KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

Coimbatore – 641 021.

SYLLABUS
DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

Semester-IV

16CHU403   ORGANIC CHEMISTRY IV (Organic spectroscopy)   4H 4C

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

Scope
It deals with various spectroscopic techniques like UV Spectroscopy, IR Spectroscopy and NMR spectroscopy which are used to identify the organic molecules. It also deals with the carbohydrates, dyes and polymers

Methodology
Blackboard teaching, Powerpoint presentation and group discussion.

Programme Outcome

1. To Understand the principle and the theory behind the UV spectroscopy.
2. Understand the principle and the theory behind the IR spectroscopy.
3. Understand the principle and the theory behind the NMR spectroscopy.
4. Understand about the occurrence, classification and their biological importance carbohydrates
5. Understand about the classification of dyes and polymers.

Programme Learning Outcome

1. The students understood the principle and the theory behind the UV spectroscopy.
2. They gain the knowledge about the principle and the theory behind the IR spectroscopy.
3. They understood the principle and the theory behind the NMR spectroscopy.
4. They learned about the occurrence, classification and their biological importance carbohydrates

UNIT 1 Organic Spectroscopy
General principles to absorption and emission spectroscopy.

UV Spectroscopy: Types of electronic transitions, λmax, Chromophores and Auxochromes, Bathochromic and Hypsochromic shifts, Intensity of absorption; Application of Woodward Rules for calculation of λmax for the following systems: α,β-unsaturated aldehydes, ketones, carboxylic acids and esters; Conjugated dienes: alicyclic, homoannular and heteroannular; Extended conjugated systems (aldehydes, ketones and dienes); distinction between cis and trans isomers.

UNIT II
IR Spectroscopy: Fundamental and non-fundamental molecular vibrations; IR absorption positions of O, N and S containing functional groups; Effect of H-bonding, conjugation, resonance and ring size on IR absorptions; Fingerprint region and its significance; application in functional group analysis.

UNIT III
NMR Spectroscopy: Basic principles of Proton Magnetic Resonance, chemical shift and factors influencing it; Spin – Spin coupling and coupling constant; Anisotropic effects in alkene, alkyne, aldehydes and aromatics, Interpetation of NMR spectra of simple compounds. Applications of IR, UV and NMR for identification of simple organic molecules.

UNIT IV Carbohydrates
Occurrence, classification and their biological importance.
Monosaccharides: Constitution and absolute configuration of glucose and fructose, epimers and anomers, mutarotation, determination of ring size of glucose and fructose, Haworth projections and conformational structures; Interconversions of aldoses and ketoses; Killiani- Fischer synthesis and Ruff degradation;
Disaccharides – Structure elucidation of maltose, lactose and sucrose.
Polysaccharides – Elementary treatment of starch, cellulose and glycogen.

UNIT V
Dyes -Classification, Colour and constitution; Mordant and Vat Dyes; Chemistry of dyeing; Synthesis and applications of: Azo dyes – Methyl orange; Triphenyl methane dyes - Malachite green and Rosaniline ; Phthalein Dyes – Phenolphthalein; Natural dyes – structure elucidation and synthesis of Alizarin and Indigotin; Edible Dyes with examples.

Polymers - Introduction and classification including di-block, tri-block and amphiphilic polymers; Polymerisation reactions -Addition and condensation -Mechanism of cationic, anionic and free radical addition polymerization; Metallocene-based Ziegler-Natta polymerisation of alkenes;
Preparation and applications of plastics – thermosetting (phenol-formaldehyde, Polyurethanes) and thermosoftening (PVC, polythene); Fabrics – natural and synthetic (acrylic, polyamido, polyester); Rubbers – natural and synthetic: Buna-S, Chloroprene and Neoprene; Vulcanization; Polymer additives; Introduction to; Biodegradable and conducting polymers with examples.

Suggested Readings

Text Book:
1. Kalsi, P. S.(2009). *Textbook of Organic Chemistry*. 1st Ed. New Age International (P) Ltd. Pub.
2. Morrison, R. T. & Boyd, R. N.(1992). *Organic Chemistry*. Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
3. Billmeyer, F. W.(1984). *Textbook of Polymer Science*. John Wiley & Sons, Inc.
4. Gowariker, V. R., Viswanathan, N. V. & Sreedhar, J.(2003). *Polymer Science*. New Age
   International (P) Ltd. Pub.

Reference Books
1. Finar, I. L.(2002). *Organic Chemistry: Stereochemistry and the Chemistry of Natural Products.* Volume 2. Dorling Kindersley (India) Pvt. Ltd. (Pearson Education).
2. Clayden, J., Greeves, N., Warren, S. & Wothers, P.(2000). *Organic Chemistry*. Oxford University Press.
3. Singh, J.; Ali, S.M. & Singh, J. (2010). *Natural Product Chemistry*. PrajatiPrakashan.

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LESSION PLAN
DEPARTMENT OF CHEMISTRY
B.Sc CHEMISTRY

STAFF NAME   : **Dr. M.MAKESWARI AND Mr.R.KUMAR**
SUBJECT NAME   : **ORGANIC CHEMISRY-IV(Organic Spectroscopy)**
SUB. CODE   : **16CHU403**
SEMESTER   : **IV**
CLASS   : **II- B. Sc-CHEMISTRY**

S.No	Lecture Duration Period	Topics to be Covered	Support Material/Page Nos
		UNIT-I	
1	1	**Organic Spectroscopy** General principles to absorption and emission spectroscopy.	**T1:** 335-338, **R1:** 9-12
2	1	UV Spectroscopy: Introduction	**T1:** 38-341, **R1:** 12-15
3	1	Types of electronic transitions, λmax,	**T1:** 341-344, **R1:** 15-19
4	1	Chromophores and Auxochromes	**T1:** 344, **R1:** 19-21
5	1	Bathochromic and Hypsochromic shifts	**T1:** 344-345, **R1:** 21-22
6	1	Intensity of absorption	**R1:** 12-15
7	1	Application of Woodward Rules for calculation of λmax for α,β-unsaturated aldehydes	**R1:** 36-42
8	1	Application of Woodward Rules for calculation of λmax for ketones	**R1:** 38-42
9	1	Application of Woodward Rules for calculation of λmax for carboxylic acids and esters	**R1:** 38-42
10	1	Conjugated dienes: alicyclic, homoannular and heteroannular; Extended conjugated systems	**R1:** 26-33,
11	1	Distinction between cis and trans isomers.	**R1:** 47-48, 51-54
12	1	Recapitulation and Discussion of important questions	

		Total No of Hours Planned For Unit 1=12	
		Bathochromic and Hypsochromic shifts	**T1:** 344-345, **R1:** 21-22
1	1	IR Spectroscopy: Introduction	**T1:** 352-354, **R1:** 69
2	1	Fundamental and non-fundamental molecular vibrations	**T1:** 359-360, **R1:** 70-76
3	1	IR absorption positions of O, containing functional groups	**R1:** 117
4	1	IR absorption positions of N containing functional groups	**R1:** 124
5	1	IR absorption positions of S containing functional groups	**R1:** 132
6	1	Effect of H-bonding, conjugation	**T1:** 356-359, **R1:** 77
7	1	resonance and ring size on IR absorptions	**T1:** 357-359, **R1:** 80, 82
8	1	Fingerprint region and its significance	**R1:** 89-90
9	1	application in functional group analysis	**T1:** 361, **R1:** 137
10	1	Recapitulation and Discussion of important questions	
		Total No of Hours Planned For Unit II=10	
		UNIT-III	
1	1	*NMR Spectroscopy*: Basic principles of Proton Magnetic Resonance,	**T1:** 263-266,
2	1	chemical shift	**T1:** 271-275,
3	1	Factors influencing chemical shift	**R1:** 194-198
4	1	Spin – Spin coupling	**R1:** 202-206
5	1	coupling constant	**R1:** 213-222
6	1	Anisotropic effects in alkene, alkyne, aldehydes and aromatics	**R1:** 195-197
7	1	Interpetation of NMR spectra of simple compounds	**T1:** 288-296
8	1	Applications of IR, UV and NMR for identification of simple organic molecules.	**R1:** 256-260
9	1	Applications of IR, UV and NMR for identification of simple organic molecules.	**R1:** 261-265
10	1	Recapitulation and Discussion of important questions	

