C}}=\underset{|}{\overset{|}{C}}$ group must be present in the compound.

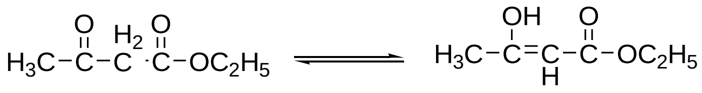
Evidence in favour of Frankland – Duppa formula (reactions of a ketone)

a) Acetoacetic ester forms cyanohydrins with hydrogen cyanide.

b) It gives a bisulphite addition compound with sodium bisulphite.

c) It gives a phenylhydrazone with phenylhydrazine.

The controversy continued until 1910, when chemists concluded that both the formulae were correct and that the two formed existed in equilibrium in solution or in the liquid state.

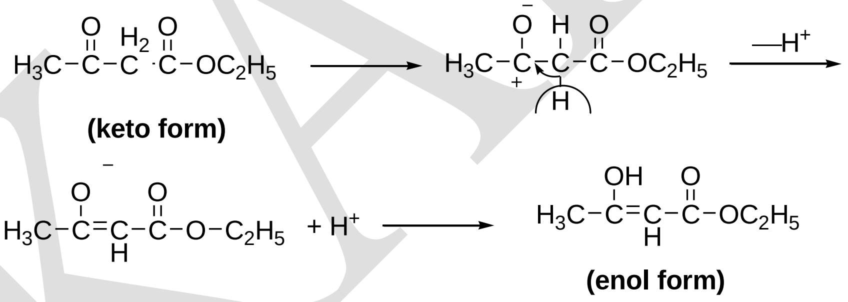


$$H_3C-\overset{O}{\overset{\|}{C}}-\overset{H_2}{C}-\overset{O}{\overset{\|}{C}}-OC_2H_5 \rightleftharpoons H_3C-\overset{OH}{\overset{|}{C}}=\underset{H}{C}-\overset{O}{\overset{\|}{C}}-OC_2H_5$$

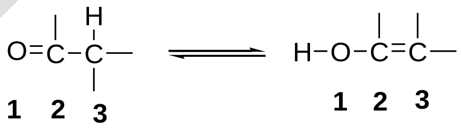
It was *Knorr* who settled this problem. He has isolated both the forms. He cooled a solution of the ester in light petrol to 95 K. He was able to obtain the crystals of this compound which gave no colouration with ferric chloride, but formed cyanohydrin. It was therefore, the pure keto form.

Knorr then passed hydrogen chloride through the suspension of the sodio derivative of the ester in hexane cooled to 195 K. He obtained a glassy solid which decolourised bromine water and gave a violet colour with $FeCl_3$ but formed neither a bisulphite compound nor a phenylhydrazone. It was, therefore, the pure enol form.

It is evident from the foregoing discussions that acetoacetic ester behaves as two structural isomers, each isomer being capable of changing rapidly into other when the equilibrium is disturbed. This is an instance of *dynamic isomerism* and is referred to as *tautomerism.* The two forms are known as *tautomers.* In acetoacetic ester, the tautomerism exists between a *keto form* and *an enol form* and is called *keto-enol tautomerism.* The probable mechanism is as follows:



The tautomerism seen above is called the *keto-enol triad* system. In this system a hydrogen atom migrates from first atom to third atom (1,3 shift):



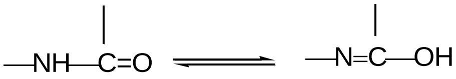
When one tautomer is more stable than the other, the former is known as *stable form* and the latter is called the *labile form.* Tautomerism is very rare in the solid state, but in the liquid or gaseous state or in solution the two forms exist as an equilibrium mixture.

Other common types of tautomeric system which we frequently come across are:

a) Nitroso-oximino system

$> CH-N=O \rightleftharpoons > C=N-OH$

b) Amido-imidol system

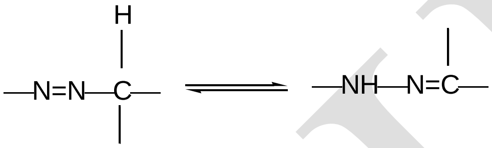


$-NH-\overset{|}{C}=O \rightleftharpoons -N=\overset{|}{C}-OH$

c) Nitro-acinitro (pseudo nitro) system

$> CH-NO_2 \rightleftharpoons > C=NO-OH$

d) Diazo-amino (triazen) system



$-N=N-\underset{|}{\overset{\overset{H}{|}}{C}}- \rightleftharpoons -NH-N=\overset{|}{C}-$

Some of the very important differences between resonance and tautomerism are given in Table.

S.No.	Resonance	Tautomerism
1.	Resonance hybrids are hypothetical.	Tautomers are definite compounds.
2.	Resonance hybrids have same atomic arrangement.	Tautomers differ in atomic arrangements.
3.	It is due to the displacement of electrons on different atoms.	It involves the movement of a labile hydrogen between two polyvalent atoms.
4.	Bond order as well as bond lengths vary much.	Bond length dose not vary.
5.	It stabilises a molecule by minimizing energy.	It does not stabilise a molecule.
6.	It is represented by a double headed arrow (↔) between its contributing structures.	Tautomer is in dynamic equilibrium between two forms and hence is represented by ⇌ between them.

Text Book:

1. Thangamani, A. (2019). *Text Book on Allied Chemistry* (I Edition). Coimbatore: Karpagam Publication.

Reference Book:

1. Gopalan, R., and Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions
(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. Explain why chloroacetic acid is more acidic than acetic acid.
2. Define electromeric effect.
3. Define the following terms (a) Resolution (b) Tautomerism.
4. Explain why ground state of carbon is divalent but excited state of carbon is tetravalency.
5. What is Inductive effect?
6. Explain racemisation.
7. Write the state of hybridization and shape of methane, ethylene and acetylene.
8. Explain why benzoic acid forms an ester but not 2, 6-dimethyl benzoic acid.
9. Explain why the dipole moment of crotonaldehyde is 3.68 D while it is 2.72 D for acetaldehyde.
10. Explain why phenol is acidic in nature.
11. Explain why vinyl chloride is a polar compound.
12. What are the methods employed to distinguish a *cis* compound from a *trans* compounds.
13. Explain why aniline is a weaker base than the primary aliphatic amines.

14. Explain why tertiary free radical is the most stable radical. Write the relative stability order of free radical.
15. Explain (a) plane of symmetry (b) centre of symmetry.

PART-C (Each Question Carry Six Marks)

1. Explain the structure of methane, ethylene and acetylene molecules.
2. (i) What are the difference between resonance and tautomerism?
   (ii) Explain steric effect with an example.
3. Explain why-
   (i) Among various chlorobutyric acids, α-chlorobutyric acid is the strongest.
   (ii) Mesityl acetic acid forms ester easily with ethanol.
   (iii) The dipole moment of acetaldehyde is 2.72 D while it is 2.27 D for formaldehyde.
4. (i) Explain resonance effect with an example.
   (ii) Write note on the effects of resonance.
5. Explain why-
   (i) Formic acid is stronger than acetic acid.
   (ii) Acetic acid is stronger than trimethyl acetic acid.
   (iii) Trichloroacetic acid is stronger than acetic acid.
   (iv) Chloroacetic acid is stronger than iodoacetic acid.
6. (i) Write the order of basic strength of different aliphatic amines.
   (ii) Discuss the acidic nature of acetylene.
   (iii) Write the conditions of resonance.
7. Explain the following
   (i) Aniline forms a Schiff's base but not 2, 4, 6-tribromo aniline.
   (ii) Phenyl cyanide easily forms benzoic acid on hydrolysis but not 2, 6-dimethylphenyl cyanide.
   (iii) *N*, *N*- dimethyl aniline undergoes coupling reaction but not 2, 6- dimethyl-*N*, *N*-dimethyl aniline.

(iv) *N*, *N*-dimethyl-o-toluidine is a stronger base than *N*, *N*-dimethyl aniline.

8. (i) Explain why maleic acid forms readily an anhydride but not fumaric acid.

(ii)Write notes on tautomerism.

9. Explain the following with suitable examples.

(i) Inductive effect.

(ii) Mesomeric effect.

10. (i) Explain the Hyperconjugation effect.

(ii) Explain the optical isomerism of tartaric acid.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(*Deemed to be University*)
(*Established Under Section 3 of UGC Act, 1956*)
Pollachi Main Road, Eachanari Post, Coimbatore–641 021.

DEPARTMENT OF CHEMISTRY

UNIT-II

COVALENT BOND AND STEREOISOMERISM

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. Trichloroacetic acid is a strong acid because of

a) mesomeric effect b) electromeric effect c) hyperconjugative effect **d) inductive effect**

2. The hyperconjugative effect is the largest in

a) $^{+}CH_3$ **b)** $^{+}C(CH_3)_3$ c) $^{+}CH(CH_3)_2$ d) $^{+}CH_2\text{-}CH_3$

3. No bond resonance is another name for

a) hyperconjugative effect b) electromeric effect c) mesomeric effect d) inductive effect

4. Inductive effect is a

a) temporary effect b) weak effect c) strong effect **d) permanent effect**

5. The term no bond resonance refers to

a) inductive effect b) mesomeric effect **c) hyperconjugative effect** d) electromeric effect

6. A chiral molecule may be defined as one that is not super imposable on its

a) mirror reflection b) mirror rotation c) mirror vibration **d) mirror image**

7. Plane of symmetry is denoted by

a) i b) S_n **c) σ** d) η

8. Plane of symmetry is also called a

a) mirror plane b) center plane c) inversion center d) imaginary plane

9. The beam of light is said to be

a) polarizer b) angle of rotation c) specific rotation **d) plane polarized**

10. Substance which rotate the plane polarized light are called as

a) optically active substance b) optically inactive substance c) isomers d) enantiomers

11. Substance which rotate the plane polarized light to the right are called

a) laevo rotatory **b) dextro rotatory** c) specific rotation d) angle of rotation

12. Cinnamic acid is an example of

a) cis-trans isomerism b) optical isomerism c) linkage isomerism d) keto-enol tautomerism

13. Acetoacetic ester was first discovered by

a) Mullikan **b) Geuther** c) Baker and Nathan d) Frankland-Duppa

14. The electron displacement occurring in saturated compounds along a carbon chain is termed as

a) inductive effect b) electromeric effect c) steric effect d) resonance effect

15. The compound changes from one isomeric modification to the other due to the presence of a mobile hydrogen atom is called

a) recemisation b) resolution **c) tautomerism** d) isomerism

16. Inductive effect is represented by

a) single arrow head b) double arrow head c) reverse arrow head

d) equilibrium arrow head

17. Inductive effect is represented by arrow head pointing towards the more

a) electro positive atom **b) electro negative atom** c) neutral atom d) hydrogen atoms

18. The atoms or groups having greater electron affinity than hydrogen are said to

a) +I effect **b) -I effect** c) +E effect d) –E effect

19. The atoms or groups having lesser electron affinity than hydrogen are said to

a) +I effect b) -I effect c) +E effect d) –E effect

20. Which of the following can exhibit keto-enol tautomerism?

a) acetyl chloride b) acetic acid c) acetamide **d) acetone**

21. Relative strength of various aliphatic monocarboxylic acids can be explained with the help of

a) inductive effect b) electromeric effect c) steric effect d) resonance effect

22. The acid dissociation constant is represented as

a) K b) K_b **c) K_a** d) K_c

23. The pKa value is lower indicate that

a) lower acid strength **b) greater acid strength**

c) lower base strength d) higher base strength

24. pK_a value of formic acid is

a) 3.75 b) 4.76 c) 4.87 d) 4.92

25. 1,2-dichloroethane can exhibit

a) optical isomerism b) tautomerism c) functional group isomerism

d) geometrical isomerism

26. Lactic acid can exist in

a) 4 forms **b) 3 forms** c) 2 forms d) only one form

27. The hybridization of acetylene molecule is

a) sp^2 hybridisation **b) sp hybridisation** c) sp^3 hybridisation d) dsp^2 hybridisation

28. Formic acid is stronger than acetic acid due to

a) +I effect b) –I effect c) +E effect d) –E effect

29. Chloroacetic acid is much stronger than acetic acid due to

a) +I effect **b) –I effect** c) +E effect d) –E effect

30. Meso-tartaric acid is

a) optically inactive b) optically active c) chiral d) pro-chiral

31. Lactic acid exists in

a) only one optically active form b) three optically active forms

c) two optically active forms d) four optically active forms

32. The tertiary amine is more basic than ammonia is due to

a) +I effect b) –I effect c) +E effect d) –E effect

33. The complete transfer of a shared pair of electrons in one of the atom joined by a double or triple bond at the requirement of attacking reagent is known as

a) inductive effect **b) electromeric effect** c) steric effect d) resonance effect

34. The reaction of acetone with HCN is an example of

a) inductive effect **b) electromeric effect** c) steric effect d) resonance effect

35. The electromeric effect is indicated by

a) +I b) -I **c) E** d) -E

36. When several structures may be assumed to contribute to the true structure of a molecule then the molecule is referred as

a) resonance hybrid b) conjugation c) hyperconjugation d) hybrid orbitals

37. Resonance effect is also known as

a) inductive effect **b) mesomeric effect** c) steric effect d) electromeric effect

38. The isomer which rotates the plane of polarized light to the right is called

a) laevo rotatory b) specific rotation c) walden inversion **d) dextro rotatory**

39. (+)-Tartaric acid is

a) laevo rotatory b) specific rotation **c) dextro rotatory** d) walden inversion

40. Aniline is a weaker base than the primary aliphatic amines due to

a) resonance effect b) inductive effect c) hyperconjugative effect d) electromeric effect

41. The aliphatic alcohols are neutral whereas phenol is acidic due to

a) inductive effect **b) resonance effect** c) steric effect d) electromeric effect

42. The phenoxide ion is stabilized by

a) inductive effect b) steric effect c) electromeric effect **d) resonance effect**

43. Steric effect is also known as

a) mesomeric effect **b) overcrowding effect** c) inductive effect d) electromeric effect

44. Tartaric acid can exist in

a) 4 forms b) 3 forms c) 2 forms d) only one form

45. Benzaldehyde reacts with aniline to form an

a) enamine b) di-imine c) amide **d) anil**

46. Meso-tartaric acid is optically inactive because

a) it has two asymmetric carbon **b) it has a plane of symmetry**

c) it is a mixture of (+) and (-) acid d) its mirror image is non-superimposable on it

47. (-)Tartaric acid is

a) laevo rotatory b) dextro rotatory c) specific rotation d) walden inversion

48. Triethylamine is a weaker base than diethylamine due to

a) inductive effect b) mesomeric effect **c) steric effect** d) electromeric effect

49. The hydrolysis of phenylcyanide gives

a) benzoic acid b) acetophenone c) benzophenone d) benzaldehyde

50. Tartaric acid contains

a) only one asymmetric carbon atoms **b) two asymmetric carbon atoms**

c) three asymmetric carbon atoms d) four asymmetric carbon atoms

51. Hyperconjugation effect was discovered by

a) Mullikan b) H. Davy **c) Baker and Nathan** d) E.G. Rochow

52. The vinyl chloride is polar due to

a) resonance effect b) inductive effect c) electromeric effect d) steric effect

53. The dipole moment value of formaldehyde is

a) 2.27 D b) 2.72 D c) 3.68 D d) 4.21 D

54. The double bond in ethylene is made up of

a) one sigma and one pi bond b) two sigma bond c) one pi bond d) one sigma bond

55. The separation of a racemic mixture into its enantiomers is termed

a) racemisation **b) resolution** c) inversion d) retention

56. The process of producing a racemic modification starting with one of the pure enantiomers is termed as

a) racemisation b) resolution c) retention d) inversion

57. The oxidation of maleic acid with alkaline potassium permanganate gives

a) meso-tartaric acid b) racemic-tartaric acid c) d-tartaric acid d) l-tartaric acid

58. The racemic mixture is

a) optically inactive b) optically active c) chiral d) asymmetric

59. The alkaline potassium permanganate oxidation of fumaric acid gives

a) meso-tartaric acid **b) racemic-tartaric acid** c) d-tartaric acid d) l-tartaric acid

60. The geometrical isomerism is also termed as

a) optical isomerism **b) cis-trans isomerism** c) functional group isomer d) tautomerism

UNIT-III

SYLLABUS

Industrial Chemistry: Silicones: Synthesis, properties and uses. Fuels gases: Natural gas-water gas-semi water gas-carbureted water gas-producer gas- oil gas (Manufacturing details not required).Fertilizers: NPK fertilizer-ammonium sulphate-urea-superphosphate of lime-triple superphosphate- potassium nitrate-ammonium nitrate. Pollution: Water, air and soil pollution-sources and remedies-acid rain-ozone hole-greenhouse effect.

CHAPTER-1

SILICONES

The silicones are the condensation polymeric organo silicon compounds having silicon, oxygen and carbon. These materials have highly stable Si –O backbones. Though the interests in silicones were prevailing even in the nineteenth century, industrial interests did not begin until 1935’s. The silicones have the general formula:

$[R_nSiO_{(4-n)/2}]_m$ Where n is between 0 and 3 and m is 2 or larger.

Preparation

The manufacture of silicones involves the following three steps:

a) Formation of alkyl or aryl chlorosilanes.

b) Hydrolysis of alkyl chlorosilanes to silicols.

c) Condensation of silicols in the presence of acids or heating.

a) Formation of alkyl or aryl chlorosilanes

Alkyl or aryl chlorosilanes can be formed in more than one of the following methods:

(i) **Direct silicone process**: E.G. Rochow in 1945 discovered that a silicon-copper alloy will react exothermally with alkyl chlorides to produce organo chlorosilanes at about 573 K.

$$nCH_3Cl + Si \xrightarrow[573\ K]{Cu} CH_3SiCl_3 + (CH_3)_2SiCl_2 + (CH_3)_3SiCl + \text{Other compounds}$$

The individual components are separated by fractionation.

(ii) **Using Grignard Reagent**: By this method silicon tetrachloride can be converted into alkyl or aryl derivatives as below:

$$SiCl_4 + RMgCl \longrightarrow RSiCl_3 + MgCl_2$$

$$RSiCl_3 + RMgCl \longrightarrow R_2SiCl_2 + MgCl_2$$

$$R_2SiCl_2 + RMgCl \longrightarrow R_3SiCl + MgCl_2$$

$$SiCl_4 + C_6H_5{-}MgCl \longrightarrow C_6H_5SiCl_3 + MgCl_2 \text{ etc.}$$

(iii) **Using unsaturated hydrocarbons:** Quite a number of olefines and acetylenes are capable to undergo reaction with halosilanes or organohalosilanes having one or more Si-H bonds under suitable conditions.

$$Cl_3SiH + CH_2{=}CH_2 \longrightarrow Cl_3SiC_2H_5$$

b) Hydrolysis of alkyl or aryl chlorosilanes to silicols

Under controlled condition, the alkyl or aryl chloro silanes readily react with water and the chlorine atoms are replaced by hydroxyl groups:

$$RSiCl_3 + 3H_2O \longrightarrow RSi(OH)_3 + 3HCl$$

$$R_2SiCl_2 + 2H_2O \longrightarrow R_2Si(OH)_2 + 2HCl$$

$$R_3SiCl + H_2O \longrightarrow R_3SiOH + HCl$$

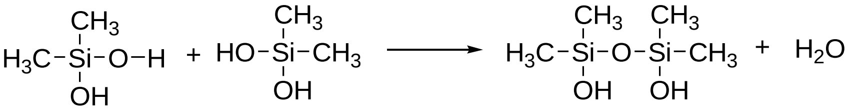
$$C_6H_5SiCl_3 + 3H_2O \longrightarrow C_6H_5Si(OH)_3 + 3HCl$$

c) Condensation of silicols

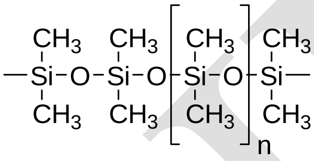
The condensation of trialkyl hydroxosilane $R_3Si(OH)$ results in a linear dimer:

$$R_3Si{-}O{-}H + HO{-}SiR_3 \longrightarrow R_3Si{-}O{-}SiR_3 + H_2O$$

Two hydroxysilane molecules condense in the following way and the resulting Si-O-Si linkage is as strong as in silica.