		Total No of Hours Planned For Unit III=10	
		UNIT-IV	
1	1	**Carbohydrates -**Occurrence,	**T1:** 450
2	1	**Carbohydrates** -classification and their biological importance.	**T1:** 451-452
3	1	Monosaccharides: Constitution and absolute configuration of glucose and fructose	**T1:** 471-472
4	1	Epimers, anomers and mutarotation of Glucose	**T1:** 456-459, 490
5	1	determination of ring size, Haworth projections and conformational structures of glucose	**T1:** 460-463
6	1	Epimers, anomers and mutarotation of Fructose	**T1:** 465-467, 490-492
7	1	determination of ring size, Haworth projections and conformational structures of Fructose	**T1:** 467-468, 490-492
8	1	Interconversions of aldoses and ketoses; Killiani-Fischer synthesis and Ruff degradation	**T1:** 468-471
9	1	Disaccharides – Structure elucidation of maltose, lactose	**T1:** 482-484
10	1	Structure elucidation of sucrose	**T1:** 481-482
11	1	Polysaccharides – Elementary treatment of starch,	**T1:** 485-487
12	1	Cellulose and glycogen.	**T1:** 487-490, **R2:** 97
13	1	Recapitulation and Discussion of important questions	
		Total No of Hours Planned For Unit IV=13	
		UNIT-V	
1	1	Dyes-Classification, Colour and constitution	**T1:** 584-587, 584-595
2	1	Mordant and Vat Dyes; Chemistry of dyeing	**T1:** 498-499
3	1	Synthesis and applications of: Azo dyes – Methyl orange; Triphenyl methane dyes - Malachite green and Rosaniline, Phthalein Dyes – Phenolphthalein	**T1:** 595, 597-598, 599-600
4	1	Natural dyes – structure elucidation and synthesis of Alizarin	**T1:** 601-605
5	1	structure elucidation and synthesis of Indigotin, Edible Dyes with examples	**T1:** 605-609
6	1	**Polymers -**Introduction and classification including di-block, tri-block and amphiphilic polymers	**T1:** 555-557
7	1	Polymerisation reactions -Addition and condensation - Mechanism of cationic polymerization	**T1:** 557-558, 562-563

8	1	Free radical addition and anionic polymerization	**T1:** 560-564
9	1	Metallocene-based Ziegler-Natta polymerisation of alkenes	**T1:** 564 **R3:** 46-52
10	1	Preparation and applications of plastics – thermosetting (phenol-formaldehyde, Polyurethanes) and thermosoftening (PVC, polythene)	**T1:** 572, 575-576, 569, 565
11	1	Fabrics – natural and synthetic (acrylic, polyamido, polyester); Rubbers – natural and synthetic: Buna-S, Chloroprene and Neoprene;	**T1:** 570-571
12	1	Vulcanization; Polymer additives; Introduction to; Biodegradable and conducting polymers with examples.	**T1:** 576-579
13	1	Recapitulation and Discussion of important questions	
14	1	End semester question paper discussion	
15	1	End semester question paper discussion	
16	1	Discussion of Previous ESE Question Papers.	
	Total No of Hours Planned for unit V=15		
Total Planned Hours	**60**		

TEXT BOOK

T1 : Madan, R.L. (2015). *Chemistry for Degree Students.* India. S. Chand and Company (New Delhi) Pvt, Ltd.

REFERENCE BOOK

R1: Sharma,Y.R.(2010). Elementary Organic Spectroscopy. S. Chand and Company (New Delhi) Pvt, Ltd.

R2: Agarwal, O.P. (2003). Chemistry of organic Natural products**,** Goel Publishing House, Meerut

R3: Gowariker, V. R., Viswanathan, N. V. & Sreedhar, J. (2003). *Polymer Science*. New Age International (P) Ltd.

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CLASS: II B SC CHEMISTRY   COURSE NAME: ORGANIC CHEMISTRY- IV (Organic Spectroscopy)
**COURSE CODE: 16CHU403   UNIT: I (UV Spectroscopy)   BATCH-2016-2019**

UNIT I

SYLLABUS

General principles to absorption and emission spectroscopy.
UV Spectroscopy: Types of electronic transitions, λmax, Chromophores and Auxochromes, Bathochromic and Hypsochromic shifts, Intensity of absorption; Application of Woodward Rules for calculation of λmax for the following systems: α,β-unsaturated aldehydes, ketones, carboxylic acids and esters; Conjugated dienes: alicyclic, homoannular and heteroannular; Extended conjugated systems (aldehydes, ketones and dienes); distinction between cis and trans isomers.

Ultraviolet and Visible Spectroscopy

An obvious difference between certain compounds is their color. Thus, quinone is yellow; chlorophyll is green; the 2,4-dinitrophenylhydrazone derivatives of aldehydes and ketones range in color from bright yellow to deep red, depending on double bond conjugation; and aspirin is colorless. In this respect the human eye is functioning as a spectrometer analyzing the light reflected from the surface of a solid or passing through a liquid. Although we see sunlight (or white light) as uniform or homogeneous in color, it is actually composed of a broad range of radiation wavelengths in the ultraviolet (UV), visible and infrared (IR) portions of the spectrum. As shown on the right, the component colors of the visible portion can be separated by passing sunlight through a prism, which acts to bend the light in differing degrees according to wavelength.
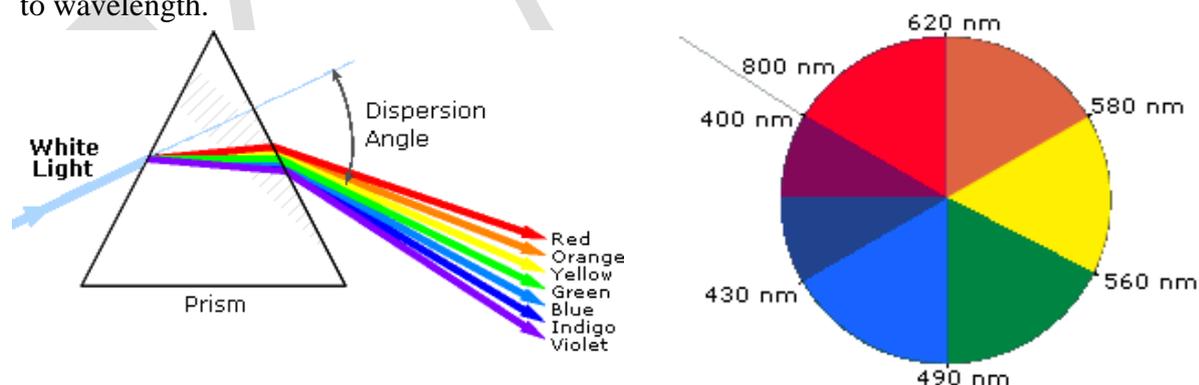
Electromagnetic radiation such as visible light is commonly treated as a wave phenomenon, characterized by a wavelength or frequency. **Wavelength** is defined on the left below, as the distance between adjacent peaks (or troughs), and may be designated in meters, centimeters or

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nanometers (10^{-9} meters). **Frequency** is the number of wave cycles that travel past a fixed point per unit of time, and is usually given in cycles per second, or hertz (Hz). Visible wavelengths cover a range from approximately 400 to 800 nm. The longest visible wavelength is red and the shortest is violet. Other common colors of the spectrum, in order of decreasing wavelength, may be remembered by the mnemonic: **ROY G BIV**. The wavelengths of what we perceive as particular colors in the visible portion of the spectrum are displayed and listed below. In horizontal diagrams, such as the one on the bottom left, wavelength will increase on moving from left to right.
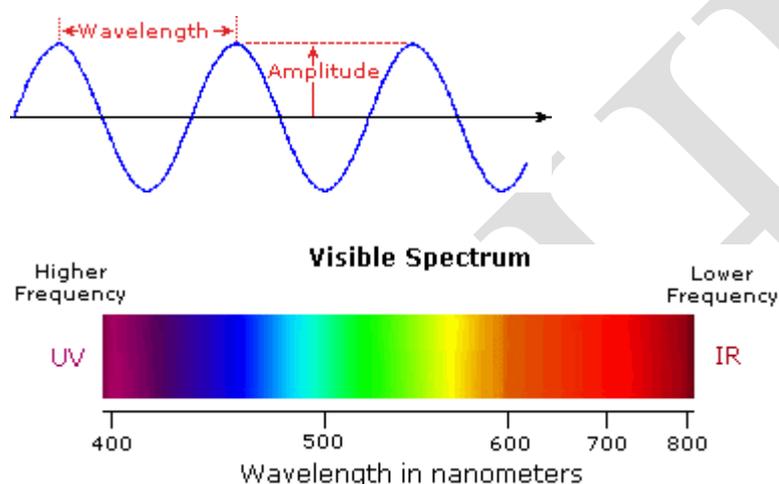

- **Violet:** 400 - 420 nm
- **Indigo:** 420 - 440 nm
- **Blue:** 440 - 490 nm
- **Green:** 490 - 570 nm
- **Yellow:** 570 - 585 nm
- **Orange:** 585 - 620 nm
- **Red:** 620 - 780 nm

When white light passes through or is reflected by a colored substance, a characteristic portion of the mixed wavelengths is absorbed. The remaining light will then assume the complementary color to the wavelength(s) absorbed. This relationship is demonstrated by the color wheel shown on the right. Here, complementary colors are diametrically opposite each other. Thus, absorption of 420-430 nm light renders a substance yellow, and absorption of 500-520 nm light makes it red. Green is unique in that it can be created by absoption close to 400 nm as well as absorption near 800 nm. Early humans valued colored pigments, and used them for decorative purposes. Many of these were inorganic minerals, but several important organic dyes were also known. These included the crimson pigment, kermesic acid, the blue dye, indigo, and the yellow saffron pigment, crocetin. A rare dibromo-indigo derivative, punicin, was used to color the robes of the royal and wealthy. The deep orange hydrocarbon carotene is widely distributed in plants, but is not sufficiently stable to be used as permanent pigment,

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other than for food coloring. A common feature of all these colored compounds, displayed below, is a system of **extensively conjugated pi-electrons**.


Some Natural Organic Pigments
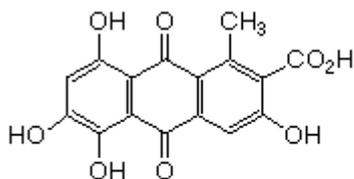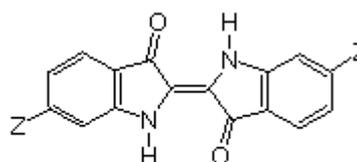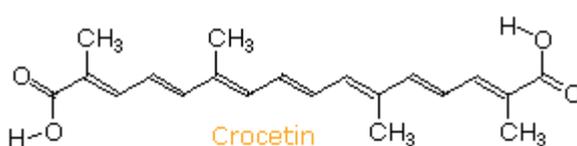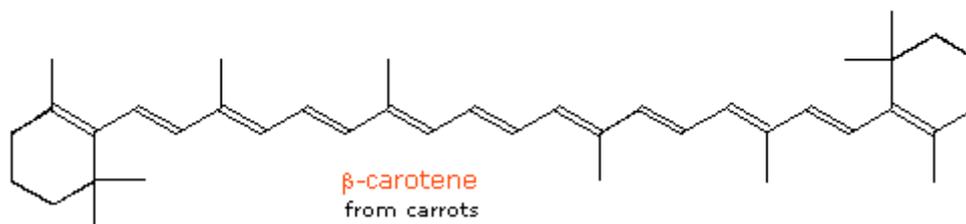
**The Electromagnetic Spectrum**

The visible spectrum constitutes but a small part of the total radiation spectrum. Most of the radiation that surrounds us cannot be seen, but can be detected by dedicated sensing instruments. This **electromagnetic spectrum** ranges from very short wavelengths (including gamma and x-rays) to very long wavelengths (including microwaves and broadcast radio waves). The following chart displays many of the important regions of this spectrum, and demonstrates the inverse relationship between wavelength and frequency (shown in the top equation below the chart).

The energy associated with a given segment of the spectrum is proportional to its frequency. The bottom equation describes this relationship, which provides the energy carried by a photon of a given wavelength of radiation.

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$\upsilon = c/\lambda$ υ=frequency, λ=wavelength, c=velocity of light (c=3•10^{10} cm/sec)
$\Delta E = h\upsilon$ E=energy, υ=frequency, h=Planck's constant (h=6.6•10^{-27} erg sec)

To obtain specific frequency, wavelength and energy values use this calculator.

The Electromagnetic Spectrum
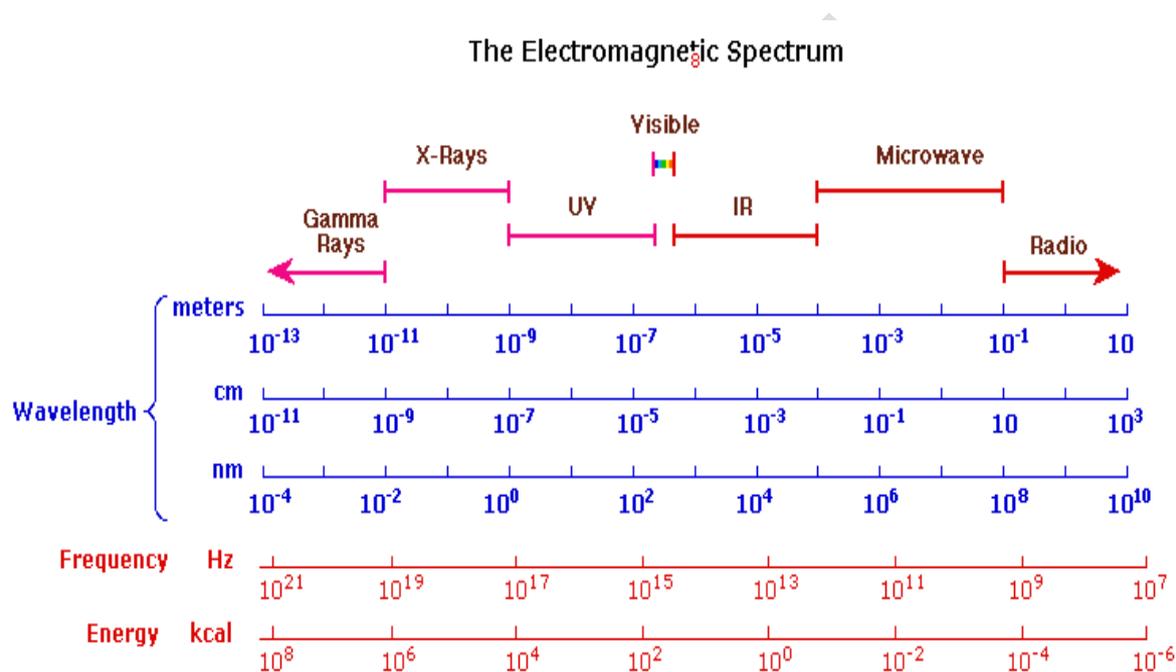
Introduction

Many compounds absorb ultraviolet (UV) or visible (Vis.) light. The diagram below shows a beam of monochromatic radiation of radiant power P_0, directed at a sample solution. Absorption takes place and the beam of radiation leaving the sample has radiant power P.
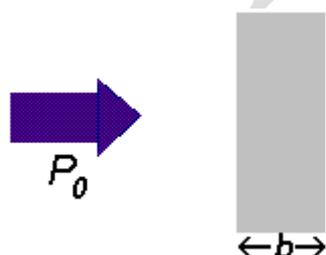
The amount of radiation absorbed may be measured in a number of ways:

Transmittance, T = P / P_0
% Transmittance, *%T = 100 T*

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Absorbance,

$$A = log_{10} P_0 / P$$
$$A = log_{10} 1 / T$$
$$A = log_{10} 100 / \%T$$
$$A = 2 - log_{10} \%T$$

The last equation, $A = 2 - log_{10} \%T$, is worth remembering because it allows you to easily calculate absorbance from percentage transmittance data.