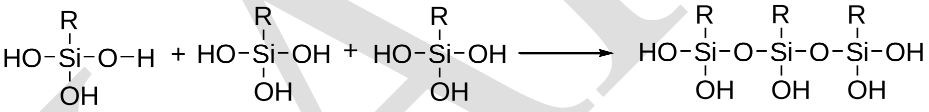


Repeated condensations results in the formation of polymers called *silicones*.

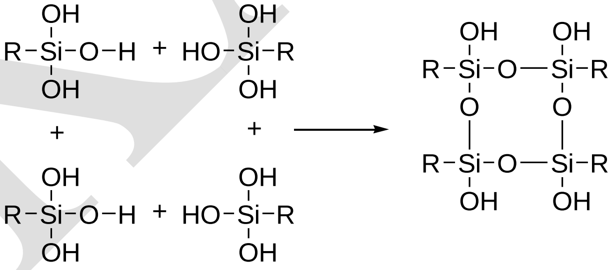


A complex cross linked polymer is obtained by the condensation of alkyltrihydroxy silane, $RSi(OH)_3$:

i)



ii)



It is evident that the structure can be extended in two dimensions, to any manner. These organosilicon polymers grow further by reaction with other molecules containing one silicon atom. It is possible to control the nature of the polymer formed. The dihalides tend to establish linear chains. The trihalides crosslink the chains and the mono halides act as chain terminators.

Properties

The amount of cross linking as well as the nature of group determines the properties of the polymer. Materials ranging from oils, viscous fluids, resins to rubber like solids are known. There are certain common properties to all silicones:

1) They are water repellent.

2) They have high thermal stability.

3) All have high dielectric strength.

4) All have good electrical insulating properties.

5) They are resistant to oxidation and thermal decomposition.

6) All are unaffected by the majority of the chemicals, weak acids and alkalies and salt solutions.

Uses

The uses of silicones are determined by their physical characteristics. These are -

1) Silicones provide excellent insulating material for electric motors and other electrical appliances which can withstand high temperature without charring.
2) Since silicones are water repellent, they are used for making water proof cloth and paper.
3) Silicone rubber, after proper vulcanization, retains its shape and elasticity which finds many applications in industries.
4) Silicones are mixed in paints and enamels which make them resistant to the effect of high temperature, sun light and chemicals.
5) Vaseline like greases obtained from silicones are very useful as lubricants in aeroplanes. They are extremely useful for low temperature lubrication.
6) Various types of silicone resins can withstand temperatures upto 773 K and above. They find wide applications in industries.

CHAPTER-2

FUEL GASES

Any combustible substance which may be burnt to supply heat energy without the production of excessively objectionable by–products is called a *fuel*. The *calorific value* of a fuel is the quantity of heat produced by a given mass of the fuel on complete combustion. It is the same as the enthalpy of combustion. Formerly, it was measured either in calories or in British Thermal Units (B.Th.U). In the S.I system, it is kilojoules per kilogram. The calorific value is an important criterion of all fuels.

Requisites of a good fuel are —

1) It should be cheap and easily available.
2) It should have a high heat content.
3) It should yield as little ash as possible.
4) It should not give any offensive odour while burning.
5) It should not have undesirable products when burnt.

Different types of fuels that we come across are –

(a) *Solid fuels* such as wood, coal, coke and charcoal.

(b) *Liquid fuels* such as petroleum, alcohol and kerosene.

(c) *Gaseous fuels* (or fuel gases) such as natural gas, water gas, semi water gas and carburetted water gas.

Fuel gases have the following special advantages over other types of fuels -

1) They burn easily.

2) They leave no residue.

3) They produce no smoke.

4) They have high calorific value.

5) Complete combustion is possible.

6) They readily flow through pipes and tubes.

Some of the important gaseous fuels are discussed in this section:

Natural gas

It is a mixture of gaseous hydrocarbons. Methane is the principal constituent which issues from wells mainly situated in the oil producing regions. It is an excellent fuel and can be stored at relatively low cost. It is conducted from the producing centres to distant places through long pipe lines.

It has a calorific value of about 3160 kJ m^{-3}.

A typical natural gas might have the following composition:

Methane (85%), Ethane (8%),

Propane (4%), Butane (1.5%) and higher hydrocarbon (1.5%).

Water gas

It is essentially a mixture of carbon monoxide and hydrogen. However, the composition is -

Carbon monoxide 40 to 50%, Hydrogen 50 to 44 %

Carbondioxide 7 to 3% and nitrogen 3 %.

The calorific value is about 13100 kJ m^{-3}.

It is prepared by passing steam over hot coke or coal:

$$C_{(s)} + H_2O_{(g)} \longrightarrow H_{2\,(g)} + CO_{(g)} \quad -121.3\ \text{kJ}$$

The above reaction is endothermic and hence coke is rapidly cooled. A blast of air is sent at intervals to heat coke again when CO_2 is formed:

$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \quad +393.7\ \text{kJ}$$

Uses

1) For lighting purposes.

2) As a good source of heat.

3) For making carburetted water gas.

4) In the manufacture of synthetic petrol.

5) In the manufacture of H_2 (*Bosch Process*).

6) In the manufacture of methyl alcohol: (*Patart's Process*).

$$CO + 2H_2 \xrightarrow[723\ \text{K}]{ZnO\ \text{(or)}\ Cr_2O_3} CH_3OH$$

Semi water gas

In order to improve the calorific value of water gas, it is mixed with producer gas ($CO + N_2$). It is obtained by passing a mixture of steam and air through white hot coke continuously. The probable composition of this gas is -

Nitrogen (50%), Carbon monoxide (28%)

Hydrogen (14%) and Carbon dioxide (8%).

Uses

1) It is employed as fuel in steel industry as well as in internal combustion engines.

2) It is used as a source of nitrogen and hydrogen for Haber's synthesis of ammonia.

Carburetted water gas

The calorific value of water gas is increased by mixing small quantities of coal gas with it. It is essentially the water gas enriched with gaseous hydrocarbons obtained by cracking of kerosene oil. The approximate composition of the carbureted water gas is –

Hydrogen (30-40%), Saturated hydrocarbons (15-20%),

Unsaturated hydrocarbons (10-15%), Carbon monoxide (20-28%),

Nitrogen (2.5-5%) and Carbon dioxide (0-2%).

Uses

1) It is used as industrial fuel.

2) It is used for heating and lighting purposes.

Producer gas

Producer gas is essentially a mixture of carbon monoxide and nitrogen which is prepared by burning coke (or even low grade coal) in a limited supply of air. The main constituents of the gas are -

Carbon monoxide (30-25%), Nitrogen (50-60%),

Hydrogen (2-5%), Methane and Carbon dioxide (rest percentage).

It is the cheapest fuel gas of all gaseous fuels. Its calorific value is low and is about 4500 kJ m^{-3}. This is due to the presence of large percentage of nitrogen.

Production

It is produced by blowing air through incandescent coke in a special type of furnace known as *producer*. It consists of an air tight cylindrical structure lined with fire bricks and provided with an air inlet at the bottom and an exit for gases at the top.

The following reactions take place in the furnace:

$$C_{(s)} + 1/2\, O_{2\,(g)} \longrightarrow CO_{(g)} \quad +110 \text{ kJ}$$
$$C_{(s)} + O_{2\,(g)} \longrightarrow CO_{2\,(g)} \quad + 393.7 \text{ kJ}$$

Uses

1) As an illuminant.

2) As a gaseous fuel.

3) As a cheap industrial fuel.

4) As a substitute for petrol in motor engines.

5) As a reducing agent in metallurgical operations.

Oil gas

The gaseous fuel used in the laboratories is the oil gas which is obtained by the cracking of kerosene in an oil gas plant. A thin stream of oil is dropped on the red hot iron retort when a mixture of gaseous hydrocarbons is evolved. The oil gas thus produced goes up and passes through a hydraulic arrangement and is finally stored in a gas holder by downward displacement of water. Here it is mixed with air and then supplied. Oil gas is a mixture of hydrocarbons of ethane and ethylene series.

Gobar Gas

Gobar gas is the gaseous fuel obtained by the fermentation of cattle dung and water inside a circular pit in the absence of air. The fermentation is brought about by the bacteria present in the dung.

Gobar gas mainly consists of methane and a little ethane.

Gobar gas is clean and odourless. It can be transported to the kitchen through G.I pipe and can be used for cooking by means of specially designed burners. It is safe to use since it is less likely to cause an explosion.

CHAPTER-3

FERTILIZERS

Fertilizers are materials that contain one or more nutrient elements essential for plant growth. They are used chiefly to compensate natural deficiencies in the soil and to replace nutrients removed in cropping regimes. Plants need besides water and sun light, few chemical elements for their healthy growth. Nitrogen, phosphorus and potassium are usually called *primary nutrients* and are most vital.

Calcium, magnesium and sulphur are *secondary nutrients* which are also used by plants.

Iron, copper, manganese, boron, zinc and chlorine which are needed in relatively small amounts and are therefore called *minor* or *micro nutrients*.

Nitrogen is very essential for rapid growth of plants and in improving the yield of crops. It also raises the protein content of the crops and the lack of nitrogen in the soil can easily be detected by the dearth of green colour on the leaves.

Phosphates promote early growth as well as early maturity of plants and protect plants from frosts and diseases. Its deficiency is indicated by poverty of fruits on the trees.

Potassium develops a healthy root system and helps in the formation of carbohydrates, albumins in various plants. Lack of potassium can be seen by the unhealthy appearance on the different parts of the plants.

All compounds containing nitrogen, phosphorus and potassium cannot be used as a fertilizer.

The requisites of a good fertilizer are -

1) The elements present in it must readily be available to the plants.

2) It should be soluble in water and must be stable so that the nutrient element present in it is available to the plants over a long period.

Some of the important fertilizers have been described in this chapter.

Ammonium sulphate

1) It is manufactured from the ammoniacal liquor obtained from the dry distillation of bituminous coal. The ammonium salts present in the liquor are - ammonium carbonate, ammonium sulphate etc. The liquor is mixed with lime and heated in stills by steam when the salts decompose evolving ammonia which is passed through 60 percent sulphuric acid when crystals of ammonium sulphate separate out:

$$2NH_4Cl + Ca(OH)_2 \longrightarrow CaCl_2 + 2H_2O + 2NH_3$$

$$(NH_4)_2SO_4 + Ca(OH)_2 \longrightarrow CaSO_4 + 2H_2O + 2NH_3$$

$$2NH_3 + H_2SO_4 \longrightarrow (NH_4)_2SO_4$$

2) It is also manufactured by absorbing synthetic ammonia in sulphuric acid

3) A new method consists in passing carbon dioxide gas through a suspension of calcium sulphate in aqueous ammonia:

$$2NH_3 + CO_2 + H_2O \longrightarrow (NH_4)_2CO_3$$

$$CaSO_4 + (NH_4)_2CO_3 \longrightarrow CaCO_3 + (NH_4)_2SO_4$$

Calcium carbonate precipitates out and is removed by filtration. It is called "*precipitated chalk*" an important by product. The solution is concentrated and crystallized.

It is the chief fertilizer in India and contains theoretically over 25% ammonia but 20% ammonia is found in the commercial products. It is a valuable nitrogenous manure for rice and potatoes. It should not be used too often on soils poor in lime since the loss of ammonia makes the soil acidic.

Urea, $CO(NH_2)_2$

It is perhaps the best amongst all the nitrogenous fertilizers since, after its assimilation by plants, it leaves behind only CO_2 in the soil which has no harmful effect.

$$CO(NH_2)_2 + H_2O \longrightarrow CO_2 + 2\ NH_3$$

On the other hand, the sulphate and nitrate ions render the soil acidic. Another advantage of urea is its high nitrogen content, i.e., 46.6%. There is no risk in storage of urea, as it is not subjected to fire or explosion hazards.

Urea is synthesized by mixing ammonia and carbon dioxide with a little moisture in an autoclave at 408 K. Ammonium carbamate NH_2-COO-NH_4 is first formed which gets transformed into urea under reduced pressure:

$$2NH_3 + CO_2 \xrightarrow[408\ K]{200\ atm} NH_2COONH_4$$

$$NH_2COONH_4 \longrightarrow NH_2CONH_2 + H_2O$$

Urea is also a valuable raw material for synthetic resins.

Superphosophate of Lime

Natural phosphorus compounds, phosphate rock and apatites contain phosphorus in the form of insoluble $Ca_3(PO_4)_2$ which is difficult for plants to assimilate. These are, therefore, converted into calcium dihydrogen phosphate, $Ca(H_2PO_4)_2$ which is commonly known as "*super phosphate*" It is manufactured by treating finely ground phosphate rocks or bone ash with calculated quantity of nearly 70 percent sulphuric acid in large revolving autoclaves. The product consists of a dry mixture of primary or mono calcium phosphate and gypsum.

$$Ca_3(PO_4)_2 + 2H_2SO_4 + 5H_2O \longrightarrow \underbrace{\underbrace{Ca(H_2PO_4)_2 . H_2O}_{\textbf{Soluble}} + \underbrace{2CaSO_4 . 2H_2O}_{\textbf{gypsum}}}_{\textbf{Superphosphate of lime}}$$

Superphosphate contains 16 to 18 percent of available phosphorus as P_2O_5.

Triple super phosphate

It is an excellent phosphate fertilizer and contains as much as 48 to 49 percent of available phosphorus as P_2O_5 which is three times that of superphosphate of lime. It has the advantage (in freight charges) of not containing the dead weight of calcium sulphate as superphosphate does. It is obtained by adding 45% phosphoric acid to calcium phosphate.

$$Ca_3(PO_4)_2 + 4H_3PO_4 \longrightarrow \underset{\textbf{Triple superphosphate}}{3Ca(H_2PO_4)_2}$$

Potassium nitrate

It is an excellent fertilizer since it contains both potassium and nitrogen. It occurs abundantly in India in the soil.

Ammonium nitrate (Calcium Ammonium Nitrate (CAN), nitro chalk)

Hydrogen is obtained by the electrolysis of water and nitrogen from the fractional distillation of liquid air. The two gases are mixed and ammonia is formed by Haber’s process. A part of ammonia is used to obtain nitric acid by Ostwald’s process. Another part of ammonia reacts with nitric acid to form ammonium nitrate. The nitrate liquor so formed contains some nitric acid. To this some calcium carbonate is added to obtain granular calcium ammonium nitrate.

Haber's Process: $N_2 + 3H_2 \xrightleftharpoons{\text{Fe, 773 K, 200 atm}} 2NH_3$

Ostwald's Process: $4NH_3 + 5O_2 \xrightleftharpoons{\text{Pt, 1073 K}} 4NO + 6H_2O$

$$4NO + 2O_2 \longrightarrow 4NO_2$$

$$2H_2O + 4NO_2 + O_2 \longrightarrow 4HNO_3$$

$$NH_3 + HNO_3 \longrightarrow NH_4NO_3$$

$$CaCO_3 + 2HNO_3 \longrightarrow Ca(NO_3)_2 + H_2O + CO_2$$

$$CaCO_3 + NH_3 + 3HNO_3 \longrightarrow \underbrace{Ca(NO_3)_2 .NH_4NO_3}_{\text{CAN}} + H_2O + CO_2$$

These grains of calcium ammonium nitrate are coated with thin layers of powdered soap stone to protect from moisture. Ammonium nitrate is explosive. The function of lime stone is to prevent it from explosion. Calcium ammonium nitrate is superior to ammonium sulphate, since it is more soluble in water and the presence of calcium prevents the development of acidity in the soil.

CHAPTER-4

POLLUTION

The presence of one or more contaminants or combination thereof in small amounts in the atmosphere is called Pollution. The contaminants known as *pollutants* are harmful to living organisms. The pollutants originate usually from industries, automobiles, thermoelectric power plants and nuclear power plants.

Classification of pollution

Pollution is broadly classified into three types -

(i) Land or soil pollution (ii) Water pollution. (iii) Air pollution

Due to industrial revolution and modern scientific discoveries, water pollution and air pollution have become the major hazards to mankind.

WATER POLLUTION

Water of good quality is required for living organisms and industries. But, nowadays industries discharge their wastes (effluents) into rivers. Hence, water is contaminated with different toxic chemicals. Moreover, the inadequate sewage disposal system also causes water pollution. They harm water in several ways. Water pollutants are harmful to health. For instance -

(i) Some organic pollutants present in water are toxins and carcinogens.

(ii) They increase biological oxygen demand (BOD) thereby less oxygen is available to aquatic life.

(iii) They impart objectionable odour and taste to drinking water.

(iv) The bacteria present in drinking water cause diseases.

(v) They produce toxic and inflammable vapours.

(vi) They spoil the fertility of the soil.

(vii) They weaken up the pipe joints.

Control of water pollution

(i) Organic wastes are destroyed using biochemical methods.

(ii) Toxic chemicals are destroyed by chemical reactions.

(iii) Inorganic wastes are treated at the source itself.

(iv) Nuclear wastes are buried in the land or at the deep sea.

Sewage water

Sewage is the liquid waste of the community. It contains mainly human and domestic wastes, industrial wastes, ground wastes and storm wastes.

Treatment of sewage

(i) The sewage may be diverted to agricultural fields.

(ii) The sewage effluents are subjected to biochemical oxidation.

(iii) The acidic effluents are neutralized.

(iv) The suspended organic pollutants are removed by chemical coagulation.

(v) The organic compounds that cannot be treated are buried underground.

(vi) The complex organic compounds present in the sewage are decomposed to form stable, harmless inorganic compounds such as carbon dioxide and nitrate.

(vii) The sewage is conveyed to the sea or rivers through underground drainage pipes. This is called *sewerage*.

AIR POLLUTION

Air pollution is mainly due to the presence of smoke, dust, radioactive wastes, acids and chemical fumes. Some important air pollutants are discussed in this section.

1. **Carbon monoxide:** This is produced by the incomplete combustion of gasoline in automobiles, mines etc. It is very treacherous and deadly poisonous gas. It induces a variety of symptoms like headache, visual difficulty, paralysis and coma. It ties up the hemoglobin in the blood thereby the normal transport of oxygen from the lungs to the other parts of body is prevented.

2. **Sulphur dioxide**: When coal and sulphur containing fuel oil are burnt, sulphur dioxide is liberated. It is a highly irritating gas. It prevents the movement of air in and out of the lungs. It causes respiratory diseases to man, chlorosis and dwarfing to plants. Metals are corroded by this gas.

3. **Hydrogen fluoride**: It is produced in large volumes in aluminium and chemical industries. It causes bone, teeth and respiratory diseases. It affects crops also.

4. **Hydrogen sulphide**: It is very common in petroleum industry. It causes respiratory diseases and paralysis to man. It spoils the painted surfaces. It causes corrosion to metals.

5. **Nitrogen dioxide**: it is produced during the combustion of fossil fuels. The large electric power plants, explosive factories and fertilizer companies give out this gas profusely. This gas causes chronic lung condition and even death. It causes chlorosis and extensive leaf drop in plants.

6. **Dust:** Dust is produced in larger amounts in chemical industries, mines and ceramic industries. This leads to respiratory diseases and silicosis to man. This spoils the soil and corrode the metals.

7. **Hydrocarbons:** Automobiles, petroleum refineries and photochemical industries release more than 50% hydrocarbons to the atmosphere. There are very poisonous. Ex. Benzopyrine, a hydrocarbon forms photochemical smog. Aromatic hydrocarbons are carcinogenic in nature.

Control of air pollution

(a) The best way of controlling air pollution is by reducing the amounts of pollutants at the sources itself.

For example: (a) smoke formation is prevented by –

(i) Feeding the fuel uniformly and continuously

(ii) Burning the fuel at high temperature

(iii) Burning the fuel with optimum amount of air.

(b) Dust is removed or reduced using cyclone dust separator, bag filter, electrostatic precipitator, washers, settling chamber, centrifugal separators, extraction and ventilation method, carttel precipitators etc.

SOIL POLLUTION

Nature has provided enough resources on the earth. But, man in his greed to amass more wealth become short sighted in his approach and exploited it. This has resulted in irreparable loss.

Man in his ambition to increase the productivity uses fertilizers and pesticides in his fields and is necessary when the population increases exponentially. When a field is sprayed with pesticides to control the diseases in paddy, the diseases causing organisms are not only the target but all the components of the network of the ecosystem is affected.

Deforestation, over grazing and dumping of non-degradable wastes are the major sources of mismanagement of soil. Oil spillage, disposal of radioactive materials, garbages and municipal discards add to soil pollution.

Man made deserts increased carbon dioxide level and disturbances of ozone are the unpardonable acts against nature. These can be definite threat to the very existence of human race.

Acid rain

Sulphur dioxide is a major pollutant of our environment. It is released by burning of oil and coal together with that discharged by industries. It causes severe damage to the plant and animal life particularly the respiratory organ. About 200 million tonnes of the gas released annually over the world and nearly an equal amount is released by the natural processes. Localities near sulphuric acid plants also often contain a higher level of this gas in the air. The pollution is thus severe in highly populated urban areas. SO_2 is partially oxidized to SO_3 in air by photolytic and catalytic processes initiated by ozone, hydrocarbon, nitrogen oxides and soot or dust. The SO_3 gives rise to H_2SO_4 with water particles causing “acid rain”. In addition to general plant and aquatic life, buildings especially archaeological specimens are severely damaged by acid rains.

Ozone hole

Ozone is an important constituent of the upper atmosphere (15-25 km above the earth) where it is formed from oxygen by solar ultraviolet radiation of very high energy.

$$O_2 + h\upsilon \longrightarrow 2O$$
$$O_2 + O \longrightarrow O_3$$

The ozone molecules absorb moderately high energy ultraviolet radiation and decompose to oxygen:

$$O_3 \longrightarrow O_2 + O$$

$$\text{At equilibrium,} \quad 3O_2 \rightleftharpoons 2O_3$$

is maintained thereby a steady concentration of ozone is (27% by weight) maintained. This layer in effect protects the earth and its biosphere from the harmful ultraviolet radiations. Any significant decrease in this concentration may have severe adverse effects on the biosphere e.g. increased surface temperature, high incidence of skin cancer etc. Nitrogen oxides from supersonic aircrafts and industries catalyse the conversion of O_3 to O_2. Similarly chlorofluoro carbons (CFC, Freons) used as foam blowing agents, aerosol propellants and refrigerants are photochemically decomposed to give chlorine atoms which break the ozone molecules. It may be observed that the nitrogen oxides or chlorine atoms are continuously regenerated, causing permanent damage to the ozone balance.

Green house effect

There is now a serious concern about the increase of CO_2 content of the atmosphere which is causing a slow rise in global temperature. The effect is called the Green house effect in analogy with the "green house" maintained in winter countries by artificial heating. The CO_2 molecules in the atmosphere permit the passage of visible light but absorb strongly in the infra red region, thereby hindering heat radiation from the earth.

In the early age of the earth, the concentration of CO_2 in the atmosphere remained more or less steady. But with increased burning of carbonaceous fuels and decrease in forest areas (trees consume CO_2 of photosynthesis) the CO_2 content of the atmosphere has been increasing in an alarmingly higher rate.

It has been estimated that if the present rate of warming continues, average temperature of the earth's atmosphere will rise by about 5°C in the next 30 years–resulting in major climatic changes. The polar ice caps will melt with a consequent rise in the sea level whereby main sea side localities will be completely submerged.

Forestation and use of non-fossil fuels as energy source (e.g. wind and atomic energy) seem to be the only remedy.

Text Book:

1. Thangamani, A. (2019). *Text Book on Allied Chemistry* (I Edition). Coimbatore: Karpagam Publication.

Reference Book:

1. Gopalan, R., and Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions
(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. What is water gas? How it is prepared.
2. How Triple superphosphate is prepared.
3. Mention any four uses of silicones.
4. What is meant by direct silicone process?
5. Define Fuel. What are the different types of fuels with examples?
6. Write notes on (i) primary nutrients (ii) secondary nutrients
7. Mention any three properties of silicones
8. How is oil gas synthesized?
9. What are the requisites of fertilizer?
10. What are requisites of a good fuel?
11. How is superphosphate manufactured?

12. How can water pollution be controlled?

13. What are silicones and mention its general formula.

14. Define pollution. What are the health hazards of water pollution?

15. What is sewage? How is it treated?

PART-C (Each Question Carry Six Marks)

1. What are silicones? How it is prepared. What are its uses?

2. How are the following manufactured?

   (i) Water gas (ii) Semi water gas (iii) Oil gas.

3. Explain in detail on the preparation of silicones. Mention their uses.

4. How are the following manufactured?

   (i) Natural gas (ii) Carbureted water gas (iii) Producer gas.

5. Write note on water pollution.

6. Write the composition and uses of

   (i) Natural gas (ii) Carbureted water gas (iii) Producer gas (iv) Water gas (v) Semi Water gas.

7. (i) In what way fuel gases are superior to other types of fuels.

   (ii) How is urea synthesized? Mention its uses?

8. Write note on acid rain, ozone hole and green house effect.

9. Write note on (i) Ammonium sulphate (ii) NPK fertilizers.

10. (i) Discuss the methods adopted to control air pollution.

    (ii) Write note on ammonium nitrate.

KARPAGAM ACADEMY OF HIGHER EDUCATION
(*Deemed to be University*)
(*Established Under Section 3 of UGC Act, 1956*)
Pollachi Main Road, Eachanari Post, Coimbatore–641 021.

DEPARTMENT OF CHEMISTRY

UNIT-III

INDUSTRIAL CHEMISTRY

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. $[R_nSiO_{(4-n)/2}]_m$ is the general formula of

a) boranes b) carbenes **c) silicones** d) zircons

2. How many steps are involved in the preparations of silicones?

a) 1 **b) 3** c) 2 d) 5

3. The alkyltrihydroxy silane is represented as

a) $C_6H_5Si(OH)_3$ **b) $RSi(OH)_3$** c) $R_3Si(OH)$ d) $R_2Si(OH)_2$

4. The hydrolysis of alkyl chlorosilanes to gives

a) silicols b) silica c) silicones d) alkyl silanes

5. Silicones have high stability due to

a) Si-O backbone b) Si-Si- backbone c) O-O backbone d) S-O backbone

6. Which of the following is a gaseous fuel?

a) lignite b) helium c) carbon dioxide **d) natural gas**

7. Producer gas is a/an

a) petroleum product b) compound **c) mixtures of two gases** d) element

8. Among the first four alkanes, the one with maximum calorific value is

a) CH_4 b) C_2H_6 c) C_3H_8 **d) C_4H_{10}**

9. The fuel which is a mixture of H_2 and CO is called

a) natural gas b) producer gas **c) water gas** d) indane gas

10. The formula of triple superphosphate is

a) $3Ca(H_2PO_4)_2$ b) $Ca_3(PO_4)_2$ c) $Ca(H_2PO_4)_2.CaSO_4$ d) $CaH_2(PO_4)_2$

11. Natural gas is a mixture of

a) gaseous hydrocarbons b) gaseous unsaturated compounds

c) gaseous aromatic compounds d) gaseous heterocyclic compounds

12. Producer gas is a mixture of

a) CO and N_2 b) CO and H_2 c) CO, N_2 and H_2 d) gaseous hydrocarbons

13. Which fertilizers continuous uses increase the soil acidity?

a) urea **b) ammonium sulphate** c) ammonium nitrate d) superphosphate of lime

14. Water gas is used as a in the manufacture of

a) ethyl alcohol b) nitric acid **c) synthetic petrol** d) ammonia

15. The manufacture of ethyl alcohol from

a) Haber's process b) Bosch process **c) Patart's process** d) Ostwald's process

16. The fuel which is a mixture of water gas and producer gas is called

a) semi water gas b) natural gas c) carburetted water gas d) indane gas

17. Semi water gas is used as a source of nitrogen and hydrogen for Haber's synthesis of

a) hydrogen b) methyl alcohol **c) ammonia** d) nitric acid

18. Calcium, magnesium and sulphur are called

a) primary nutrients **b) secondary nutrients** c) micro nutrients d) minor nutrients

19. Calcium dihydrogen phosphate is commonly known as

a) triple superphosphate **b) superphosphate** c) gypsum d) superphosphate of lime

20. Superphosphate of lime is a dry mixture of

a) $Ca_3(PO_4)_2$ and urea b) urea and ammonium sulphate

c) calcium dihydrogen phosphate and gypsum d) triple superphosphate and potassium nitrate

21. The manufacture of nitric acid from

a) Ostwald's process b) Patart's process c) Bosch process d) Haber's process

22. Calcium ammonium nitrate is a mixture of

a**) calcium nitrate and ammonium nitrate** b) cerium nitrate and ammonium nitrate

c) cuprous nitrate and ammonium nitrate d) cupric nitrate and ammonium nitrate

23. Calcium ammonium nitrate is also called as

a) nitro chalk b) precipitated chalk c) gypsum d) plaster of Paris

24. Which of the following is an air pollutant?

a) oxygen b) hydrogen **c) carbon monoxide** d) nitrogen

25. Which one of the following is a likely source of carbon monoxide pollutant?

a) paper industry **b) automobiles** c) fertilizer industry d) leather industry

26. Acid rain is mainly caused by

a) dust particles b) sand particles **c) oxides of nitrogen and sulphur**

d) oxides of antimony and phosphorus

27. Which fertilizers have highest nitrogen content?

a) ammonium sulphate b) ammonium nitrate c) ammonium sulphate **d) urea**

28. An example for non-biodegradable pollutant is

a) garbages b) fruit c) vegetable d) wood

29. Freon's are used in

a) preservative **b) refrigerants** c) flame retardants d) food additives

30. An example for Freon is

a) DDT **b) CFC** c) DDQ d) chloranil

31. Hydrogen sulphide causes

a) chronic lung condition b) bone diseases **c) respiratory diseases** d) chlorosis to plants

32. Which catalyst is used for the synthesis of nitric acid from Ostwald's process?

a) Fe b) Mo **c) Pt** d) Co

33. Silicones have

a) low thermal stability **b) high thermal stability** c) low dielectric strength

d) bad electrical insulating

34. Calorific value is an important criterion of all

a) fuels b) gases c) oils d) liquids

35. Example for solid fuel is

a) glass b) sand **c) charcoal** d) rubber

36. Advantage of fuel gases

a) produce smoke **b) burn easily** c) low calorific value d) leave residue

37. Calorific value of water gas is

a) 31100 kJm^{-3} b) 13300 kJm^{-3} **c) 13100 kJm^{-3}** d) 11300 kJm^{-3}

38. Nitrogen, phosphorus and potassium are called

a) primary nutrients b) secondary nutrients c) micro nutrients d) minor nutrients

39. Reagents used for the preparation of urea is

a) NH_3 and O_2 **b) NH_3 and CO_2** c) NH_3 and CO d) NH_3 and H_2SO_4

40. Contamination of environment is called

a) corrosion b) deforestation c) revolution **d) pollution**

41. CAN is

a) calcium ammonium nitrate b) cerium ammonium nitrate

c) carbon ammonium nitrate d) chlorine ammonium nitrate

42. Which catalyst is used for the synthesis of ammonia from Haber's process?

a) Fe b) Mo c) Pt d) Co

43. Silicones was discovered by

a) Lennard Jones b) H. Davy c) Mullikan **d) E.G. Rochow**

44. Calcium sulphate dihydrate is called as

a) nitro chalk b) precipitated chalk c) triple superphosphate **d) gypsum**

45. Iron, copper, manganese, boron zinc and chlorine are called

a) primary nutrients b) secondary nutrients **c) micro nutrients** d) tertiary nutrients

46. Which one is the example for secondary nutrients?

a) calcium b) iron c) copper d) boron

47. The molecular formula for urea is

a**) $CO(NH_2)_2$** b) $CO(NH_2)_3$ c) $CS(NH_2)_2$ d) NH_4NO_3

48. Silicones are resistant to

a) reduction b) redox reaction **c) oxidation** d) auto oxidation

49. Example for liquid fuel is

a) water **b) alcohol** c) LPG d) distilled water

50. The Hydrogen manufacture from

a) Patart's process b) Ostwald's process c) Haber's process **d) Bosch process**

51. Gaseous fuel is also called as

a) fuel gases b) solid fuels c) liquid fuels d) LPG

52. Which catalyst is used for the synthesis of methyl alcohol from Patart's process?

a) Fe b) CrO_3 **c) ZnO** d) Pt

53. In natural gas the major constituent is

a) butane b) ethane **c) methane** d) propane

54. The producer gas has low calorific value due to

a) large percentage of methane **b) large percentage of nitrogen**

c) large percentage of hydrogen d) large percentage of CO_2

55. Which one is the example for cheapest fuel gases?

a) natural gas b) water gas **c) producer gas** d) semi water gas

56. Urea is a valuable raw material for

a) synthetic resins b) natural resins c) synthetic petrol d) manufacture of methyl alcohol

57. Urea is an example for

a) nitrogenous fertilizers b) phosphatic fertilizers c) potash fertilizers d) calcium fertilizers

58. Calcium carbonate is known as

a) gypsum b) nitro chalk c) plaster of Paris **d) precipitated chalk**

59. Pesticides pollute

a) the soil alone b) the air alone **c) the soil and water** d) the water and air

60. Which fuel gases are used as a substitute for petrol in motor engines?

a) oil gas b) gobar gas **c) producer gas** d) water gas

UNIT-IV

SYLLABUS

Elements of Photochemistry, Chemical Kinetics and Chromatography: Elements of Photochemistry: Photochemical laws-Beer Lambert's law-Grotthuss-Draper law-Stark-Einstein law (statement only).

Chemical Kinetics: Rate-order-molecularity-pseudo first order reactions-zero order reactions-determination of order of reaction-measurement of order and rates of reactions-effect of temperature on reaction rate-energy of activation.

Chromatography: Principles and applications of Column, Paper and Thin Layer Chromatography.

CHAPTER-1

ELEMENTS OF PHOTOCHEMISTRY

Grotthuss–Draper law

The Grotthuss–Draper law (also called the Principle of Photochemical Activation) states that only that light which is absorbed by a system can bring about a photochemical change. Materials such as dyes and phosphors must be able to absorb "light" at optical frequencies. This law provides a basis for fluorescence and phosphorescence. The law was first proposed in 1817 by Theodor Grotthuss and in 1842, independently, by John William Draper.

This is considered to be one of the two basic laws of photochemistry. The second law is the Stark–Einstein law, which says that primary chemical or physical reactions occur with each photon absorbed.

Stark–Einstein law

The Stark–Einstein law is named after German-born physicists Johannes Stark and Albert Einstein, who independently formulated the law between 1908 and 1913. It is also known as the photochemical equivalence law or photo equivalence law. In essence it says that every photon that is absorbed will cause a (primary) chemical or physical reaction.

The photon is a quantum of radiation, or one unit of radiation. Therefore, this is a single unit of EM radiation that is equal to Planck's constant (h) times the frequency of light. This quantity is symbolized by γ, $h\nu$, or $\hbar\omega$.

The photochemical equivalence law is also restated as follows: for every mole of a substance that reacts, an equivalent mole of quanta of light are absorbed. The formula is

$$\Delta E_{mol} = N_A h\nu$$

where N_A is Avogadro's number.

The photochemical equivalence law applies to the part of a light-induced reaction that is referred to as the primary process (i.e. absorption or fluorescence).

In most photochemical reactions the primary process is usually followed by so-called secondary photochemical processes that are normal interactions between reactants not requiring absorption of light. As a result such reactions do not appear to obey the one quantum–one molecule reactant relationship.

The law is further restricted to conventional photochemical processes using light sources with moderate intensities; high-intensity light sources such as those used in flash photolysis and in laser experiments are known to cause so-called biphotonic processes; i.e., the absorption by a molecule of a substance of two photons of light.

Beer-Lambert Law

Introduction

The Beer-Lambert law (also called the Beer-Lambert-Bouguer law or simply Beer's law) is the linear relationship between absorbance and concentration of an absorber of electromagnetic radiation. The general Beer-Lambert law is usually written as:

$$A = a_\lambda \times b \times c$$

where A is the measured absorbance, a_λ is a wavelength-dependent absorptivity coefficient, b is the path length, and c is the analyte concentration. When working in concentration units of molarity, the Beer-Lambert law is written as:

$$A = \varepsilon_\lambda \times b \times c$$

where ε_λ is the wavelength-dependent molar absorptivity coefficient with units of M^{-1} cm^{-1}. The λ subscript is often dropped with the understanding that a value for ε is for a specific wavelength. If multiple species that absorb light at a given wavelength are present in a sample, the total absorbance at that wavelength is the sum due to all absorbers:

$$A = (\varepsilon_1 \times b \times c_1) + (\varepsilon_2 \times b \times c_2) + \ldots$$

where the subscripts refer to the molar absorptivity and concentration of the different absorbing species that are present.

Theory

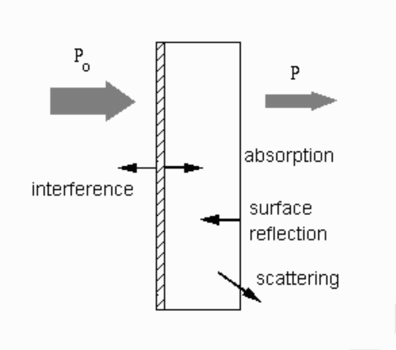
Experimental measurements are usually made in terms of transmittance (T), which is defined as:

$$T = \frac{P}{P_o}$$

where P is the power of light after it passes through the sample and P_o is the initial light power. The relation between A and T is:

$$A = -\log(T) = -\log\left(\frac{P}{P_o}\right)$$

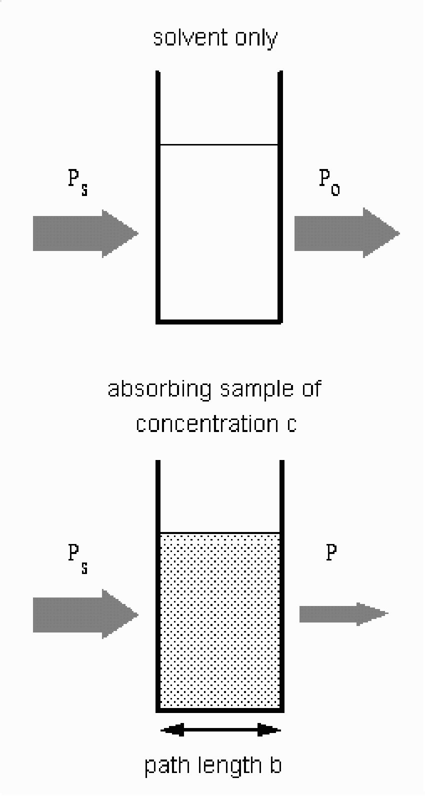
The figure shows the case of absorption of light through an optical filter and includes other processes that decrease the transmittance such as surface reflectance and scattering.