The relationship between absorbance and transmittance is illustrated in the following diagram:
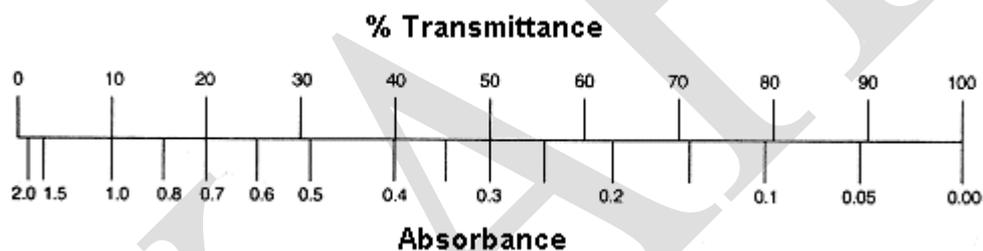
So, if all the light passes through a solution *without* any absorption, then absorbance is zero, and percent transmittance is 100%. If all the light is absorbed, then percent transmittance is zero, and absorption is infinite.

The intensity of the light passing through the sample cell is also measured for that wavelength - given the symbol, I. If I is less than Io. I$_o$, then the sample has absorbed some of the light (neglecting reflection of light off the cuvette surface). A simple bit of math is then done in the computer to convert this into something called the absorbance of the sample - given the symbol, A. The absorbance of a transition depends on two external assumptions.

1. The absorbance is directly proportional to the concentration (c) of the solution of the the sample used in the experiment.

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2. The absorbance is directly proportional to the length of the light path (l), which is equal to the width of the cuvette.

Assumption one relates the absorbance to concentration and can be expressed as

$$\log_{10} \frac{I_o}{I} = \varepsilon\, l\, c$$

- Greek letter, epsilon — ε
- concentration of solution (mol dm^{-3})
- length of solution the light passes through (cm)

Now, suppose we have a solution of copper sulphate (which appears blue because it has an absorption maximum at 600 nm). We look at the way in which the intensity of the light (radiant power) changes as it passes through the solution in a 1 cm cuvette. We will look at the reduction every 0.2 cm as shown in the diagram below. **The Law says that the fraction of the light absorbed by each layer of solution is the same.** For our illustration, we will suppose that this fraction is 0.5 for each 0.2 cm "layer" and calculate the following data:

Path length / cm	0	0.2	0.4	0.6	0.8	1.0
%T	100	50	25	12.5	6.25	3.125
Absorbance	0	0.3	0.6	0.9	1.2	1.5

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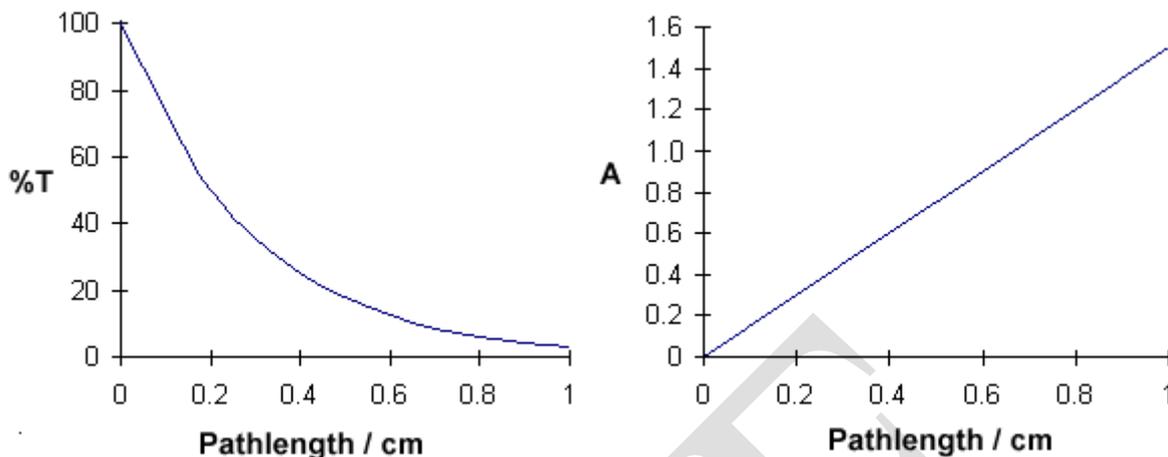
A = kbc tells us that absorbance depends on the total quantity of the absorbing compound in the light path through the cuvette. If we plot absorbance against concentration, we get a straight line passing through the origin (0,).
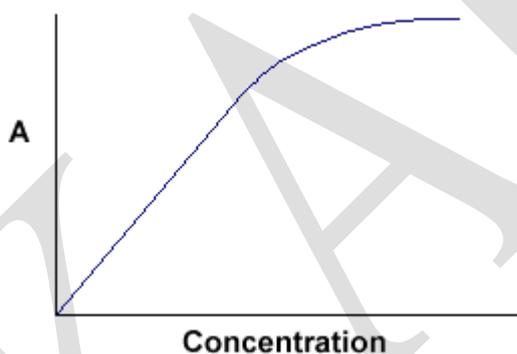
Note that the Law is not obeyed at high concentrations. This deviation from the Law is not dealt with here.

The linear relationship between concentration and absorbance is both simple and straightforward, which is why we prefer to express the Beer-Lambert law using absorbance as a measure of the absorption rather than %T.

Types of electronic transitions

To understand why some compounds are colored and others are not, and to determine the relationship of conjugation to color, we must make accurate measurements of light absorption at different wavelengths in and near the visible part of the spectrum. Commercial optical

spectrometers enable such experiments to be conducted with ease, and usually survey both the near ultraviolet and visible portions of the spectrum.

The visible region of the spectrum comprises photon energies of 36 to 72 kcal/mole, and the near ultraviolet region, out to 200 nm, extends this energy range to 143 kcal/mole.
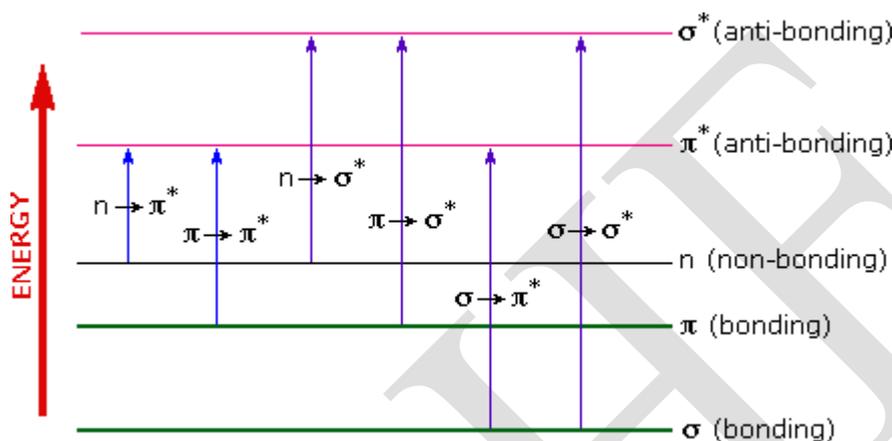
Ultraviolet radiation having wavelengths less than 200 nm is difficult to handle, and is seldom used as a routine tool for structural analysis.

The energies noted above are sufficient to promote or excite a molecular electron to a higher energy orbital. Consequently, absorption spectroscopy carried out in this region is sometimes called "electronic spectroscopy". A diagram showing the various kinds of electronic excitation that may occur in organic molecules is shown on the left. Of the six transitions outlined, only the two lowest energy ones (left-most, colored blue) are achieved by the energies available in the 200 to 800 nm spectrum. As a rule, energetically favored electron promotion will be from the **highest occupied molecular orbital (HOMO)** to the **lowest unoccupied molecular orbital (LUMO)**, and the resulting species is called an **excited state**. For a review of molecular orbitals.

When sample molecules are exposed to light having an energy that matches a possible electronic transition within the molecule, some of the light energy will be absorbed as the electron is promoted to a higher energy orbital. An optical spectrometer records the wavelengths at which absorption occurs, together with the degree of absorption at each

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wavelength. The resulting spectrum is presented as a graph of absorbance (A) versus wavelength, as in the isoprene spectrum shown below. Since isoprene is colourless, it does not absorb in the visible part of the spectrum and this region is not displayed on the graph. **Absorbance** usually ranges from 0 (no absorption) to 2 (99% absorption), and is precisely defined in context with spectrometer operation.

Because the absorbance of a sample will be proportional to the number of absorbing molecules in the spectrometer light beam (e.g. their molar concentration in the sample tube), it is necessary to correct the absorbance value for this and other operational factors if the spectra of different compounds are to be compared in a meaningful way. The corrected absorption value is called "molar absorptivity", and is particularly useful when comparing the spectra of different compounds and determining the relative strength of light absorbing functions (chromophores). **Molar absorptivity** (ε) is defined as:

Molar   (where *A*= absorbance, **c** = sample concentration in moles/liter & **l** =
Absorptivity, ε =   length of light path through the sample in cm.)
A **/ c l**

If the isoprene spectrum on the right was obtained from a dilute hexane solution (c = $4 * 10^{-5}$ moles per liter) in a 1 cm sample cuvette, a simple calculation using the above formula indicates a molar absorptivity of 20,000 at the maximum absorption wavelength. Indeed the entire vertical absorbance scale may be changed to a molar absorptivity scale once this information about the sample is in hand. Clicking on the spectrum will display this change in units.

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| Chromophore	Example	Excitation	λ_{max}, nm	ε	Solvent
C=C	Ethene	$\pi \longrightarrow \pi^*$	171	15,000	hexane
C≡C	1-Hexyne	$\pi \longrightarrow \pi^*$	180	10,000	hexane
C=O	Ethanal	$n \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$	290 180	15 10,000	hexane hexane
N=O	Nitromethane	$n \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$	275 200	17 5,000	ethanol ethanol
C-X X=Br X=I	Methyl bromide Methyl Iodide	$n \longrightarrow \sigma^*$ $n \longrightarrow \sigma^*$	205 255	200 360	hexane hexane
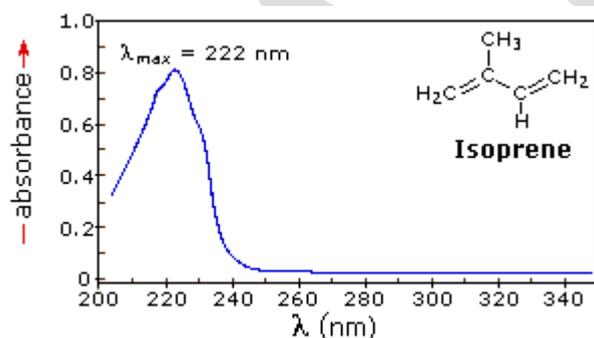
From the chart above it should be clear that the only molecular moieties likely to absorb light in the 200 to 800 nm region are pi-electron functions and hetero atoms having non-bonding valence-shell electron pairs. Such light absorbing groups are referred to as **chromophores**. A list of some simple chromophores and their light absorption characteristics is provided on the left above. The oxygen non-bonding electrons in alcohols and ethers do not give rise to absorption above 160 nm. Consequently, pure alcohol and ether solvents may be used for spectroscopic studies. The presence of chromophores in a molecule is best documented by UV-Visible spectroscopy, but the failure of most instruments to provide absorption data for

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wavelengths below 200 nm makes the detection of isolated chromophores problematic. Fortunately, conjugation generally moves the absorption maxima to longer wavelengths, as in the case of isoprene, so conjugation becomes the major structural feature identified by this technique. Molar absorptivity's may be very large for strongly absorbing chromophores (>10,000) and very small if absorption is weak (10 to 100). The magnitude of ε reflects both the size of the chromophore and the probability that light of a given wavelength will be absorbed when it strikes the chromophore.

The Importance of Conjugation

A comparison of the absorption spectrum of 1-pentene, λ_{max} = 178 nm, with that of isoprene (above) clearly demonstrates the importance of chromophore conjugation. Further evidence of this effect is shown below. The spectrum on the left illustrates that conjugation of double and triple bonds also shifts the absorption maximum to longer wavelengths. From the polyene spectra displayed in the center diagram, it is clear that each additional double bond in the conjugated pi-electron system shifts the absorption maximum about 30 nm in the same direction. Also, the molar absorptivity (ε) roughly doubles with each new conjugated double bond. Spectroscopists use the terms defined in the table on the right when describing shifts in absorption. Thus, extending conjugation generally results in bathochromic and hyperchromic shifts in absorption. The appearance of several absorption peaks or shoulders for a given chromophore is common for highly conjugated systems, and is often solvent dependent. This fine structure reflects not only the different conformations such systems may assume, but also electronic transitions between the different vibrational energy levels possible for each electronic state. Vibrational fine structure of this kind is most pronounced in vapor phase spectra, and is increasingly broadened and obscured in solution as the solvent is changed from hexane to methanol.

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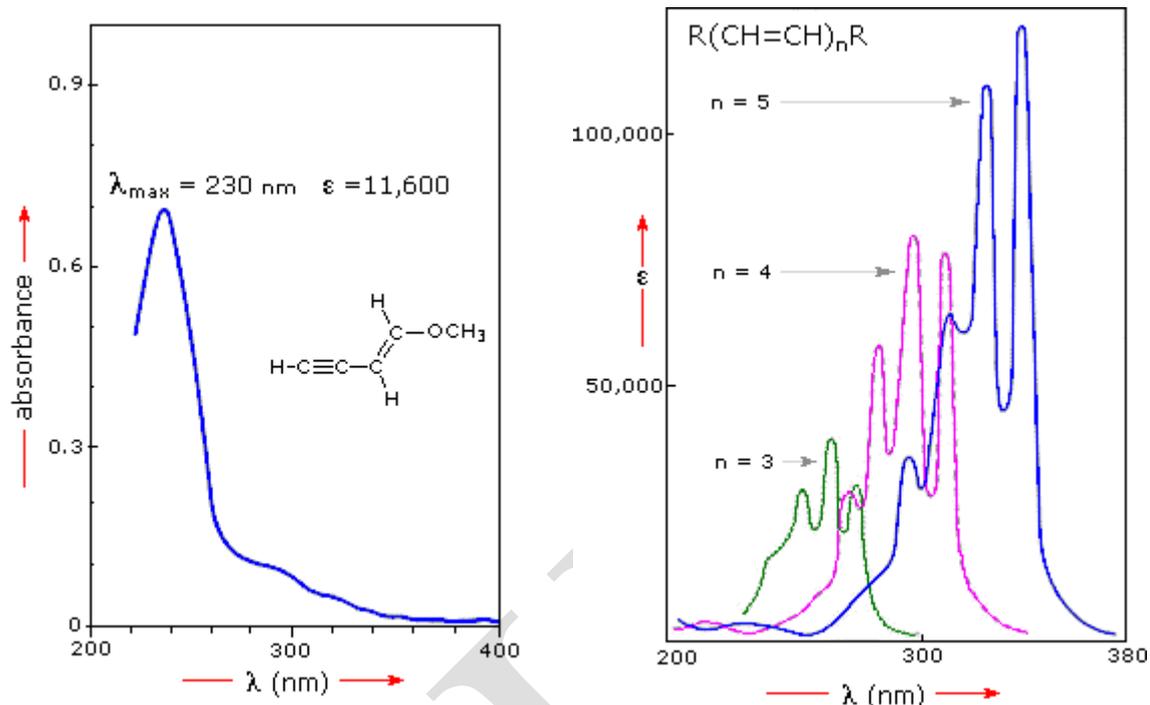
Types of Shifts

Terminology for Absorption Shifts	
Nature of Shift	**Descriptive Term**
To Longer Wavelength	Bathochromic
To Shorter Wavelength	Hypsochromic
To Greater Absorbance	Hyperchromic
To Lower Absorbance	Hypochromic

To understand why conjugation should cause bathochromic shifts in the absorption maxima of chromophores, we need to look at the relative energy levels of the pi-orbitals. When two double bonds are conjugated, the four p-atomic orbitals combine to generate four pi-molecular orbitals (two are bonding and two are antibonding). This was described earlier in the section concerning diene chemistry. In a similar manner, the three double bonds of a conjugated triene create six pi-molecular orbitals, half bonding and half antibonding. The energetically most favorable $\pi \rightarrow \pi^*$ excitation occurs from the highest energy bonding pi-orbital (**HOMO**) to the lowest energy antibonding pi-orbital (**LUMO**).