In analytical applications we often want to measure the concentration of an analyte independent of the effects of reflection, solvent absorption, or other interferences. The figure to the right shows the two transmittance measurements that are necessary to use absorption to determine the concentration of an analyte in solution. The top diagram is for solvent only and the bottom is for an absorbing sample in the same solvent. In this example, P_s is the source light power that is incident on a sample, P is the measured light power after passing through the analyte, solvent, and sample holder, and P_o is the measured light power after passing through only the solvent and sample holder. The measured transmittance in this case is attributed to only the analyte.

Depending on the type of instrument, the reference measurement (top diagram) might be made simultaneously with the sample measurement (bottom diagram) or a reference measurement might be saved on computer to generate the full spectrum.

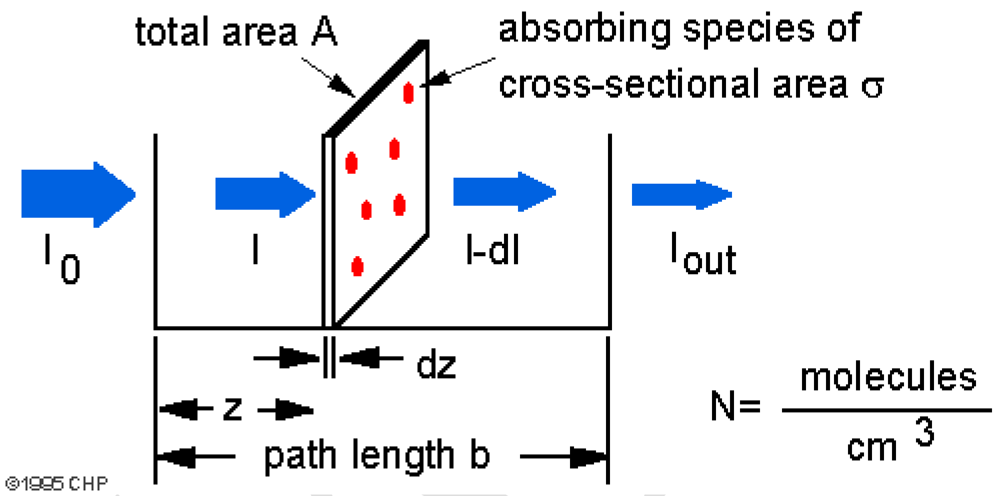
Absorption of light by a sample



Modern absorption instruments can usually display the data as either transmittance, %-transmittance, or absorbance. An unknown concentration of an analyte can be determined by measuring the amount of light that a sample absorbs and applying Beer's law. If the absorptivity coefficient is not known, the unknown concentration can be determined using a working curve of absorbance versus concentration derived from standards.

Derivation of the Beer-Lambert law

The Beer-Lambert law can be derived from an approximation for the absorption coefficient for a molecule by approximating the molecule by an opaque disk whose cross-sectional area, σ, represents the effective area seen by a photon of frequency *w*. If the frequency of the light is far from resonance, the area is approximately 0, and if *w* is close to resonance the area is a maximum. Taking an infinitesimal slab, dz, of sample:



I_o is the intensity entering the sample at z=0, I_z is the intensity entering the infinitesimal slab at z, dI is the intensity absorbed in the slab, and I is the intensity of light leaving the sample. Then, the total opaque area on the slab due to the absorbers is σ × N × A × dz. Then, the fraction of photons absorbed will be σ× N × A × dz / A so,

$$\frac{dI}{I_z} = -\sigma N dz$$

Integrating this equation from z = 0 to z = b gives:

$$\ln(I) - \ln(I_0) = -\sigma N b$$

or

$$-\ln\left(\frac{I}{I_0}\right) = -\sigma N b$$

Since N (molecules/cm^3) × (1 mole / 6.023x10^{23} molecules) × 1000 cm^3 / liter = c (moles/liter) and 2.303 × log(x) = ln(x), then

$$-\log\left(\frac{I}{I_0}\right) = -\sigma\left(\frac{6.023x10^{20}}{2.303}\right) c b$$

or

$$-\log\left(\frac{I}{I_0}\right) = A = \varepsilon c b$$

where $\varepsilon = \sigma \times (6.023 \times 10^{20} / 2.303) = \sigma \times 2.61 \times 10^{20}$

Typical cross-sections and molar absorptivities are:

	σ (cm^2)	ε (M^{-1} cm^{-1})
absorption - atoms	10^{-12}	$3x10^{8}$
absorption - molecules	10^{-16}	$3x10^{4}$
absorption - infrared	10^{-19}	3x10
Raman scattering	10^{-29}	$3x10^{-9}$

Limitations of the Beer-Lambert law

The linearity of the Beer-Lambert law is limited by chemical and instrumental factors. Causes of nonlinearity include:

- deviations in absorptivity coefficients at high concentrations (>0.01M) due to electrostatic interactions between molecules in close proximity
- scattering of light due to particulates in the sample
- fluoresecence or phosphorescence of the sample
- changes in refractive index at high analyte concentration
- shifts in chemical equilibria as a function of concentration
- non-monochromatic radiation, deviations can be minimized by using a relatively flat part of the absorption spectrum such as the maximum of an absorption band
- stray light

CHAPTER-2

CHEMICAL KINETICS

Introduction

Chemical kinetics is concerned with the study and measurement of the rate of chemical reactions. There are many reactions which proceed at a very high speed that their rates cannot be measured. Such reactions are known as **fast reactions.** Familiar examples for fast reactions are- the neutralisation of a base by an acid, precipitation of silver chloride on mixing a solution of silver nitrate with sodium chloride.

There are also reactions which are very slow.

Ex: *rusting of iron.*

In between these two extremes, there are many reactions whose rates can be measured in the laboratory. The study of chemical kinetics helps us to know about the mechanism of chemical reactions i.e., the path followed by the reactants to form the products. This may also help us to know the various factors like temperature, pressure which affect the rate of chemical reactions.

The rate of a chemical reaction is the variation in the concentration of either reactants or the products with time.

i.e.,

$$\text{rate} = \frac{\text{change in concentration}}{\text{time taken}} = \frac{\text{moles/lit}}{\text{time}}$$

The unit for the rate is, mole lit^{-1} $\text{sec}^{-1}$and is mathematically expressed as **dc/dt**.

According to Law of Mass Action, the speed or the velocity of a chemical reaction is directly proportional to the active mass of the reactants. For every reaction, rate equation connecting the rate of the reaction and the active mass of the reactants can be written. For example, consider the reaction -

$$A \rightarrow \text{Products} \qquad \text{-----------} \; (1)$$

The rate equation for this reaction is

$$\frac{-\,d[A]}{dt} = k\,[A]^1 \qquad \text{-----------} \; (2)$$

Here, the –ve sign indicates the decrease in the concentration of the reactants with time.

The order of reaction is defined as the sum of the powers of the concentration of the reactants in the rate equation.

OR

It is the number of molecules whose concentrations determine the rate of the reaction.

Evidently, in the above example, the rate is proportional to the first power of the concentration of A and the reaction is of first order.

Examples for first order reaction -

1) Radioactive decay.
2) Decomposition of hydrogen peroxide.
3) Thermal decomposition of nitrogen pentoxide.

For the reaction,

$$A + B \rightarrow \text{Products} \qquad \ldots\ldots\ (3)$$

The rate equation is

$$-\frac{d[A]}{dt} = -\frac{d[B]}{dt} = k\,[A]^1\,[B]^1 \qquad \text{-----------} \; (4)$$

By our definition, the order of the reaction is 1+1 =2

Examples for second order reaction -

1) Base catalysed ester hydrolysis (**saponification)**.
2) Benzoin condensation.
3) Conversion of ammonium cyanate into urea.
4) Conversion of ozone into oxygen at 373 K.

In general, for the reaction

$$aA + bB + cC\ldots\ldots\ldots\rightarrow \text{Products} \qquad \ldots\ldots\ldots\ldots\ldots (5)$$

The order is, a + b + c +… It must remembered here that the rate equation of a reaction is written on the basis of experimental results only. These are no necessary connection between the order and the balanced chemical equation of a reaction. This is exemplified by the following reaction,

$$2N_2O_5 \rightarrow 4\,NO_2 + O_2 \qquad \ldots\ldots\ldots\ldots\ldots (6)$$

This may seem to be a second order reaction, but experimentally it is a first order reaction.

The order of a reaction need not be a whole number. It may be fraction or even zero. For example, the ortho-para hydrogen conversion is fractional with the order equal to 2/3. Many photochemical reactions are found to be of zero order. The order of a reaction is greatly influenced by factors like temperature, pressure, and concentration.

Theoretically speaking reactions of higher order are possible. But reactions of order more than three are very rare. This is because such reactions should involve simultaneous collisions of more than three molecules. The probability for such collisions is limited. Therefore our study is limited to reactions up to order three. The rate equations for the first, second and third order reactions are given in the table.

Order	Type of reaction	Rate equation
1	A → Products	$k_1 = \frac{2.303}{t} \log \frac{a}{(a-x)}$
2	2A → Products	$k_2 = \frac{1}{at} \frac{x}{(a-x)}$
3	3A → Products	$k_3 = \frac{1}{2t} \{\frac{1}{(a-x)} - \frac{1}{a^2}\}$

Note: The derivation of the above rate equations is beyond the scope of this book.

Order and molecularity of a reaction

Order of a reaction is defined as the sum of the power of the concentration terms that occurs in the rate equation and is purely experimental quantity. It may be a whole number, fraction or even zero.

The molecularity of a reaction is the number of species (atoms or molecules) of the reactants that participate in the step leading to the chemical reaction. In many cases the order and molecularity are equal. Molecularity is always a small whole number and cannot be zero or fraction.

Pseudo unimolecular reactions

For many reactions, the order and molecularity are often identical but in some cases, the order is not the same as that of molecularity of the reaction.

Consider the hydrolysis of ethyl acetate in presence of dilute hydrochloric acid. Here, hydrochloric acid acts as a catalyst.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{HCl} CH_3COOH + C_2H_5OH$$

Evidently, the molecularity of this reaction is two. The rate equation for this reaction will be,

$$\text{rate} = k\,[CH_3COOC_2H_5]\,[H_2O]$$

But the concentration of water does not alter the rate of reaction and the reaction rate is determined by ethyl acetate only. Hence, the reaction is of first order.

This type of first order, bimolecular reactions are called pseudo unimolecular reaction.

Other examples

1) Inversion of cane sugar

$$\underset{\text{(sucrose)}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\text{(glucose)}}{C_6H_{12}O_6} + \underset{\text{(fructose)}}{C_6H_{12}O_6}$$

2) The oxidation of citric acid by perdisulphate ion.

Zero order reactions

These are the reactions in which the concentration of the reactants do not change with time i.e., the rate is unaffected by concentration. In other words, the rate remains constant throughout the reaction. For a reaction of this type, the rate of disappearance of reactant may be given by the relationship,

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

As the concentration remains constant throughout, the rate of zero order reaction is determined by some other limiting factors like intensity of the absorbed light in some photochemical reactions or the area of catalyst in certain surface reactions.

Examples for zero order reaction

i) Photochemical combination of H_2 and Cl_2 gas when exposed to sun light.

$$H_2 + Cl_2 \xrightarrow{h\upsilon} 2HCl$$

ii) Iodination of acetone in presence of an acid.

iii) The decomposition of HI in which Au acts as catalyst.

$$2HI \xrightarrow{Au} H_2 + I_2$$

iv) The decomposition of NH_3 in presence of Mo or W

$$2NH_3 \xrightarrow[W]{Mo\ or} N_2 + 3H_2$$

v) All enzyme catalysed reactions.

Determination of order of reaction

Method of integration (or) trial and error method

The progress of the chemical reaction under study is followed by measuring the change in concentration of the reactant/reactants with time. These values are substituted in the rate equations for first, second and third order reactions.

The order of the reaction is equal to that equation which gives a fairly constant value of the rate constant, k.

This method is applicable only to simple reactions.

Graphical Method

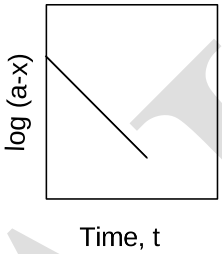
The order of a reaction in this method is determined from a plot of concentration versus time.

In the case of a first order reaction, a straight line is obtained by plotting log (a-x) against time, t.

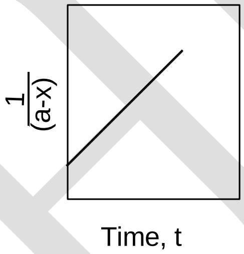
In the case of a second order reaction, a plot of $\frac{1}{(a-x)}$ Vs time, t gives a straight line,

Whereas a straight line is obtained if $\frac{1}{(a-x)^2}$ is plotted against time, t for a third order reaction.

The plots are shown in the following diagrams.



I order reaction



II order reaction

Time for half change method

The time for half change is the time required for the completion of half of the reaction. It is denoted by $t_{1/2}$.

The first order rate equation is,

$$k_1 = \frac{2.303}{t} \log \frac{a}{(a-x)} \qquad \text{.....................} (7)$$

When time is $t_{1/2}$, $x = a/2$

$$k_1 = \frac{2.303}{t_{1/2}} \log \frac{a}{(a-a/2)} \qquad \text{.........................} (8)$$

$$k_1 = \frac{2.303}{t_{1/2}} \log \frac{a}{a/2} \qquad \text{.........................} (9)$$

or,

$$t_{1/2} = \frac{2.303}{k_1} \log 2 \qquad \text{...........................} (10)$$

i.e.,

$$t_{1/2} = \frac{0.6932}{k_1} \qquad \text{...............................}(11)$$

It is seen that the time for half changes is independent of initial concentration a in the case of a first order reaction. Similarly it can be shown that for a second order reaction,

$$t_{1/2} = \frac{1}{k_2 a} \qquad \text{............................} (12)$$

and for third order reaction,

$$t_{1/2} = \frac{1}{k_3 a^2} \qquad \text{...........................} (13)$$

In general for a reaction of nth order

$$t_{1/2} \; \alpha \; \frac{1}{a^{(n-1)}} \qquad \text{.............................} (14)$$

To determine the order of a reaction in this method, the time for half change t_1 and t_2 is measured at two different initial concentrations a_1 and a_2. According to equation 14.

$$t_1 \; \alpha \; \frac{1}{a_1^{(n-1)}} \qquad \text{..............................} (15)$$

$$t_2 \;\alpha\; \frac{1}{a_2^{(n-1)}} \qquad \text{.......................................} (16)$$

15 ÷ 16 gives,

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

Taking log on both sides,

$$\log \frac{t_1}{t_2} = (n-1) \log \left(\frac{a_2}{a_1}\right)$$

$$(n-1) = \frac{\log (t_1 / t_2)}{\log (a_2 / a_1)} \qquad \text{.......................................} (17)$$

$$n = 1 + \frac{\log (t_1 / t_2)}{\log (a_2 / a_1)} \qquad \text{.......................................} (18)$$

It can be noted that for a first order reaction, the time for half change remains the same irrespective of the initial concentration.

In the case of a second order reaction, the product of $t_{1/2}$ and initial concentration, a is a constant.

For a third order reaction, $t_{1/2} \times a^2$ is a constant.

Ostwald's isolation method

The method, introduced by Ostwald (1902) is applicable when two or more than two reactants are involved in a chemical reaction. It is based on the fact that if a reaction involves **"a"** molecules of A, **b** molecules of B and **c** molecules of C, the total orders will be, **a+b+c.** The usual method is to take B and C in excess, then the order will be with respect to A i.e., **a** since when all but one of the reactants are taken in large excess so that their active masses remain constant and the concentration changes only to the isolated reactant A only. Then A and C are taken in excess, so that the order will be with respect to B i.e., **b.** Finally A and B are taken in excess, then the order will be **c.** The total order of the reaction will be, **a+b+c**.

It should be noted that the result obtained should be accepted with caution.

Effect of temperature on reaction rate

The rates of chemical reactions are influenced by many factors like nature of reactants, temperature, catalyst, concentration of the reactants. But the effect of temperature on reaction rates has been studied in great detail.

With rise in temperature, the rate of a chemical reaction also increases. A rises of 10°C in temperature usually doubles the rate of a reaction.

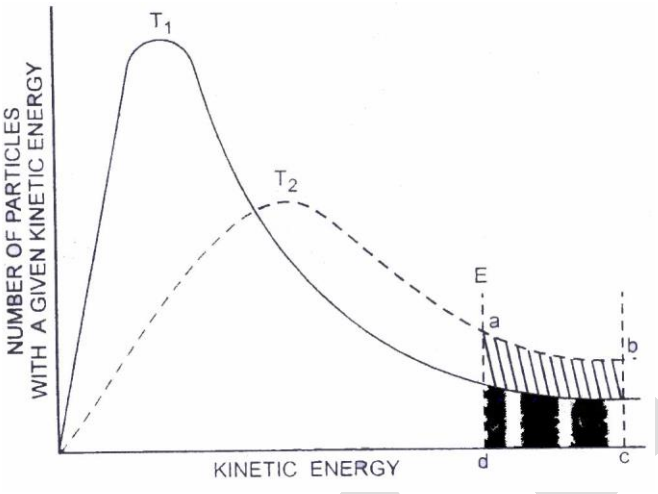
The ratio of the rate-constants of a chemical reaction at two different temperatures differing by 10K is known as the temperature coefficient of the reaction.

The temperatures usually taken are 298 K and 308 K

Thus, temperature coefficient=K_{308K}/K_{298K}

and almost all the reactions have a positive temperature coefficient. This rise in the reaction rate with rise in temperature is explained by collision theory.

According to the collision theory, chemical reactions take place due to collisions between the reactant molecules. At low temperatures the molecules move with low velocity and so possess low kinetic energy. Therefore, the number of molecules colliding will be few and so the number of collisions. As temperature increases, thermal energy is supplied to the molecules, this result in an increase in the kinetic energy of the molecules. Hence, at a higher temperature more molecules will collide with each other thereby converting more reactants into products.

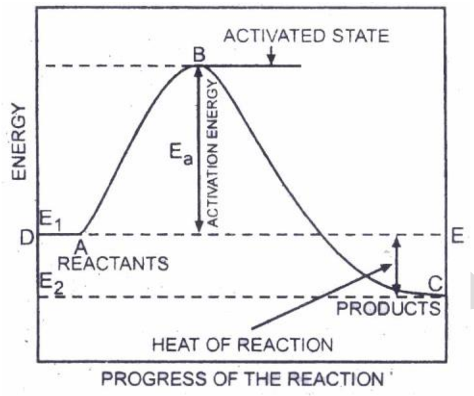


The figure depicts the relationship between kinetic energy and the number of molecules with a given kinetic energy. It is seen in the figure that at a higher temperature, T_2 the number of molecules possessing a particular value of kinetic energy increases.

Arrhenius activation energy

The first quantitative explanation for the effect of temperature on reaction rate was put forward by the Swedish Chemist Arrhenius. According to him, the prime condition for a molecule to take part in a chemical reaction is that it must possess energy in excess of the average kinetic energy. This energy is called the energy of activation, E_a. Molecules possessing this activation energy are referred to as activated molecules. The number of activated molecules in a system is directly proportional to the temperature. As the temperature increases, the kinetic energy of the molecules increases, thereby increasing the number of collisions between the molecules. As a result of collisions between the molecules, energy distribution between the colliding molecules takes place thereby increasing the fraction of activated molecules. This results in an increase in the rate.

The above facts are explained with the help of the following figure.



In the figure, A represents the reactants, B the activated state and C the products. The reactants A are converted into products C not directly. But the reactants must get activated to go to the activated state B. At this state, two chances are possible-decomposition to products or to reactants. But, mainly products are formed. This is because, the products have less energy than the reactants. The difference in energy between the activated state and the reactants given by E_a is the activation energy of the reaction. The energy difference between the product and reactants is the heat of the reaction at the constant volume, ΔE. The above explanation holds good for an exothermic reaction.

Arrhenius derived quantitatively an equation connecting the rate constant, k of a reaction and temperature in the following way:

As stated earlier, the rate and/ or rate constants of a reaction is directly proportional to the fraction of the activated molecules.

i.e., k α fraction of activated molecules

k = A x fraction of activated molecules

Where A is the proportionality constant known as Arrhenius frequency factor.

It can be shown using Boltzmann's theory that the fraction of the molecules possessing energy, E_a in excess of the average energy = $e^{-Ea/RT}$

When this is applied to the present case,

$$k = A.e^{-E_a / RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(19)$$

Where, E_a is the activation energy,

Taking logarithm on both sides,

$$\log k = \log A - \frac{E_a}{2.303\,RT} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (20)$$

Let k_1 and k_2 be the rate constants of a reaction at two different temperatures, T_1 and T_2 respectively.

Substituting them in equation (20).

$$\log k_1 = \log A - \frac{E_a}{2.303\,RT_1} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (21)$$

$$\log k_2 = \log A - \frac{E_a}{2.303\,RT_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (22)$$

(22) – (21) gives,

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

$$\log \frac{k_2}{k_1} = \frac{E_a\,(T_2 - T_1)}{2.303\,R\,T_1\,T_2} \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ (23)$$

If the rate constants of a reaction at two different temperatures T_1 and T_2 are known, then using the above equation 23, the energy of activation of the reaction, E_a can be calculated.

Worked Examples

1. For a certain reaction the values of rate constant at 455 K and 445 K are found to be 4.65×10^{-4} sec^{-1} and 2×10^{-4} sec^{-1} respectively. Calculate the energy of activation for the reaction at this temperature range.

Given:

$k_2 = 4.65 \times 10^{-4}$ sec^{-1}

$k_1 = 2 \times 10^{-4}$ sec^{-1}

$T_1 = 445$ K ; $T_2 = 455$ K

Use:

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

$$\log = \frac{4.65\text{x}10^{-4}}{2\text{x } 10^{-4}} = \frac{E_a\,(455 - 445)}{2.303 \text{ x } 8.314 \text{ x } 445 \text{ x } 455}$$

$$\log 2.325 = \frac{10E_a}{2.303 \text{ x } 8.314 \text{ x } 445 \text{ x } 455}$$

$$0.3664 = \frac{10E_a}{2.303 \text{ x } 8.314 \text{ x } 445 \text{ x } 455}$$

$$E_a = \frac{2.303 \text{ x } 8.314 \text{ x } 445 \text{ x } 455 \text{ x } 0.3664}{10}$$

$$\mathbf{E_a = 142\ kJ}.$$

2. Calculate the rate constant of a reaction at 310 K given the value of the rate constant at 300 K to be 2.5×10^{-5} sec^{-1} and the energy of activation is 83.74 kJ/mole.

Given:

$E_a = 83740$ J ; $k_1 = 2.5 \times 10^{-5}$ sec^{-1}

$T_2 = 310$ K ; $T_1 = 300$ K

$R = 8.314$ Joules / deg / mol ; $k_2 = ?$

Use:

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

$$\log \frac{k_2}{2.5\text{x}10^{-5}} = \frac{83740\ (310 - 300)}{2.303 \text{ x } 8.314 \text{ x } 310 \text{ x } 300}$$

$$\log \frac{k_2}{2.5\text{x}10^{-5}} = \frac{837400}{2.303 \text{ x } 8.314 \text{ x } 310 \text{ x } 300}$$

$$\log \frac{k_2}{2.5\text{x}10^{-5}} = 0.4703$$

$$\frac{k_2}{2.5\text{x}10^{-5}} = \text{antilog } 0.4693 = 2.899$$

$$k_2 = 2.899 \text{ x } 2.5 \text{ x}10^{-5}\text{sec}^{-1}$$

$$k_2 = 7.383 \text{ x}10^{-5}\text{sec}^{-1}$$

The rate constant at 310 K is 7.383 x 10^{-5}sec^{-1}

3. The rate of a reaction gets doubled when the temperature is raised from 300 K to 310 K. Calculate the activation energy.

Use:

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

Given:

$k_2/k_1 = 2$; R = 8.314 Joules / deg / mol

T_1 = 27°C = 300 K; T_2 = 37°C = 310 K.

$$\log 2 = \frac{E_a\ (310 - 300)}{2.303 \text{ x } 8.314 \text{ x } 310 \text{ x } 300}$$

$$E_a = \frac{2.303 \text{ x } 0.3019 \times 8.314 \text{ x } 310 \text{ x } 300}{10} \text{ Joules}$$

E_a = **53.60 kJ.**

4. A first order reaction is 40% complete at the end of 50 min. What is the value of rate constant? In how many minutes will the reaction be 80% complete?

Use:

$$k = \frac{2.303}{t} \log \frac{a}{(a\text{-}x)}$$

Given:

t = 50 min, a = 100% x = 40%

Therefore (a-x) = 60%

$$\text{Rate constant, } k = \frac{2.303}{50} \log \frac{100}{60} \text{ min}^{-1}$$

$$= \frac{2.303}{50} \times 0.2218 = \mathbf{0.01021\ min^{-1}}$$

Use:

$$t = \frac{2.303}{k} \log \frac{a}{(a\text{-}x)}$$

Given:

a = 100% ; x = 80% ; (a-x) = 20%

k = 0.01021 min^{-1}

$$t = \frac{2.303}{0.01021} \log \frac{100}{20}$$

$$= \frac{2.303}{0.01021} \log 5$$

$$= \frac{2.303 \times 0.6990}{0.01021}$$

$$t = \mathbf{157.6\ min.}$$

CHAPTER –3

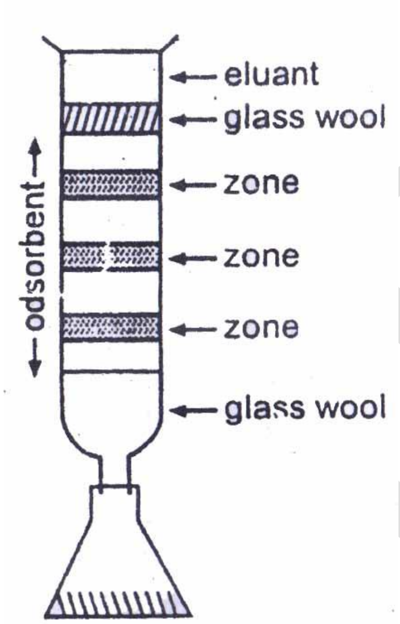
CHROMATOGRAPHY

Chromatography is a recent method of separating substances from one another that is widely used in analytical and preparative chemistry. This is based on differences in some physical properties like adsorption, partitioning between two immiscible solvents. Chromatography is commonly understood to involve the flow of a liquid or gas over a solid or liquid stationary phase. Thus, we may distinguish, on the basis of mobile phase, *liquid chromatography* and *gas chromatography*. Liquid chromatography is applicable to soluble substances and gas chromatography to volatile substances.

As the mobile phase flows past the stationary phase, a solute will undergo repeated sorption and desorption and move along at a rate depending among other factors, on its ratio of distribution between the two phases. If their distribution ratios are sufficiently different, components of mixture will migrate at different rates and produce a characteristic *chromatogram*. Liquid chromatography may be performed either in a tube filled with a sorbent (*column chromatography)*, on a sheet of paper (*paper chromatography)* or one layer of sorbent spread over a solid support *(thin layer chromatography).*

Column chromatography

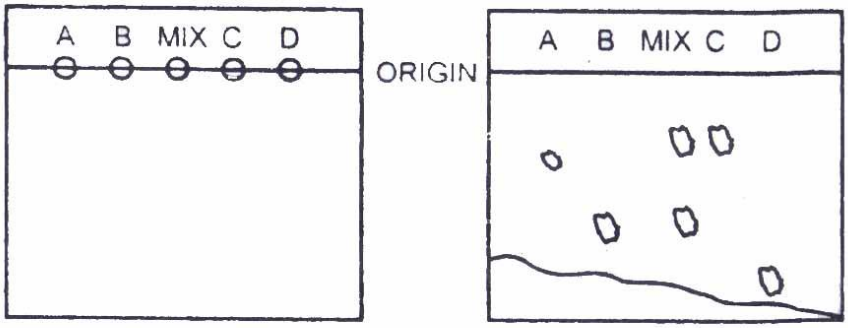
Column chromatography is based on the adsorption of different constituents of a mixture on solid adsorbents like MgO, Al_2O_3 Kieselguhr, silica gel, active charcoal etc. The common type of apparatus is shown in the figure. It consists of a column of a paste of any one of the above said adsorbents filled air tight. Above the column is placed a concentrated solution of the mixture and is *eluted* with a suitable solvent. The mixture of components dissolve in the solvent and run down the column. Depending upon the extent of adsorption, individual components get adsorbed at different heights in the column. The various zones of adsorption are made visible by running a suitable solvent through the column which produces different colour. The various zones thus developed are called a *chromatogram*. The solution which is used to separate the zone to various distances or give colouration with zone is known as *developer*. The solvent which removes a particular component from the column by elution is an *eluant*.



Partition chromatography

In this type, the solute gets distributed between a fixed liquid called the stationary phase and a mobile liquid (solvent) known as mobile phase. Paper chromatography is a special case of this type.

In paper chromatography a spot is made with the solution of the mixture in the centre of a circular paper or at the edge of a sheet of paper. The drop spreads out into a circular spot. When the spot has dried, the sheet of paper is introduced into a suitably closed apparatus with a portion of the paper immersed in the solvent which is chosen as the mobile phase. Care must be taken that the solvent spreads very slowly on the paper. The solvent percolates through the fibres of the paper and the different components of the mixture are moved to varying distance in the direction of the flow of the solvent.



In the case of a circular paper, the distribution of the solvent being circular in nature, the components move radially from the centre and a series of rings are formed.

The distance moved by the solvent is marked when it reaches a suitable distance. The paper is dried. If the substances are coloured, they can be located directly. Colourless substances are treated with reagents to produce coloured products. For example, ninhydrin is used to identify the amino acids.

The relative flow, the rate ratio or the distance moved by the component to the distance travelled by the solvent in a given time is determined. This is known as R_f value. Mathematically, it is expressed as

$$R_f = \frac{\text{Distance moved by the spot from the starting point}}{\text{Distance moved by the solvent from the same point}} \quad \text{during the same time}$$

Once the R_f values are known, they are compared with standard R_f values and the type of component in the mixture is identified. Quantitatively, it is determined by the intensity of the colour developed. The R_f values are independent of concentration but depends on the nature of the solvent and substance, temperature and quality of the paper used.

The advantages of paper chromatography are that a number of sample can be developed simultaneously under identical conditions on the same sheet and the possibility of multiple development.

Other advantages of paper chromatography are that filter paper is cheap and readily available and that it is easier to recover material by elution from pieces of paper.

Using two dimensional chromatography, the resolution can be increased i.e., the sample is placed near one corner of a square sheet and developed first is one direction and then in a second direction, perpendicular to the first.

Thin layer chromatography

Technically thin layer chromatography differs from paper chromatography mainly in requiring the preparation of a uniform layer of sorbent. A powder either dry or more frequently in a *slurry* is spread on a plate or other solid supports such as plastic or aluminum foil. Many types of mechanical spreading devices, ready made thin layer plates and sheets are commercially available. Usually a binder such as plaster or starch is incorporated in the powder to give mechanical stability.

A solution of the sample to be tested is prepared in a volatile solvent and is applied at one end of the plate as a drop. After drying the spot, the plate is supported vertically in a suitable glass tank with its lower edge touching the required mobile phase. The solvent ascends by capillary action and chromatogram develops. The plate is removed and the solvent is evaporated. The individual spots are identified as in paper chromatography.

Thin layer chromatography has the following advantages over paper chromatography.

1) The sorbent particles are smaller and more regular than paper fibres and produce less zone distortion.
2) They are less permeable and concentrate the solutes on the surface. This increases the sensitivity of the method and gives smaller and more compact zones.
3) The reagents those are too corrosive for paper chromatography may be used on thin layer Plate.

4) The eluates from thin layer chromatogram are contaminated by the material usually washed out of the filter paper.
5) The chromatogram can be heated to high temperatures, if necessary, without affecting the chromatogram.
6) This method of separation is the sharpest.

Application of Chromatography

1) Chromatography has been particularly valuable for the separation of mixtures containing a large number of compounds.
2) Gas- liquid chromatography is a very sensitive method to analyse the components of a complex mixture of volatile substances.
3) Chromatography is used in -
   a) Purification of substances from their contaminants.
   b) Concentration of solutes from dilute solutions.
   c) Identification of technical products.

The ion-exchange chromatography is used in -

1) The separation of lanthanides.
2) The softening of water.
3) The complete removal of ions (*demineralisation)* of water.
4) The removal of certain interfering radicals.
5) The purification of organic compounds extracted in water.

Text Book:

1. Thangamani, A. (2019). *Text Book on Allied Chemistry* (I Edition). Coimbatore: Karpagam Publication.

Reference Books:

1. Gopalan, R., and Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

2. Puri, B. R., Sharma, L. R., and Pathania, M. S. (2014). *Elements of Physical Chemistry* (46th Edition). Jalandhar: Vishal Publishing Company.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. What is Beer Lambert's Law?
2. What are the difference between order and molecularity of a reaction?
3. Write some examples of first order reaction.
4. Define (i) fast reaction (ii) rate.
5. Define order of a reaction. Write any two examples for first order reaction.
6. What is meant by zero order reactions?
7. State and explain Grotthus-Draper Law?
8. Define molecularity of a reaction.
9. Write some examples of zero order reaction.
10. State Stark-Einstein Law?
11. Define energy of activation. What is temperature coefficient?
12. What are the uses of ion-exchange chromatography?
13. Why acid hydrolysis of ester is called the pseudo unimolecular reaction?

14. How is order of a reaction found out by graphical method?

15. (i) Mention the names of few adsorbent.

 (ii) What are the uses of column chromatography?

PART-C (Each Question Carry Six Marks)

1. Explain (i) first order (ii) second order (iii) zero order reaction.

2. (i) Describe column chromatography.

 (ii) What are the applications of chromatography?

3. Discuss pseudo unimolecular reaction and zero order reaction with an example.

4. (i) Describe paper chromatography.

 (ii) Describe Ostwald's isolation method.

5. (i) Discuss the graphical method and trial and error method of determinations of order of reaction.

 (ii) Explain time for half change method.

6. (i) Discuss thin layer chromatography.

 (ii) Define R_f value.

7. Write notes on

 (i) Effect of temperature on reaction rate

 (ii) Arrhenius activation energy.

8. Write notes on

 (i) Beer-Lamberts law.

 (ii) Grotthus-Draper law.

 (iii) Stark-Einstein law.

 (iv) How is thin layer chromatography superior to paper chromatography?

9. (i) For a certain reaction the values of rate constant at 455 K and 445 K are found to be 4.65×10^{-4} sec^{-1} and 2×10^{-4} sec^{-1} respectively. Calculate the energy of activation for the reaction at this temperature range.

(ii) Calculate the rate constant of a reaction at 310 K given the value of the rate constant at 300 K to be 2.5×10^{-5} sec^{-1} and the energy of activation is 83.74 kJ/mole.

10. (i) The rate of a reaction gets doubled when the temperature is raised from 300 K to 310 K. Calculate the activation energy.

(ii) A first order reaction is 40% complete at the end of 50 min. What is the value of rate constant? In how many minutes will the reaction be 80% complete?

KARPAGAM ACADEMY OF HIGHER EDUCATION
(*Deemed to be University*)
(*Established Under Section 3 of UGC Act, 1956*)
Pollachi Main Road, Eachanari Post, Coimbatore–641 021.

DEPARTMENT OF CHEMISTRY

UNIT-IV

ELEMENTS OF PHOTOCHEMISTRY, CHEMICAL KINETICS AND CHROMATOGRAPHY

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. A photochemical reaction takes place by the absorption of

a) visible and ultraviolet radiations b) infrared radiations c) heat energy

d) microwave radiations

2. Photochemistry deals with the study of

a) photons b) photos **c) reactions which proceed with absorptions of UV light**

d) reactions which proceed with absorb of IR light

3. The wavelength of UV and visible regions of electromagnetic spectrum is

a) less than 2000 Å b) more than 8000 Å **c) 2000 to 8000 Å** d) 200 to 400 nm

4. The Grotthuss-Draper law is also called as

a) Lambert law b) photochemical equivalence law c) photo equivalence law

d) principle of photochemical activation

5. Grotthuss-Draper law was discovered by

a) Theodor Grotthuss and John William Draper b) Johannes Stark and Albert Einstein

c) Beer and Lambert d) Planck's

6. The only light is absorbed by a system can bring about a photochemical change. This statement was given by

a) Lambert law b) Beer-Lambert law **c) Grotthuss-Draper law** d) Stark-Einstein law

7. Stark-Einstein law is also known as

a) Lambert law **b) photochemical equivalence law** c) Beer law

d) principle of photochemical activation

8. “In a photochemical reaction each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products” This is the statement of

a) Beer- Lambert law b) Grotthuss-Draper law **c) Stark-Einstein law** d) Lambert law

9. The photon is a

a) two unit of radiation b) three unit of radiation c) four unit of radiation

d) one unit of radiation

10. The Beer- Lambert law is also called as

a) photochemical equivalence law b) photo equivalence law

c) principle of photochemical activation **d) Beers law**

11. The biphotonic processes means

a) molecule absorbed two photons of light b) molecule absorbed one photon of light

c) one quantum of radiation d) non quantum of radiation

12. The energy associated with a photon is given by the equation

a) $E = hv$ b) $E = mc^2$ c) $E = hc$ d) $E = hc^2$

13. Beer-Lambert law follows the

a) non-linear relationship **b) linear relationship** c) linear free energy relationship

d) zigzag relationship

14. Which one is affect the rate of chemical reaction?

a) volume b) time c) mass **d) temperature**

15. The rusting of iron is an example for

a) pseudo unimolecular reaction b) zero order reaction c) fast reaction **d) slow reaction**

16. The order of reaction is defined as the sum of the powers of the concentrations of the

a) products in the rate equation b) rate **c) reactants in the rate equation**

d) reactants and products in the rate equation

17. Many reactions which proceed at a very high speed that their rates cannot be measured such reactions are known as

a) complex reaction **b) fast reaction** c) slow reaction d) elementary reaction

18. The rate of chemical reaction is the variation in the concentration of either reactants or the products with

a) time b) mass c) temperature d) pressure

19. The unit for the rate is

a) mole lit^{-1} sec^{-1} b) mole c) sec^{-1} d) mole lit^{-1}

20. The neutralization of a base by an acid is an example for

a) unimolecular reaction **b) fast reaction** c) bimolecular reaction d) slow reaction

21. The unit for the rate is mathematically expressed as

a) dr/dt b) dp/dt **c) dc/dt** d) drp/dt

22. The speed or velocity of a chemical reaction is directly proportional to the active mass of the reactants is known as

a) Ostwalds law b) Arrhenius law c) Einstein law **d) Law of mass action**

23. The rate equation the negative sign indicates the

a) decrease in the concentration of the reactants with time b) decrease in the concentration of the products with time c) increase in the concentration of the products with time

d) increase in the concentration of the reactants with time

24. Decomposition of hydrogen peroxide is an example for

a) zero order reaction **b) first order reaction** c) second order reaction d) third order reaction

25. Benzoin condensation is an example for

a) zero order reaction b) first order reaction **c) second order reaction** d) third order reaction