The following diagram illustrates this excitation for an isolated double bond (only two pi-orbitals) and, on clicking the diagram, for a conjugated diene and triene. In each case the HOMO is colored blue and the LUMO is colored magenta. Increased conjugation brings the HOMO and LUMO orbitals closer together. The energy (ΔE) required to effect the electron

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promotion is therefore less, and the wavelength that provides this energy is increased correspondingly (remember $\lambda = h \cdot c/\Delta E$).
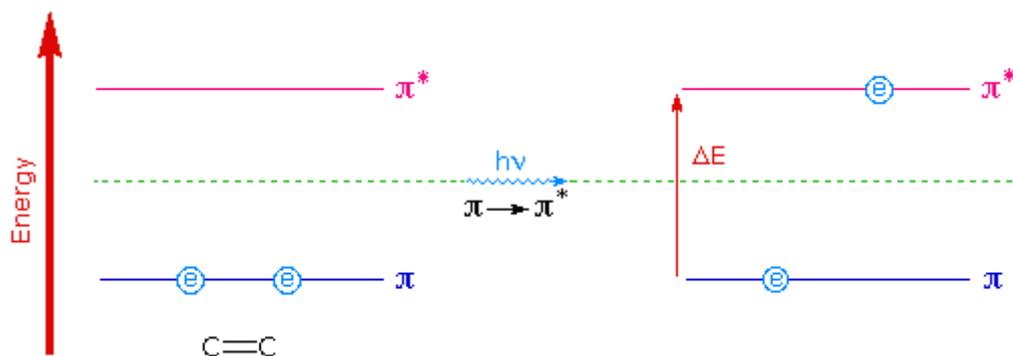

Examples of $\pi \longrightarrow \pi^*$

Many other kinds of conjugated pi-electron systems act as chromophores and absorb light in the 200 to 800 nm region. These include unsaturated aldehydes and ketones and aromatic ring compounds. A few examples are displayed below. The spectrum of the unsaturated ketone (on the left) illustrates the advantage of a logarithmic display of molar absorptivity. The $\pi \longrightarrow \pi^*$ absorption located at 242 nm is very strong, with an $\varepsilon = 18,000$. The weak n $\longrightarrow \pi^*$ absorption near 300 nm has an $\varepsilon = 100$.

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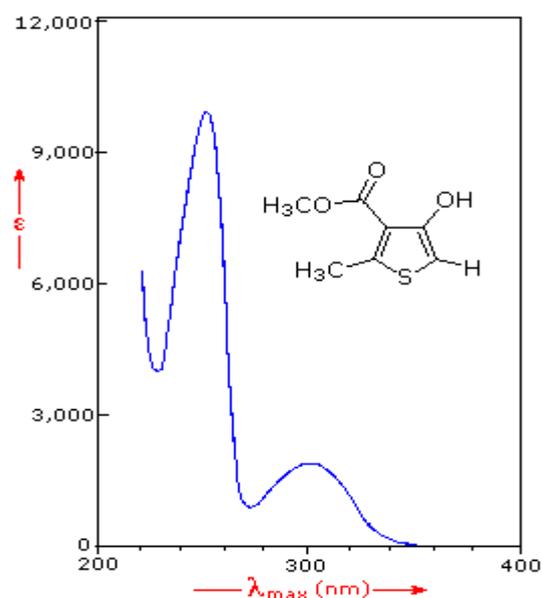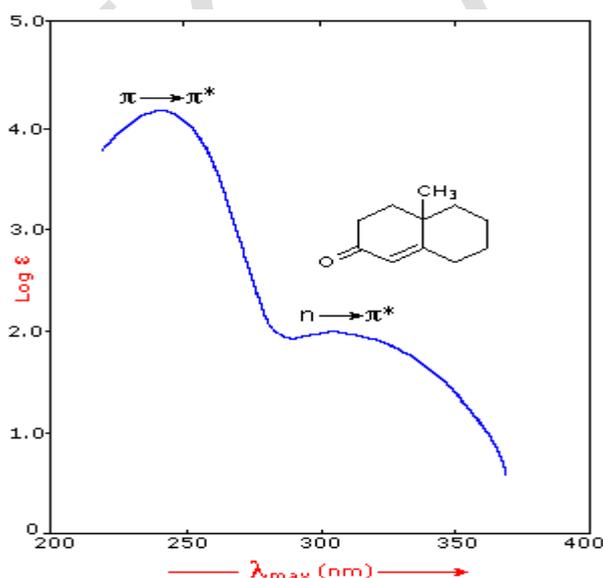
Benzene exhibits very strong light absorption near 180 nm ($\varepsilon > 65,000$) , weaker absorption at 200 nm ($\varepsilon = 8,000$) and a group of much weaker bands at 254 nm ($\varepsilon = 240$). Only the last group of absorptions are completely displayed because of the 200 nm cut-off characteristic of most spectrophotometers. The added conjugation in naphthalene, anthracene and tetracene causes bathochromic shifts of these absorption bands, as displayed in the chart on the left below. All the absorptions do not shift by the same amount, so for anthracene (green shaded box) and tetracene (blue shaded box) the weak absorption is obscured by stronger bands that have experienced a greater red shift. As might be expected from their spectra, naphthalene and anthracene are colorless, but tetracene is orange.
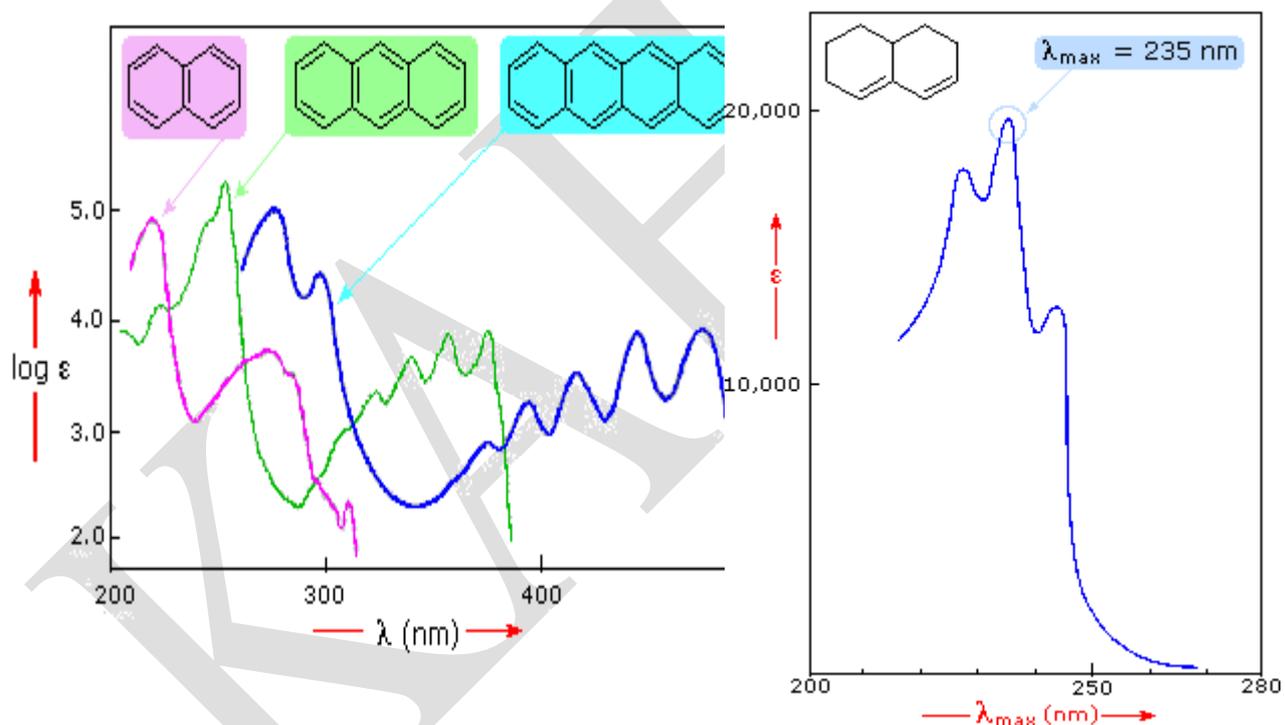
The spectrum of the bicyclic diene (above right) shows some vibrational fine structure, but in general is similar in appearance to that of isoprene, shown above. Closer inspection discloses that the absorption maximum of the more highly substituted diene has moved to a longer wavelength by about 15 nm. This "substituent effect" is general for dienes and trienes, and is even more pronounced for enone chromophores.