26. Example for second order reaction is

a) radioactive decay b) thermal decomposition of nitrogen pentoxide

c) decomposition of HI **d) base catalyzed ester hydrolysis**

27. Example for first order reaction is

a) thermal decomposition of nitrogen pentoxide b) benzoin condensation

c) conversion of ammonium nitrate into urea d) base catalyzed ester hydrolysis

28. The order of a reaction is

a) cannot be whole number b) cannot be zero **c) whole number, fraction or even zero**

d) cannot be fraction

29. Molecularity of a reaction is always a

a) not a whole number b) zero c) fraction **d) small whole number**

30. The number of species (atoms or molecules) of the reactants that participate in the step leading to the chemical reaction is known as

a) molecularity of a reaction b) order of a reaction c) pseudo unimolecular reaction d) zero order reaction

31. Many photochemical reactions are found to be

a) second order **b) zero order** c) first order d) third order

32. The order of a reaction is greatly influenced by

a) mass b) time **c) temperature** d) volume

33. The hydrolysis of ethyl acetate in presence of dilute hydrochloric acid is an example for

a) second order reaction b) zero order reaction

c) first order reaction **d) pseudo unimolecular reaction**

34. Pseudo unimolecular reaction means

a) order is one and molecularity is two b) order is one and molecularity is one

c) order is two and molecularity is two d) order is one and molecularity is one

35. The rate is unaffected by concentration for

a) second order reaction **b) zero order reaction**

c) first order reaction d) pseudo unimolecular reaction

36. Iodination of acetone in presence of an acid is an example for

a) second order reaction b) first order reaction

c) zero order reaction d) third order reaction

37. The molecularity of a reaction

a) is always the same as its order b) could be zero c) could be fractional **d) is always integral**

38. The unit of the first order rate constant is

a) time^{-1} b) concn^{-1} c) concn^{-1} time^{-1} d) concn. time^{-1}

39. The decomposition of HI in the presence of Au catalyst is a

a) second order reaction **b) zero order reaction**

c) first order reaction d) third order reaction

40. Which one method is used to determine the order of reaction?

a) volumetric method b) conductmetric method

c) graphical method d) potentiometric method

41. The plotting log (a-x) against time, t for a first order reaction is

a) parabola b) hyperbola c) Zig-Zag line **d) straight line**

42. Time for half change method is donated by

a) $k_{1/2}$ b) $k_{3/2}$ c) $k_{2/3}$ **d) $t_{1/2}$**

43. The rise in the reaction rate with rise in temperature is explained by

a) Ostwalds dilution theory b) Lewis theory c) Bronsted theory **d) collision theory**

44. The ratio of rate constants of a chemical reaction at two different temperatures differing by 10 K is known as the

a) specific rotation b) coefficient of expansion **c) temperature coefficient**

d) extinction coefficient

45. As the temperature of a reaction is increased, the rate of the reaction increases because of

a) reactant molecules collide with greater energy b) reactant molecules collide with less energy c) reactant molecules collide less frequently and with greater energy d) activation energy is lowered

46. Molecules possessing activation energy are referred to as

a) super molecules **b) activated molecules** c) ionic molecules d) non-ionic molecules

47. The hydrolysis of ethyl acetate in presence of dilute hydrochloric acid, the order and molecularity of a reaction are

a) 3,2 b) 2,3 **c) 1,2** d) 2,2

48. Liquid chromatography is applicable to

a) volatile substance b) non-volatile substance c) insoluble substance **d) soluble substance**

49. Gas chromatography is applicable to

a) soluble substance b) non-volatile substance c) insoluble substance **d) volatile substance**

50. The relative flow, the rate ratio or the distance moved by the component to the distance travelled by the solvent in a given time is determined. This is known as

a) pH value b) pK_a value **c) R_f value** d) pK_b value

51. Chromatography is used in

a) non-purification of substances from their contaminants **b) purification of substances from their contaminants** c) non-identification of technical products d) concentration of solutes from dilution solutions not possible

52. R_f value depends on

a) solvent b) molecular weight c) concentration d) volume

53. Advantage of paper chromatography is

a) filter paper is expensive **b) it is easier to recover material by elution from paper**

c) elution is not required d) solvent tank is not required

54. Example for solid adsorbent is

a) ninhydrin **b) silica gel** c) ZnO d) CuO

55. The solvent which removes a particular component from the column by elution is an

a) eluent b) developer c) adsorbent d) sorbent

56. The solution which is used to separate the zone to various distances or give colouration with zone is known as

a) eluent **b) developer** c) adsorbent d) sorbent

57. The paper chromatography, ninhydrin is used to identify the

a) phenols b) acids **c) amino acids** d) carbohydrates

58. The ion-exchange chromatography is used in

a) identification of technical products b) purification of substances from their contaminants

c) concentration of solutes from dilution solutions **d) the separation of lanthanides**

59. The liquid used in column chromatography separation is called

a) the absorbent b) the adsorbate c) the solvent **d) the eluent**

60. The R_f value for a compound is a constant

a) at a particular temperature b) for a particular eluent

c) under constant experimental conditions d) at a particular pressure

UNIT-V

SYLLABUS

Dyes, Chemotherapy and Vitamins: Dyes: Terms used chromophore, auxochrome, bathachromic shift and hypsochromic shift- classification of dyes – based on chemical structure and application-one example each for azo, triphenylmethane, vat and mordant dyes- preparation.**Chemotherapy:** Preparation, uses and mechanism of action sulpha drugs- preparation and uses of prontosil, sulphadiazine and sulphafurazole-structure and uses of pencillins and chloromycetin. **Vitamins:** Diseases caused by the deficiency of vitamins A, B_1, B_2, C and D-sources of these vitamins.

CHAPTER-1

SYNTHETIC DYES

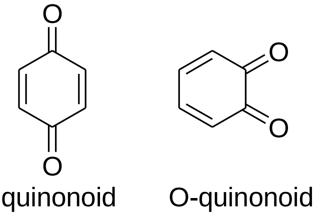
Introduction

The dyeing of cloth is one of ancient arts. Many natural dyes have been known for a long time. These were obtained from animal and vegetable sources. Today, however, practically all dyes are synthetic and are prepared from aromatic compounds. The only source of which was originally coal tar - hence, the name coal tar dyes.

All coloured compounds are not dyes. If a substance is a dye, it must fulfil the following conditions -

(a) It must have a suitable colour.
(b) It must be able to “fix” itself or capable of being “fixed” to the fabric.
(c) The fixed dye must show fastness to light, heat, washing and bleaching.

It was observed that colour in organic compounds is associated with the presence of certain groups called **chromophore** (Greek, meaning, colour bearing) in the molecule. The most effective chromophores are azo (-N=N-), nitroso (-N=O), nitro ($-NO_2$),



carbonyl (-C=O), thiocarbonyl (-C=S) and dicarbonyl (-CO-CO-).

Depth of colour increases with the number of chromophores.

Certain groups, which do not produce colours themselves, are capable of deepening the colour when present in a molecule together with a chromophore. These colour **augmenters** or **deepeners** are described as **auxochromes** (Greek, meaning, to increase). Some of them are hydroxyl (-OH), alkoxy (-OR), amino (-NH_2), alkylated amino (-NR_2). Thus, the nitrophenols and nitroanilines are more intensely coloured than nitrobenzene.

Chromophore

A covalently unsaturated group responsible for absorption in the UV or visible region is known as a chromophore. For example, C=C, C≡C, C=O, C≡N, N=N, NO_2 etc. If a compound absorbs light in the visible region (400-800 nm), only then it appears coloured. Thus, a chromophore may or may not impart colour to a compound depending on whether the chromophore absorbs radiation in the visible or UV region.

Chromophores like C=C, or C≡C, having π electrons undergo $\pi \rightarrow \pi^*$ transitions and those having both π and non bonding electrons, e.g. C=O, C≡N or N=N, undergo $\pi \rightarrow \pi^*$ and $n \rightarrow \sigma^*$ transitions. Since the wavelength and intensity of absorption depend on a number of factors, there are no set rules for the identification of a chromophore.

Auxochrome

A covalently saturated group which, when attached to a chromophore, changes both the wavelength and the intensity of the absorption maximum is known as auxochrome, e.g. NH_2, OH, SH, halogens etc. Auxochormes generally increase the value of λ_{max} well as ε_{max} by extending the conjugation through resonance. These are also called *coloured enhancing group*. An auxochrome itself does not show absorption above 200 nm. Actually, the combination of chromophore and auxochrome behaves as a new chromophore having different values of λ_{max} and $\varepsilon_{max.}$ For example, benzene shows λ_{max} 256 nm, ε_{max} 200, where aniline shows λ_{max} 280 nm, ε_{max} 1430 (both increased). Hence, NH_2 group is an auxochrome which extended the conjugation involving the lone pair of electrons on the nitrogen atom resulting in the increased values of λ_{max} and ε_{max}.

Bathochromic shift

The shift of an absorption maximum to a longer wavelength due to the presence of an auxochrome, or solvent effect is called a bathochromic shift (or) red shift. For example, benzene shows λ_{max} 256 nm and aniline shows λ_{max} 280 nm. Thus, there is a bathochromic shift of 24 nm in the λ_{max} of benzene due to the presence of auxochrome, NH_2. Similarly, a bathochromic shift of $n\rightarrow\pi^*$, band is observed in carbonyl compounds on decreasing solvent polarity e.g. λ_{max} of acetone is at 264.5 nm in water as compared to 279 nm in hexane.

Hypsochromic shift

The shift of an absorption maximum to a shorter wavelength is called hypsochrmoic or blue shift. This is caused by the removal of conjugation or change in the solvent polarity. For example, aniline shows λ_{max} 280 nm, whereas anilinium ion (acidic solution of aniline) shows λ_{max} 254 nm. This hypsochromic shift is due to the removal of $n\rightarrow \pi$ conjugation of the lone pair of electrons of the nitrogen atom of aniline with the π-bonded system of the benzene ring on protonation because the protonated aniline (anilinium ion) has no lone pair of electrons for conjugation. Similarly, there is a hypsochromic shift of 10-20 nm in the λ_{max} of $\pi\rightarrow\pi^*$ bands of carbonyl compounds on going from ethanol as solvent to hexane, i.e. on decreasing solvent polarity.

Classification

Dyes are classified according to their chemical constitution or by their application to the fibre.

Classification based on chemical constitution

This is mainly based on the nature of group present in the dye.

(a) **Nitro and nitroso dyes**: These are the oldest ones but are commercially less important.

Example: Picric acid.

(b) **Triphenylmethane dyes**: These are obtained by introducing $-NH_2$, $-NR_2$ or -OH groups into the triphenylmethane ring. They have brilliant colours but these colours fade with washing.

Example: Malachite green, pararosaniline, magenta, crystal violet.

(c) **Phthalein dyes**: These are obtained by condensing phenols with phthalic anhydride in the presence of dehydrating agents.

Example: Phenolphthalein, fluorescein, eosin.

(d) **Anthraquinone dyes**: These have anthraquinone nucleus.

Example: Alizarin.

(e) **Azo dyes**: These are the largest class of synthetic dyes. Their chromophore is an aromatic system joined to the azo group and the common auxochromes are $-NH_2$, $-NR_2$ and -OH.

According to the number of azo group in the molecule, azo dyes are classified as monazo, diaszo, trisazo–dyes etc. and are also subclassified as basic (cationic) dyes, acidic (anionic) dyes etc.

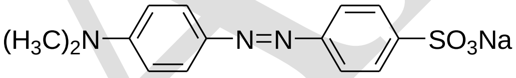
The usual method of preparation of azo dyes is direct coupling between the diazonium salt and a phenol or aniline. The structure of the dye is determined by reduction with stannous chloride and hydrochloric acid.

The common example for azo dyes and their uses are given in the following table:

Azo Dyes

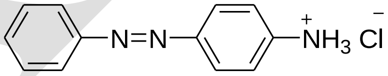
S.No.	Name	Type	Uses
1	Aniline yellow	basic	dye for oils and lacquers
2	Butter yellow	-	colouring margarine and oils
3	Resorcin yellow	-	dye for silk
4	Methyl orange	acidic	indicator
5	Orange II	acidic	dye for wool, silk, nylon, paper leather and indicator.
6	Methyl red	acidic	indicator
7	Congo red	disazo	dye for cotton and indicator
8	Para red	azoic	dye for paper, wool and silk
9	Bismarck brown	tetrazo	dye for leather, wool and cotton
10	Chrysoidine	basic	dye for paper jute, wool, leather and silk

1) Methyl orange (anionic dye)



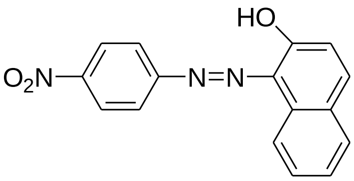
Methyl orange (anionic dye)

2) Chrysoidine (cationic dye)



Chrysoidine (cationic dye)

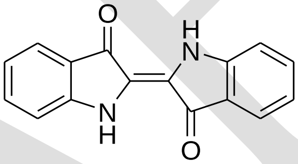
3) Para red (azoic dye)



Classification according to application

a) **Mordant dyes:** These dyes do not dye a fibre directly. They require a mordant. The mordant fixes the dye to the fibre. Commonly used mordants are hydroxides or basic salts of chromium, iron or aluminium. With basic dyes, tannic acid is used as mordant. The metal salts are referred to as lakes.

b) **Vat dyes:** These dyes are insoluble in water but on reduction with $NaHSO_3$ yield alkali soluble forms (leuco compounds) which may be colourless. It is in this form they are introduced into the fabric. The reduction was formerly carried out in wooden vats, giving rise to the name, vat dyes. After the reduced dye has been absorbed in the fibre, the original insoluble coloured dye is reformed by oxidation with air or chemicals. Indigo is an example of a vat dye and its structure is given below:



Vat dyes are used to dye cotton and are very fast, because of their insolubility in water.

Preparation of Indigo

Indigo is the oldest dye known. It was used in Egypt at the time the pyramids were built. India appears to be the birth place of Indigo.

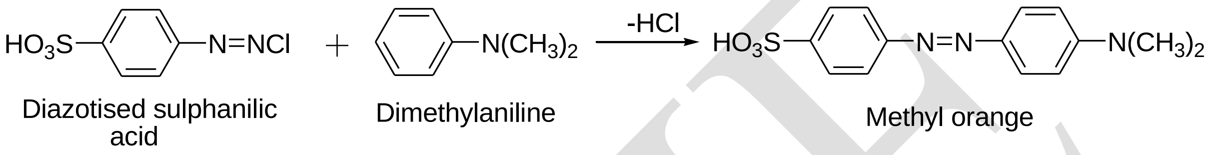
Indigo is not present as such in the plant indigofera species. It occurs only as indican, which is the beta-glucosides of indoxyl. The glucoside is extracted from the plant with water. On fermentation indoxyl is obtained. The insoluble, blue powder indigo is produced on oxidizing the indoxyl by the oxygen or air.

PREPARATION OF DYES

I. AZO DYES

Example: Methyl orange

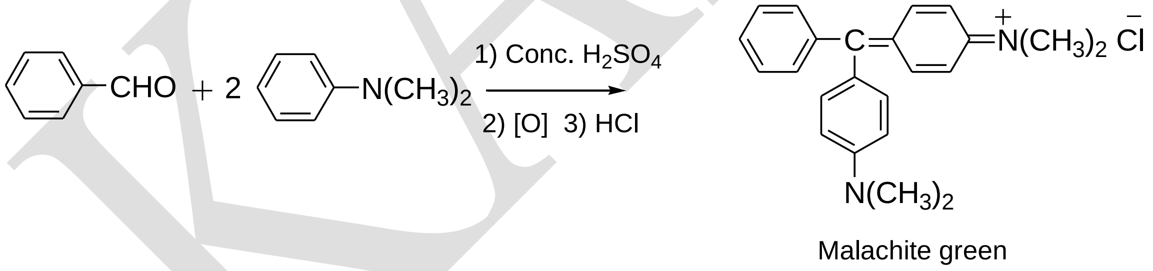
This dye is prepared by coupling diazotised sulphanilic acid with dimethylaniline.



II. TRIPHENYLMETHANE DYES

Example: Malachite green

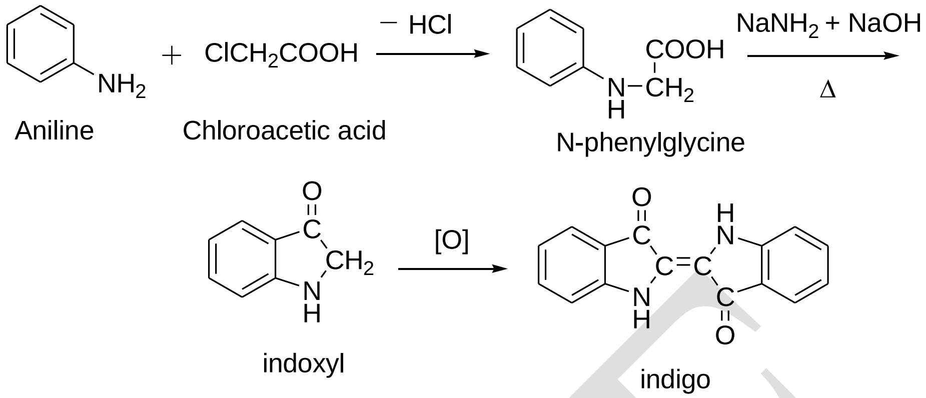
It is prepared by condensing benzaldehyde (1 molecule) with dimethylaniline (2 molecules) in presence of concentrated sulphuric acid followed by oxidation of leuco base with lead dioxide and hydrochloric acid to colour base which reacts further with hydrochloric acid to give malachite green.



III. VAT DYES

Example: Indigo

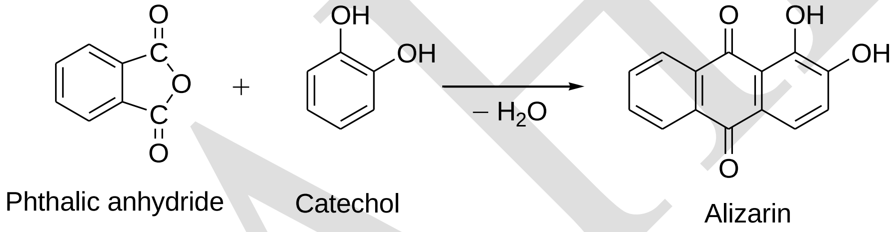
By the condensation of aniline with chloroacetic acid to get *N*-phenylglycine which is fused with caustic soda and sodamide at 570 K to produce indoxyl. This on oxidation gives indigo.



IV. MORDANT DYES

Example: Alizarin

By the condensation of catechol with phthalic anhydride to get alizarin.



CHAPTER-2

CHEMOTHERAPY

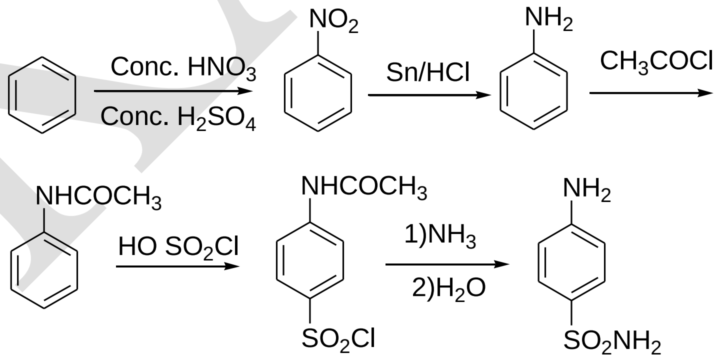
Ehrlich in 1909 introduced the term chemotherapy. It may be defined as *the treatment of disease caused by bacterial invasion by chemical compounds.* These chemicals selectivity destroy the micro-organisms without affecting the host tissues. This defenition excludes *disinfectants* like formaldehyde, phenol, iodine etc., because they are applied externally and tend to destroy the tissues.

Compounds which exert various physiological effects of therapeutic value are collectively known as *drugs*. In this section we shall discuss some *sulpha drugs*, which have great antibacterial powers.

SULPHA DRUGS

Sulphanilamide, sulphonamide or p-aminobenzene sulphonamide and its derivatives have great antibacterial powers and are commonly known as sulpha drugs. They have remarkable action against *cocci infections* like *pneumonia*, *gonorrhea*, *dysentery* and *bacterial infections* in general.

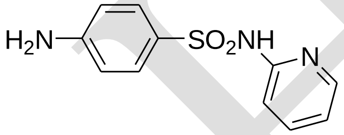
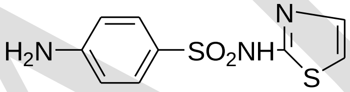
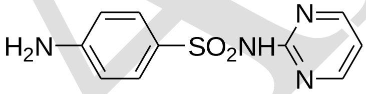
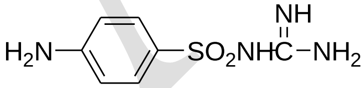
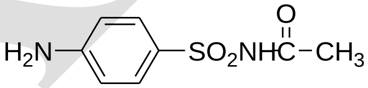
The parent compound of all sulpha drugs, namely sulphonamide, p-NH_2-C_6H_4-SO_2NH_2, is prepared from benzene in the following way:



Benzene is converted into aniline first. The acetylation of aniline with acetic anhydride or acetyl chloride forms acetanilide. This is treated with chlorosulphonic acid, $HOSO_2Cl$. The product obtained is treated with ammonia followed by hydrolysis gives sulphanilamide.

Sulphanilamide is a white crystalline solid, m.p. 439 K. The derivatives of sulphonamide have substituents on the nitrogen atom of the sulphonamide $–SO_2NH_2$ group. It will be worthwhile to note the structural formula of some sulpha drugs and the diseases they cure.

SULPHA DRUGS

Sulpha drug	Structural formula	Diseases cured
Sulpha-pyridine		Pneumonia
Sulpha-thiazole		Severe infections
Sulpha-diazine		Mild infections
Sulpha-guanidine		Bacillary dysentery
Sulpha-acetamide		Urinary tract infections

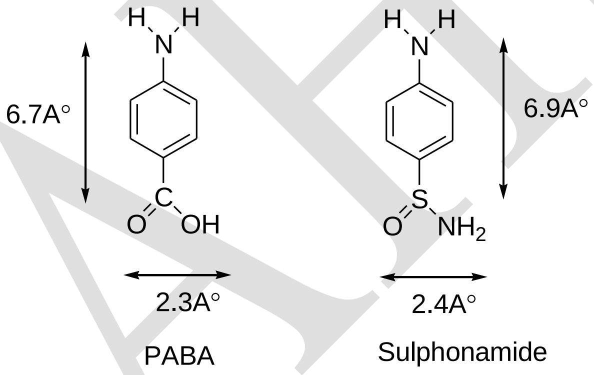
Sulpha drugs or sulphonamide are antimicrobial compounds containing sulphonamido ($-SO_2NH_2$) group.

These are synthetic chemotherapeutic agents. These were the first antibacterial drugs to be used successfully for the treatment of bacterial infection in human. These are active against certain gram positive and gram negative organisms. These are mainly bacteriostatic in action and are used in the treatment of many diseases like gonorrhoea, blood poisoning, scarlet fever, tonsillitis sinus infections, urinary tract infections etc.

Mechanism of action

Sulphonamides exhibit bacteriostatic action. Paraaminobenzoic acid (PABA) is a growth factor for micro organisms. Sulphonamides compete in the process of folic acid synthesis by micro organisms. Folic acid contains PABA unit.

PABA and sulphonamides have structural resemblance as below:

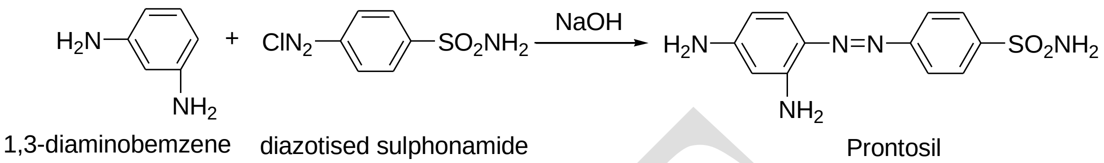


Therefore, bacteria utilise sulphonamide instead of PABA *by mistake* in the biosynthesis which prevents the growth of bacteria.

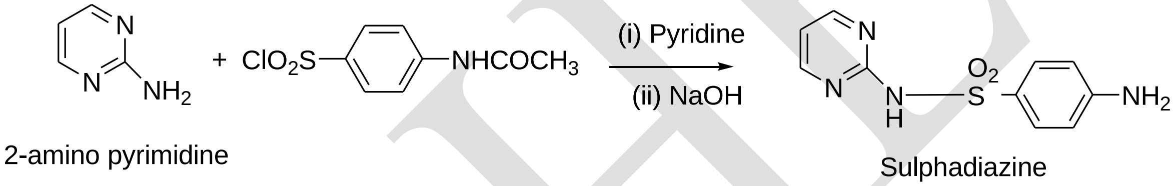
Some important sulphonamide drugs are as follows.

1. **Prontosil:** It is prepared by the coupling reaction between 1,3- diaminobenzene and diazotized sulphonamide.

Prontosil was the first prepared sulphonamide. It was used in the treatment of streptococcal sore throat, streptococcal fever, acute endocarditis etc. Due to its low solubility, it was generally used as its hydrochloride derivative as it is more soluble. Later on prontosil dye was replaced by prontosil soluble which is superior drug and has greater solubility and greater activity.

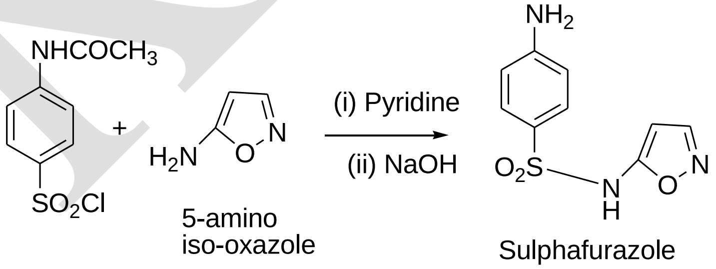


2. **Sulphadiazine:** It is prepared by condensing 2-aminopyrimidine with p- acetanilide sulphonyl chloride, (ASC) in the following manner.



It is used for general purposes as it is not toxic and is easily absorbed and excreted. It is a short acting sulpha drug and is used for systemic infections and is usually administered orally. It is used in the treatment of meningococcal meningitis.

3. **Sulphafurazole :** It is prepared by condensing 5- aminoisoxazole (or highly substituted isoxazole) with p-acetanilide sulphonyl chloride (ASC).



It is a short acting sulphonamide. It is rapidly excreted and is in high concentration in plasma. It is used in urinary tract infection.

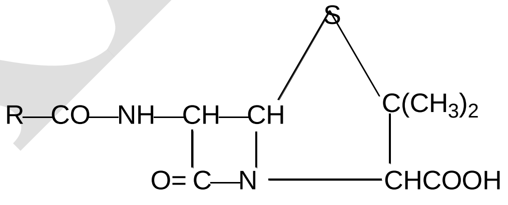
ANTIBIOTICS

An *antibiotic* is a compound produced by one micro-organism which kills another micro-organism. Hence, the more appropriate term will be *'anti-microbiotics'.* They are designed in such a way as to be more harmful to the invading organism than to the patients. They need be present only in low concentration to bring about the antibiotic action. Thus, these are chemotherapeutic agents. Antibiotics are generally produced or obtained from living cells of fungi, bacteria etc. by fermentation.

Among the micro-organisms which cause diseases, bacteria are the single cause of disease. *Gram* classified the bacteria into two main groups depending on their ability to stain as *Gram positive* (can be stained) and *Gram negative* (cannot be stained). Some antibiotic kill *Gram positive* bacteria and some *Gram negative*. But certain antibiotics treat diseases caused by both and are called *broad spectrum antibiotics*. We shall discuss few antibiotics in detail in this section.

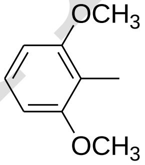
Penicillins

These are the most potent antibacterial drugs. Fleming in1929 discovered it from the mold *penicillium species.* Penicillin is the name given to the mixture of natural compounds having the general molecular formula, $C_9H_{11}O_4N_2SR$ and differing only in the nature of R. Penicillin-G is the most commonly used one among the natural penicillin. The common structure formula is given.



Penicillins

Classification based on the nature of R group is given in Table.

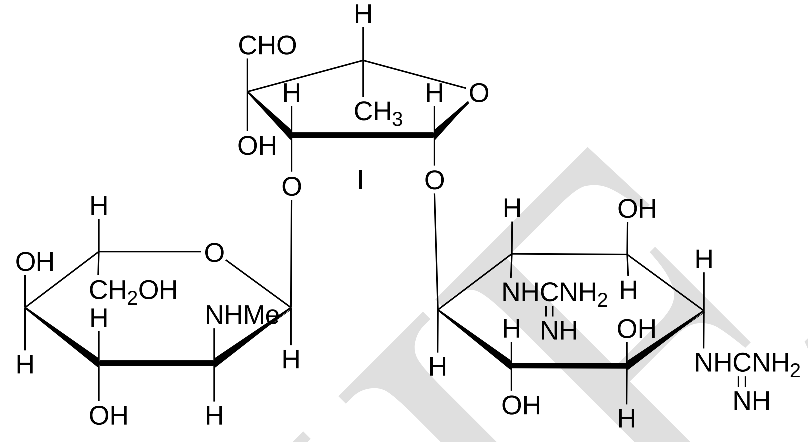
No.	Penicillin	R=
1.	F	$-CH_2-CH=CH-CH_2-CH_3$
2.	G	$-CH_2C_6H_5$
3.	K	$-CH_2-(CH_2)_5-CH_3$
4.	N	$-(CH_2)_3-CH(NH_2)-COOH$
5.	X	$-CH_2C_6H_4-OH$(p)
6.	V	$-CH_2-O-C_6H_5$
7.	Ampicillin	$-CH(NH_2)-C_6H_5$
8.	Methicillin	

Penicillins are of two classes- (1) biosynthetic and (2) semisynthetic. Biosynthetic types are formed during fermentation e.g. Penicillin G, V. Semisynthetic types are made by adding certain compounds to 6-amino penicillaric acid.

Penicillin is active only against Gram positive organism including *staphylococci*, *pneumococci*, *meningococci*, *gonococci* and against *spirochetes.* Penicillin is less toxic but it loses much of its activity when given orally and that it is excreted rapidly.

Methicillin is synthesised from minopenicillinic acid. Those micro-organisms resistance to penicillin are responsive to it.

Streptomycin, $C_{21}H_{39}O_{12}N_7$



II III

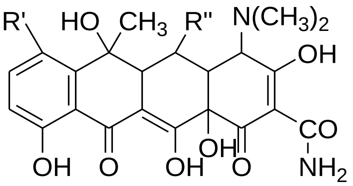
I-Streptose II-*N*-methylglucosamine III-Streptidine

Streptomycin was isolated by Waksman et al from cultures of streptomyces griseus in 1944. It is composed of three units *streptose, streptidine and N-methylglucosamine.* This antibiotic is very effective in the treatment of tuberculosis, meningitis, pneumonia, plague, tularemia, bactremia and streptococci. It is also used to treat other common infections like throat, lungs, ears and kidneys.

Prolonged used of this drug may lead to deafness.

Tetracycline antibiotics

	R’	R”
Aureomycin	Cl	H
Terramycin	H	OH



The success of streptomycin in therapy stimulated search for other antibiotic. This led to the isolation of aureomycin in 1948 from *streptomyces aurefaciens* and terramycin from *streptomyces rimosus.*

Chlorotetracycline (aureomycin) and oxytetracycline (terramycin) are derivatives of a highly complex substance containing four fused rings. Hence, they are named as tetracycline.

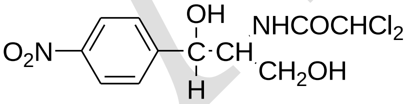
These antibiotics are used widely in various diseases -

Bacterial, viral and rickettisial. Aureomycin is used in the treatment of typhoid fever and terramycin is very effective in the treatment of *trachoma*.

Unlike penicillin and streptomycin, these can be given orally as they are absorbed from the gastro intestinal tract. Hence, they have largely replaced streptomycin and penicillin.

Chloramphenicol, chloromycetin, $C_{11}H_{15}O_5N_2Cl_2$

The chlorine containing antibiotic, chloramphenicol was isolated in 1948 by Carter et al from a *streptomyces venezuela*, a micro-organism found in the soils of Venezuela, Illinois and Japan.



Chloromycetin is very effective against Gram negative bacteria especially those producing intestinal diseases such as typhoid fever, diarrhoea and dysentery. It is as effective as aureomycin and terramycin against typhus and virus pneumonia.

HORMONES

Animal release secretions through ducts associated with glands, hence there are *duct glands or exocrine glands. e.g.* salivary, sweat glands. But hormones are secreted and released directly into the blood circulation. Hormones are chemical substances secreted in one part of the body and carried through the blood stream to other parts (organs or tissues) of the body. Hormones are called as *endocrine glands or ductless glands.* For these endocrine glands, blood serves both as a vehicle for transport and as a source of chemical raw materials. The significance of hormones (*Greek, I excite)* was known in 1902.

Properties and functions of hormones

1. Hormones are produced in very small amounts (say 10^{-9}g to 10^{-3}g) in a day.
2. Hormones act at cellular level.
3. Hormones act as *trigger substance* – i.e., they initiate biochemical reaction that persists even after their absence.
4. Hormones may be proteins, steroid or amino acid derivatives.
5. They control growth, cellular oxidation, metabolism of water, salt, carbohydrates, fats and proteins.
6. As they direct, regulate and co-ordinate the activities of the various organs in the body, they play vital role in development right from the embronic to the adult stage.

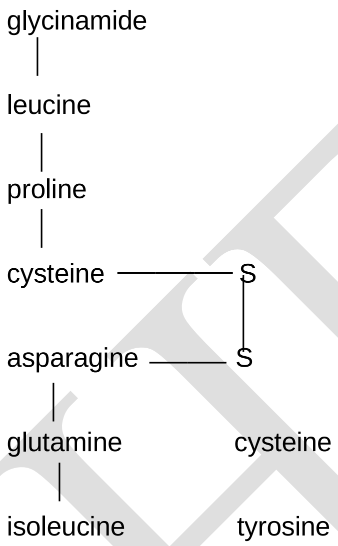
Insulin

Insulin secreted by the *pancreas*, is extremely complex. It consists of 51 amino acids and has manifold influences in the body. It facilitates the utilisation of glucose at the cellular level. i.e., it transports glucose from blood to tissues. It also prevent excessive breakdown of glycogen stored in the liver and muscles. It controls the metabolism of fats and proteins.

Oxytocin

This hormone occurs in the posterior pituitary gland. It causes rhythmic contracts of the mammalian uterus at the time of child birth. The uterus dose not response to oxytocin at any other time because of the inhibiting influence of progesterone. Oxytocin also plays a role in mammalian lactation.

The structure was established independently by du Vigneaud et al and Tuppy et al in 1953. Oxytocin is extracted from the gland by acetic acid and is purified by chromatography or electrophoresis. The molecular weight of oxytocin was about 1,000. This indicates that the molecule is an octapeptide and is shown below.



The isoelectric point of oxytocin is 7.7.

VITAMINS

Vitamins, **the assorted group of chemicals** are essential for the maintenance of normal metabolic functions. Most of these are not synthesized in the body and must therefore be supplied to the body in diet.

It was thought earlier that a diet having only proteins, fats, carbohydrates and some inorganic substance was enough for sustaining normal life. Nevertheless, when an artificial diet consisting of only above material was given to rats, they died after sometime. However, when small amount of milk was added to the above diet, the rats did not die. Thus, unspecified substance provided by milk were called **accessory dietary factor.** In 1911, Funk isolated a concentrate from rice polishing which cured the disease **beri-beri** (**Singhalese**, weakness). This was found to contain nitrogenous bases (amines). As these substances were vital for sustaining life, they were vitamines.

Later when it was discovered that all these essential substances were not exclusively amines, the letter 'e' was dropped.

When each vitamin was isolated, it was named by a letter of the alphabet. But once the structure had been established, a specific name was given.

The vitamins are divided into two major classes -

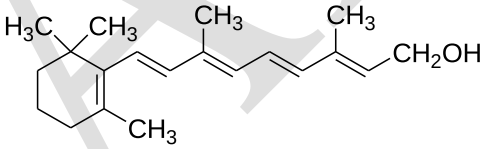
i) **Fat soluble vitamins-** vitamins A,C,D,E and K
ii) **Water soluble vitamins**-vitamin B complex i.e., vitamins B_1, B_2, B_6, B_{12} niacin etc.

A detailed study of few vitamins follows in these pages.

Vitamin A_1, Retinol, $C_{20}H_{30}O$

Vitamin A_2, Dehydroretinol, $C_{20}H_{28}O$

This vitamin is essential for vision and for the maintenance of the various epithelial cells like salivary gland, tongue, eyes.



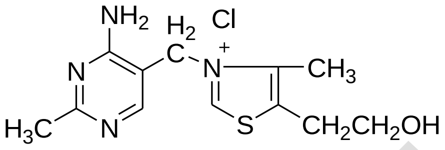
When human beings are fed on diets deficient in vitamin A, their ability for dark adaptation is lost which results in **night darkness.** Sever deficiency causes xerophthalmia i.e, hardening of cornea etc.

The daily requirement of vitamin A is 1.8 m.g. Commercial sources of this vitamin are fish liver oils (cod, shark, and halibut) milk, butter, ghee, β-carotene.

Vitamin B_1, thiamine (Aneurin), $C_{12}H_{17}ON_4$ ClS

This vitamin is necessary for carbohydrate metabolism.

Thiamine deficiency leads to a disease called **beri-beri.** It is a disease of the nervous system which is characterised by partial paralysis of the extremities and anaemia.



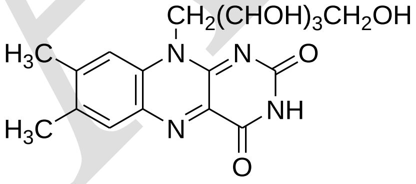
A normal person needs about one m.g. every day.

Thiamine has highest concentration in the heart, liver, kidney, brain, nuts, cereals, pulses, yeast, wheat, bran and grains.

Vitamin B$_2$, Riboflavin (Lactoflavin), C$_{17}$H$_{20}$O$_6$N$_4$

This vitamin assumes a prime place in energy metabolism as it is a component of flavoprotein enzyme.

Riboflavin deficiency results in the growth of fine blood cells in the cornea which give it at a blood shot appearance and the eyes become photophobic. It also causes **dermatitis** (skin disease).



Vitamin-B$_2$

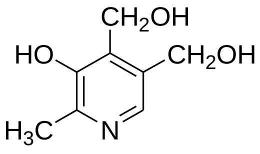
The daily requirement is about 2 m.g. The most important sources of this vitamin are peas, beans, whole grains, milk, meat, yeast, nuts, potato, liver, kidney and leafy vegetables.

Vitamin B$_6$, Pyridoxine (Adermine), C$_8$H$_{11}$O$_3$N

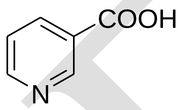
This vitamin involves in protein metabolism.