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Empirical Rules for Absorption Wavelengths of Conjugated Systems

Woodward-Fieser Rules for Calculating the λ_{max} of Conjugated Dienes and Polyenes	
Core Chromophore	**Substituent and Influence**
Transoid Diene **215 nm**	R- (Alkyl Group) .... **+5 nm** RO- (Alkoxy Group) .. **+6** X- (Cl- or Br-) .... **+10** RCO_2- (Acyl Group) ... **0** RS- (Sulfide Group) .. **+30** R_2N- (Amino Group).. **+60**
Cyclohexadiene* **260 nm**	**Further π -Conjugation** C=C (Double Bond) ... **+30** C_6H_5 (Phenyl Group) ... **+60**

(i) Each exocyclic double bond adds **5 nm**. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring B.

(ii) Solvent effects are minor.

＊ When a homoannular (same ring) cyclohexadiene chromophore is present, a base value of 260 nm should be chosen. This includes the ring substituents. Rings of other size have a lesser influence.

λ_{max} (calculated) = **Base** (215 or 260) + **Substituent Contributions**

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Some examples that illustrate these rules follow.

UV Data Sheet

Absorption maxima (λ_max) are in nanometers, molar absorptivities (ε) are in parentheses.
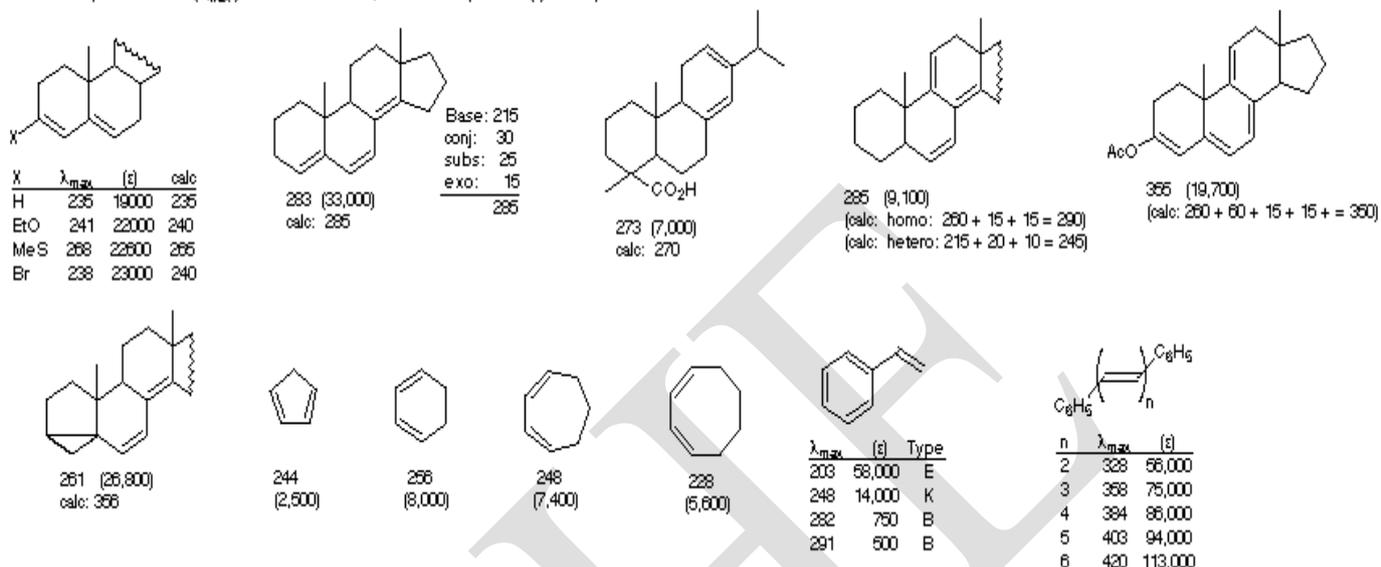
Woodward-Fieser Rules for Calculating the $\pi \longrightarrow \pi^*$ λ_{max} of Conjugated Carbonyl Compounds

Core Chromophore	Substituent and Influence			
R = Alkyl **215 nm** R = H **210 nm** R = OR' **195 nm**	α-			**Substituent**
	R-	(Alkyl Group)	**+10**	**nm**
	Cl-	(Chloro Group)		**+15**
	Br-	(Chloro Group)		**+25**
Cyclopentenone **202 nm**	HO-	(Hydroxyl Group)		**+35**
	RO-	(Alkoxyl Group)		**+35**
	RCO₂-	(Acyl Group)		**+6**

β-   **Substituent**

R-   (Alkyl   Group)   **+12   nm**

Cl-   (Chloro   Group)   **+12**

Br-   (Chloro   Group)   **+30**

HO-   (Hydroxyl   Group)   **+30**

RO-   (Alkoxyl   Group)   **+30**

RCO_2-   (Acyl   Group)   **+6**

RS-   (Sulfide   Group)   **+85**

R_2N-   (Amino   Group)   **+95**

γ   &   δ-   **Substituents**

R-   (Alkyl   Group)   **+18   nm**   (both   γ   &   δ)

HO-   (Hydroxyl   Group)   **+50   nm**   (γ)

RO- (Alkoxyl Group)   **+30 nm** (γ)

Further π -Conjugation
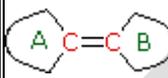
C=C   (Double   Bond)   ...   **+30**

C_6H_5 (Phenyl Group) ...   **+60**

(i) Each exocyclic double bond adds **5 nm**. In the example on the right, there are two exo-double bond components: one to ring A and the other to ring B.

(ii) Homoannular cyclohexadiene component adds **+35 nm** (ring atoms must be counted separately as substituents)

(iii) Solvent Correction: water = **–8**; methanol/ethanol = **0**; ether = **+7**; hexane/cyclohexane = **+11**

λ**max** (calculated) = **Base + Substituent Contributions and Corrections**

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Some examples that illustrate these rules follow.

UV Data Sheet

Absorption maxima (λ_{max}) are in nanometers, molar absorptivities (ε) are in parentheses.