The deficiency of this vitamin develop **seborrhea** (oily crusts or scales on the skin near eyes, nose etc.,) symptoms, nervous convulsions etc.

The daily human requirement ranges from 0.2 to 1.0 m.g. This is obtained from rice bran and yeast.



Vitamin-B_6



Niacin

Nicotinic acid, Niacin, $C_6H_5O_2N$

This vitamin is necessary for carbohydrate metabolism.

The disease caused by the deficiency is called **Pellagra (Italian, rough skin)** a condition characterized by disorder of skin, digestive and nervous system.

The daily allowance of niacin is 12 to 23 mg.

The richest sources for nicotinic acid are liver, kidney, yeast, wheat, fish, milk, meat and green vegetables.

Vitamin B_{12}, Cyanocobalamin, $C_{63}H_{88}O_{14}N_{14}$ PCo

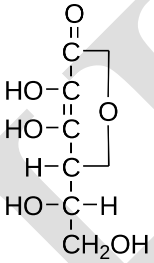
Vitamin B_{12} is necessary in nutrition and growth. This is readily converted to coenzyme B_{12} which is necessary for the function of many enzymes.

Deficiency of vitamin **B_{12}** causes pernicious anemia and the secretion of pepsin and HCl in the stomach are reduced. It also causes incomplete maturation.

The average daily requirement is only one microgram. Kidney, liver and milk contain more than the requirement.

Vitamin C, Ascorbic acid (Hexuronic acid), $C_6H_8O_6$

Ascorbic acid has an important role in the maintenance of collagen fibers, epithelial tissue, bone matrix and capillary lining. It also prevents adrenaline from being oxidized.



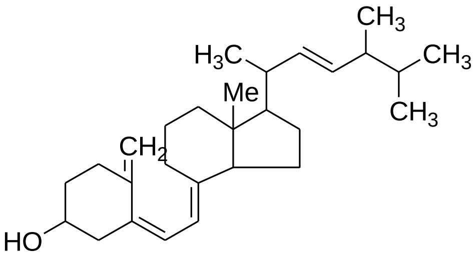
The deficiency of this vitamin causes a disease called **scurvy** characterized by spongy and bleeding gums, bleeding under the skin and extreme weakness.

Since vitamin C is continuously oxidized in the body, the daily requirement is about 30 m.g.

This vitamin is found in fruits like strawberry, oranges, lemon, guava, pineapple and papaya. Vegetable like cauliflower, cabbage, tomatoes, raddish, spinach, drum sticks also contain this vitamin.

Vitamin D_2, Calciferol, $C_{28}H_{44}O$

There are ten different substances related to Vitamin D. Vitamin D_2 helps in maintaining the level of calcium and phosphorus in the body. It is also essential for bone formation.



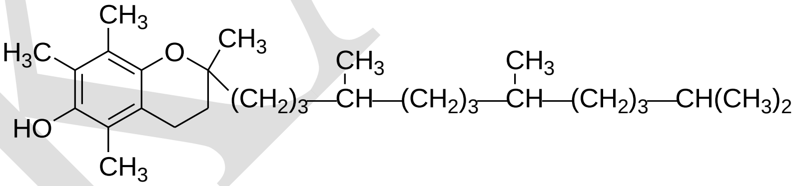
Deficiency of Vitamin D in children causes a disease called **rickets-**characterised by deformities of the skeleton especially the limbs, spine bone and skull. The daily requirement is 12.5 microgram.

The important sources of Vitamin D are the fish liver oils of tunny, halibut, cod etc. egg yolk, milk and butter. With the help of ultra violet radiation present in the sun rays, vitamin D is synthesised in the skin.

Vitamin E, Tocopherol (α- $C_{29}H_{50}O_2$)

Among eight tocopherol (Greek, to bear child birth) α-tocopherol is essential for reproduction.

The deficiency of Vitamin E results in immobile sperms in male and in female the embryo gets aborted after some time. Hence it is anti-sterility vitamin.



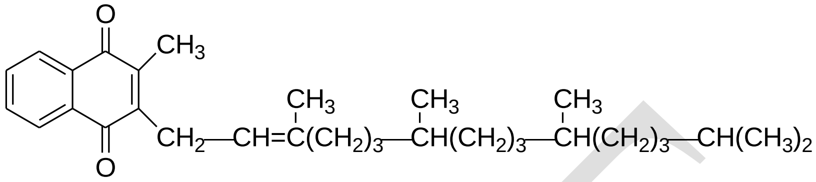
The daily life requirement is not established. Vitamin E is found in most vegetables, milk, meat and vegetable oils in general and wheat germ oil in particular.

Vitamin K_1, Phylloquinone, $C_{31}H_{46}O_2$

This vitamin occurs in two forms- Vitamin K_1 and K_2. Vitamin K plays an important role in **blood coagulation**.

Deficiency of this vitamin increases clotting time. New born infants are even in danger of bleeding to death.

The daily requirement is not known.



Vitamin K is abundantly found in green vegetables like alfalfa, cabbage, spinach, cauliflower, carrots. The intestinal bacteria are also able to synthesis this vitamin.

The various aspects of vitamins are summarized in following Table.

Vitamin	Molecular formula	Daily requirement	Deficiency Diseases	Available in
A Retinol	$C_{20}H_{30}O$	1.8 mg	**Night-blindness,** hardening of cornea	Fish liver oils, milk, butter
B_1 Thiamine	$C_{12}H_{17}ON_4$ SCl	1.0 mg	**Beri-beri**, impairment of nervous system	Heart, liver, kidney, brain, nuts, cereals, pulses, yeast, bran of rice.
B_2 Riboflavin	$C_{17}H_{20}O_6N_4$	2.0 mg	Skin diseases, retarded growth	Peas, beans, whole grain, milk, meat yeast, nut, potato, liver, kidney,
B_6 Pyridoxine	$C_8H_{11}O_3N$	0.2-1.0 mg	Impairment of protein	Rice bran, yeast, eggs, liver

B_{12} Cyanocobalamin	$C_{63}H_{88}O_{14}N_{14}PCo$	1.0 microgram	**Pernicious anemia,** secretion of pepsin is retarded, incomplete maturation	Kidney, liver, milk
Niacin	$C_6H_5O_2N$	12-23 mg	**Pellagra,** skin lesions, disorders in digestive and nervous system	Liver, kidney, yeast, wheat, fish, milk, meat, vegetables.
C Ascorbic acid	$C_6H_8O_6$	30 mg	**Scurvy,** impairment of bones, teeth, extreme weakness	Citrus fruits, cabbage, cauliflower, drum stick, raddish
D_2 Calciferol	$C_{28}H_{44}O$	12.5 micro gram	**Rickets,** impairment of bones and teeth	Fish liver oils, egg yolk, milk
E Tocopherol	$C_{29}H_{50}O_2(\alpha)$	Not established	**Sterility**	Vegetables, milk, meat, wheat, germ oil
K Phylloquinone	$C_{21}H_{46}O_2$	Not determined	**Impairment of blood clotting**	Alfalfa, cabbage, spinach, cauliflower, carrot

Text Book:

1. Thangamani, A. (2019). *Text Book on Allied Chemistry* (I Edition). Coimbatore: Karpagam Publication.

Reference Book:

1. Gopalan, R., and Sundaram, S. (2013). *Allied Chemistry* (III Edition). New Delhi: Sultan Chand & Sons.

POSSIBLE QUESTIONS

PART- A – Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

PART-B (Each Question Carry Two Marks)

1. Define chromophore with examples.
2. What are the diseases caused by the deficiency of vitamin A, and B_1?
3. How to prepare methyl orange azo dyes.
4. Define auxochrome with examples.
5. Write the preparation of methyl orange dye.
6. What is meant by sulpha drugs?
7. Define bathochromic shift with examples.
8. Write the preparation of Malachite green dye.
9. Write the preparation of sulphadiazine.
10. Define hypsochromic shift with examples.
11. How is sulphanilamide prepared from benzene?
12. How is prontosil prepared?
13. Name few sulpa drugs with their structure.
14. Explain classification of dyes according to application.
15. Write the structure of methyl orange, chrysoidine and para red and mention the chromophore and auxochrome in it.

PART-C (Each Question Carry Six Marks)

1. Explain the classification of dyes with examples.
2. Discuss the preparation and mechanism of action of sulpha drugs.
3. (i) What are the requisites of a dye.

(ii) How are dyes classified?

4. (i) What is an antibiotic? Give examples.

(ii) Write a note on penicillin.

5. (i) Write note on prontosil.

(ii) Explain atleast one preparation of triphenylmethane dyes, azo dyes, vat dyes and mordant dyes.

6. (i) What are vitamins.

(ii) How are vitamins classified? Give examples.

7. (i) How is sulphafurazole synthesized .

(ii) Write the structure formula of some sulpha drugs and the diseases they cure.

8. Write the following for (a) retinol (b) dehydroretinol (c) thiamine (d) riboflavin (e) ascorbic acid

(i) molecular formula (ii) daily requirement (iii) deficiency diseases (iv) sources.

9. Write a note on (i) pencillin (ii) chloromycetin.

10. Write the structure, sources, and diseases caused by the deficiency of the following-

(i) vitamin A (ii) vitamin B_1 (iii) vitamin B_2 (iv) vitamin C.

KARPAGAM ACADEMY OF HIGHER EDUCATION

(*Deemed to be University*)
(*Established Under Section 3 of UGC Act, 1956*)
Pollachi Main Road, Eachanari Post, Coimbatore–641 021.

DEPARTMENT OF CHEMISTRY

UNIT-V

DYES, CHEMOTHERAPY AND VITAMINS

PART-A–Multiple Choice Questions

(Each Question Carry One Mark) (Online Examinations)

1. The example for triphenylmethane dye is

a) malachite green b) alizarin c) picric acid d) congo red

2. Vat dyes are

a) soluble in water b) not suitable for dyeing fabrics **c) insoluble in water** d) unstable

3. Indigo is an example of

a) a vat dye b) a azo dye c) a mordant dye d) a nitro dye

4. Prontosil is prepared by the coupling reaction between 1,3-diaminobenzene and diazotized

a) sulphonamide b) iso-oxazole c) pyrimidine d) thiazole

5. The general molecular formula for penicillin is

a) $C_9H_{11}O_3N_2SR$ b) $C_5H_{11}O_4N_2SR$ **c) $C_9H_{11}O_4N_2SR$** d) $C_9H_{11}O_4NSR$

6. Malachite green is

a) an azo dye **b) a triphenylmethane dye** c) an anthroquinone dye d) a phthalocyanine dye

7. Vitamin B_1 deficiency leads to a disease called

a) pellagra b) night darkness c) skin disease **d) beri-beri**

8. Important source of Vitamin B_2 is

a) peas b) fish c) prawn d) shark

9. The example for azo dye is

a) methyl orange b) indigo c) malachite green d) alizarin

10. Alizarin is obtained by condensation of catechol with

a) acetic anhydride b) **phthalic anhydride** c) propanic anhydride d) phthalimide

11. The example for phthalein dye is

a) malachite green b) indigo **c) alizarin** d) phenolphthalein

12. PABA refers to

a) para aminobenzoic acid b) para azobenzoic acid

c) perchloro aminobenzoic acid d) per aminobenzoic acid

13. Chloromycetin is very effective against

a) gram negative bacteria b) gram positive bacteria

c) gram negative fungi d) gram positive fungi

14. The deficiency of vitamin C causes a disease called

a) scurvy b) beri-beri c) skin diseases d) night blindness

15. Vitamin A_1 is also called as

a) dehydroretinol **b) retinol** c) thiamine d) riboflavin

16. The daily requirement of vitamin A is

a) 2.2 m.g. **b) 1.8 m.g.** c) 1.2 m.g. d) 3.1 m.g.

17. Sulpha drugs are effective chemotherapeutic agents because

a) they contain sulfur atoms b) they are friendly to infecting organisms

c) they have a strong structural resembles to para-aminobenzoic acid used by organisms

d) they are easily absorbed in the cell walls

18. The drug of choice against typhoid fever is

a) streptomycin b) penicillin c) sulphapyridine **d) chloromycetin**

19. The example for chromophore is

a) azo b) hydroxy c) amino d) alkoxy

20. The nitro group is an example for

a) chromophore b) auxochrome c) bathochromic shift d) hypsochromic shift

21. The molecular formula for Chloromycetin is

a) $C_{21}H_{39}O_{12}N_7$ b) $C_{11}H_{15}O_5N_2D_2$ **c) $C_{11}H_{15}O_2N_2Cl_2$** d) $C_{21}H_{39}O_{11}N_7Cl$

22. The queen of drugs is

a) pencillin **b) sulpha drugs** c) streptomycin d) chloromycetin

23. Methicillin is synthesized from

a) monopenicillinic acid b) penicillin c) sulpha drugs d) streptomycin

24. Example for sulpha drug is

a) sulphapyridine b) penicillin c) methicillin d) quinine

25. $C_{20}H_{28}O$ represents as

a) Vitamin A_1 b) Vitamin B_1 c) Vitamin B_2 **d) Vitamin A_2**

26. Pneumonia disease is cured by

a) sulphathiazole **b) sulphapyridine** c) sulpha-acetamide d) sulphaguanidine

27. The term chemotherapy introduced by

a) Fleming b) Funk **c) Ehrlich** d) H. Davy

28. Vitamin B_1 is also called as

a) thiamine b) ascorbic acid c) riboflavin d) pyridoxine

29. Thiamine is also called as

a) retinol b) lactoflavin c) haxuronic acid **d) aneurin**

30. Compounds which exert various physiological effects of therapeutic values are collectively known as

a) drugs b) vitamins c) hormones d) antibiotics

31. Chloromycetin is used in the treatment of

a) pneumonia **b) typhoid fever** c) trachoma d) urinary infection

32. The treatment of disease caused by bacterial invasion by chemical compounds is known as

a) hormones b) vitamins **c) chemotherapy** d) antibiotics

33. Sulphanilamide and its derivatives have great antibacterial powers and are commonly known as

a) antibiotics b) hormones c) vitamins **d) sulpha drugs**

34. Sulpha drugs have great

a) antifungal powers b) antibiotics powers c) anti-HIV powers **d) antibacterial powers**

35. Which vitamins are necessary for carbohydrate metabolism?

a) riboflavin **b) thiamine** c) pyridoxine d) ascorbic acid

36. The example for nitro dye is

a) picric acid b) alizarin c) malachite green d) eosin

37. Methyl orange is an example for

a) cationic dye **b) anionic dye** c) neutral dye d) acidic dye

38. The example for cationic dye is

a) alizarin b) indigo **c) chrysoidine** d) methyl orange

39. The melting point of sulphanilamide is

a) 430 K b) 449 K c) 370 K **d) 439 K**

40. Sulphapyridine is an example for

a) sulpha drugs b) antibiotics c) hormones d) vitamins

41. The example for chlorine containing antibiotics is

a) penicillin **b) chloromycetin** c) streptomycin d) terramycin

42. Indigo dye is prepared from

a) aniline and dimethylaniline b) sulphailic acid and dimethylaniline

c) aniline and chloroacetic acid d) dimethylaniline and benzaldehyde

43. $C_{11}H_{15}O_5N_2Cl_2$ represents as

a) penicillin b) terramycin c) streptomycin d) **chloromycetin**

44. Sulphadiazine is prepared by condensing 2-aminopyrimidine with

a) benzene sulphonyl chloride b) p-amino benzene sulphonyl chloride

c) p-toluene sulphonyl chloride **d) p-acetanilide sulphonyl chloride**

45. Penicillin was discovered by

a) Fleming b) Funk c) Ehrlich d) H. Davy

46. The example for fat soluble vitamin is

a) Vitamin B **b) Vitamin A** c) Vitamin C d) Vitamin B

47. Vitamin A is an example for

a) oil soluble vitamin b) non-soluble vitamin **c) fat soluble vitamin** d) water soluble vitamin

48. The amino group is an example for

a) chromophore b) bathochromic shift c) hypochromic shift **d) auxochrome**

49. Which one is example for auxochrome?

a) NO_2 b) N=N **c) OH** d) C=O

50. Which group is responsible for chromophore?

a) amino group b) covalently saturated group c) hydroxyl group

d) covalently unsaturated group

51. A covalently unsaturated group responsible for absorption in the UV or visible region is known as a

a) chromophore b) bathochromic shift c) hypochromic shift d) auxochrome

52. A covalently saturated group which, when attached to a chromophore changes both the wavelength and the intensity of the absorption maximum is known as

a) chromophore b) bathochromic shift c) hypochromic shift **d) auxochrome**

53. The shift of an absorption maximum to a longer wavelength due to the

a) presence of an auxochrome b) presence of an chromophore

c) presence of an unsaturated group d) presence of an double bond

54. Red shift is also called as

a) hypsochromic shift **b) bathochromic shift** c) hypochromic shift d) chemical shift

55. Hypsochromic shift is also known as

a) red shift b) black shift **c) blue shift** d) orange shift

56. The other name for bathochromic shift is

a) resonance effect b) inductive effect c) mesomeric effect **d) solvent effect**

57. The shift of an absorption maximum to a shorter wavelength is called

a) hypsochromic shift b) bathochromic shift c) hypochromic shift d) auxochrome

58. The shift of an absorption maximum to a longer wavelength is called

a) hypsochromic shift **b) bathochromic shift** c) hypochromic shift d) auxochrome

59. The aniline shows λ_{max} value for 280 nm, whereas anilinium ion (acidic solution of aniline) shows λ_{max} value for 254 nm is due to

a) hypochromic shift b) bathochromic shift **c) hypsochromic shift** d) auxochrome

60. Which one is azoic dye?

a) methyl orange b) chrysoidine c) indigo **d) para red**

Reg. No..................................

[18BTU103]

KARPAGAM ACADEMY OF HIGHER EDUCATION
(Deemed to be University)
(Established Under Section 3 of UGC Act, 1956)
Pollachi Main Road, Eachanari Post, Coimbatore – 641 021
(For the candidates admitted from 2018 onwards)

B.Sc., DEGREE EXAMINATION, NOVEMBER 2018
First Semester

BIOTECHNOLOGY

CHEMISTRY - I

Time: 3 hours Maximum : 60 marks

PART – A (20 x 1 = 20 Marks) (30 Minutes)
(Question Nos. 1 to 20 Online Examinations)

PART B (5 x 2 = 10 Marks) (2 ½ Hours)
Answer ALL the Questions

21. How is sodium hydrosulphite is prepared.
22. What is racemization?
23. How can water pollution be controlled?
24. How is order of a reaction found out by graphical method?
25. Define the term chemotherapy? Give examples.

PART C (5 x 6 = 30 Marks)
Answer ALL the Questions

26. a. Write the preparation, properties, uses and structure of caro's acid.

Or

b. Write the preparation and properties of diborane.

27. a. Explain with an example the occurrence of Tautomerism. How does it differ from resonance?

Or

b. Explain the following with suitable examples.
i. Inductive effect. ii. Mesomeric effect.

28. a. Write note on acid rain, ozone hole and green house effect.

Or

b. How are the following fertilizers manufactured?
i. Ammonium sulphate ii. ammonium nitrate.

29. a. i. The rate of a reaction gets doubled when the temperature is raised from 300 K to 310 K. Calculate the activation energy.
ii. A first order reaction is 40% complete at the end of 50 min. What is the value of rate constant? In how many minutes will the reaction be 80% complete?

Or

b. Write notes on
i. Beer-Lamberts law.
ii. Grotthus-Draper law.
iii. Stark-Einstein law.

30. a. i. How is sulphafurazole synthesized .
ii. Write the structure formula of any four sulpha drugs and the diseases they cure.

Or

b. Explain the following terms with suitable examples
i. Chromophore ii. Auxochrome iii. Bathochromic shift.