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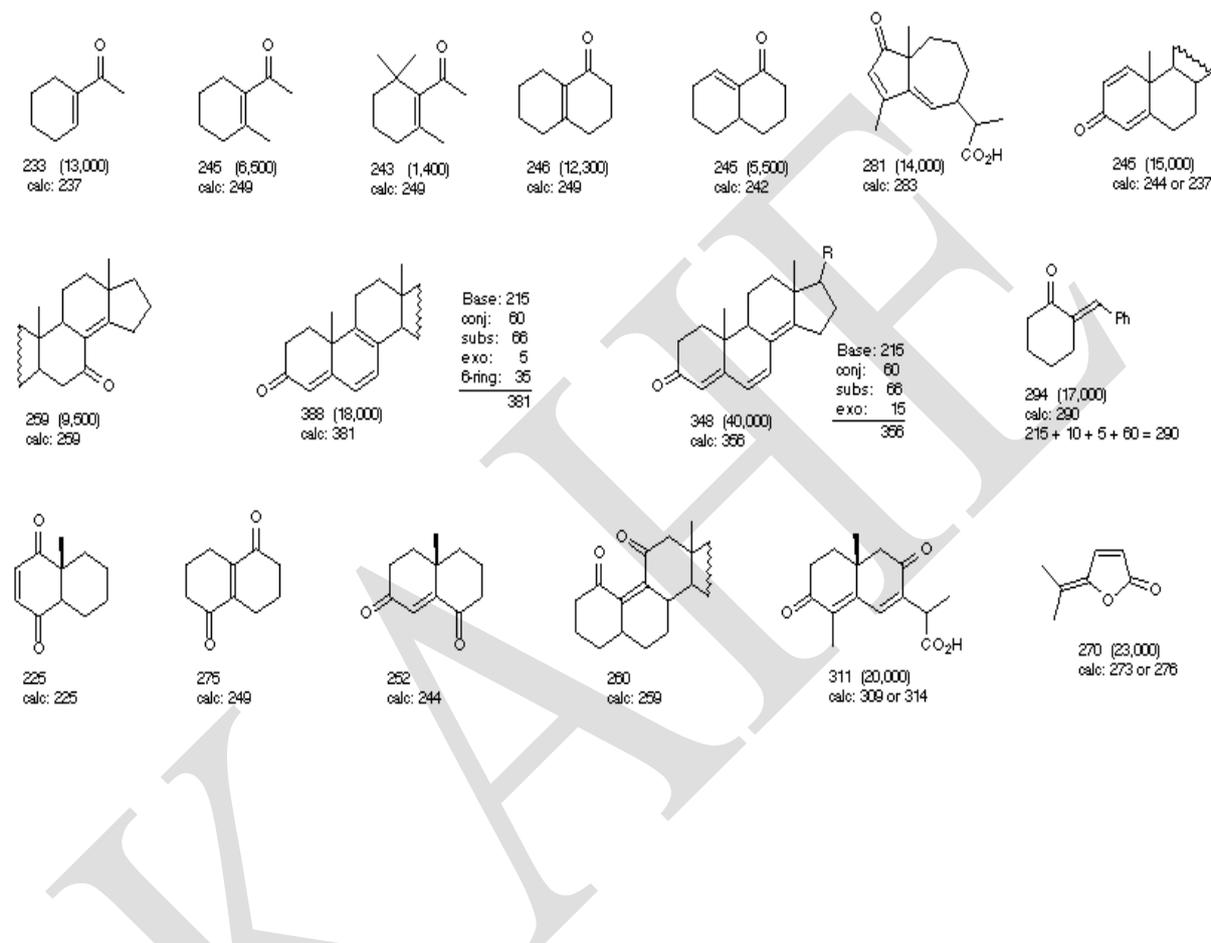
POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. What are the wavelength ranges for the ultraviolet and visible regions of the spectrum?

2. What are the absorption laws?

3. Define electronic spectroscopy

4. Explain quantisation energy.

5. Write a short note on electromagnetic spectrum.

6. Define the term chromophore.

7. Define Bathochromic shift.

8. Define auxochrome.

9. Write the relationship between wavelength and frequency.

PART C (8 Mark Questions)

1. Explain the electronic transitions involved in UV spectroscopy?

2. Explain the various parts and functions of a UV-visible spectrophotometer

3. Explain the Woodward-Fieser rules for calculating absorption maximum for α,β-unsaturated carbonyl compounds with examples.

4. Explain the description of double beam UV spectrophotometer.

5. How will you determine the structure of α, β – unsaturated compounds and conjugated dienes by   UV spectroscopy?

6. Explain the various applications of UV spectroscopy.

7. Explain the absorption laws in detail.

8. Explain the Woodward-Fieser rules for calculating absorption maximum in dienes with examples.

9. Explain absorption and intensity shifts in detail.

10. Explain the keto enol tautomerism in UV spectroscopy?

SUBJECT : **Organic Chemistry -IV (Organic Spectroscopy)**

Subject Code : **16HCU403**

Class : **II B.Sc Chemistry**

Staff Name : **Dr.M.Makeswari and Mr. R Kumar**

Batch : **2016-2018 Batch**

UNIT-I

Multiple choice Questions (Each Carry One mark)   **ANSWER**

Question	a	b	c	d	Answer
An electronic transition takes place so rapidly that a vibrating molecule does not change its internuclear distance appreciably during the transition.This principle is known as	a. Paulis principle	b. Heisenberg principle	c. Franck condon principle.	d.Uncertinity principle	c. Franck condon principle.
Which among the following is the laws of Photochemistry	a.Hooks law	b.Beer-Lambertz law	c. Charls law	d.Avagdros law.	b.Beer-Lambertz law
Reciprocal of transmittance is called	a. Absorbance	b. Opacity	c. Incidence	d.Molar exinction coefficient	b. Opacity
The quantity Ecl is known as	a.Absorbance	b.Opacity	c.Transmittance	d.absorbtivity	a.Absorbance
Structural information deducible from UV spectra is mainly about	a. Inductive effect	b.Conjugation	c.Steric hiderance	d.Mesomeric effect	b.Conjugation
UV absorption spectroscopy is powerful tool for ------------ analysis	a. Quantitative	b. qualitative	c.physical	d environmental	a. Quantitative

Question	a	b	c	d	Answer
As the number of double bonds in conjucation increases, λ_{max} --------	a. increases	b. decreases	c. remains zero	d.zero	a. increases
The alkyl subsitution in an alkene causes a ---------- shift	a.Bathochromic	b.Hypsochromic	c. isomeric	d.Chromophoric	a.Bathochromic
What is the forbidden transition in the following	a.σ- σ*	b.n-π*	c.n-σ*	d. π- π *	b.n-π*
Saturated aldehyde exhibit ------- type of transition	A.both .n-π* and π- π*	b. both .σ- σ* and π- π *	c. .both .σ- σ* and n-π*	d.only n- π *	A.both .n-π* and π-π*
Methyl chloride is an example for ------- type of transition	a. .n-π*	b.π- π*	c. .σ- σ*	d. n-σ*	d. n-σ*
In π- π* transition, solvent polarity results in------------ shift	a. Bathochromic	b. hypsochromic	c. both	d.none	a. Bathochromic
In the case of alcohol λ_{max} small, the effect due to	a.Covalent bond	b.H-bonding	c.co ordinate bonding.	D.none	b.H-bonding
Transition in UV absorption depend on	a.size of the atom	b.Electronegativity	c. H-bonding	d.all the above	d.all the above
According to Woodward-Fieser rule, the value of absorbance depend on	a.no of alkyl sustituents	b. no of double bond	c.presence of polar group	d.all the above	d.all the above
Parent value for Buta diene system is	a.217mμ	b.218 mμ	c.219 mμ	d.220 mμ	a.217mμ

According to Woodward-Fieser rule, to correct strain correction in bicyclic system----- should be added	a. 5 mµ	b.10 mµ	c.15 mµ	d.20 mµ	c.15 mµ
What is the λ_{max} for the 2,4-hexa diene	a. 217 mµ	b.227 mµ	c.272 mµ	d.271 mµ	b.227 mµ
What is the calculated value for cyclohexa 1,3-diene	a. 261 mµ	b. 262 mµ	c.263 mµ	d.264 mµ	c.263 mµ
Upon irradiation with UV-radiation, benzene displaces ----bonds due to its transition	a. 1	b.2	c. 3	d.4	c. 3
If water used as solvent in UV absorption studies, ------ nm to be added with parent value.	a. -4	b.+4	c.+ 8	d.-8	d.-8
Cycles/sec is unit for	a. Wavelength	b.frequency	c.wave number	d.energy	d.energy
The arrangement of all type of electromagnetic radiation in the order of -------- wavelength is called electromagnetic spectrum.	a.increasing	b.decreasing	c.same	d.approximate	a.increasing
Which of the following spectroscopy otherwise known as electronic spectroscopy	a.UV	b.IR	c.NMR	d.ESR	a.UV
Greater value of Molar extinction coefficient indicates that the probability of transition-------	a.less	b.more	c. nil	d.zero	b.more

Molar extinction coefficient value less than ------- is called forbidden transition	a.1	b.10	c.100	d.1000	c.100
When electronegativity increases, λ_{max} -----------	a.increases	b.decreases	c.remains same	d.becomes zero	b.decreases
Increase of solvent polarity results in --------- of λ_{max} of absorption.	a.increase	b.decrease	c. increase and decrease	d.zero	b.decrease
Sufficient condition for absorption of energy of energy is that the interaction must create	a.dipole moment	b.frequency of oscillation	c.both the above	d.none	c.both the above
According to spin conservation rule,which of the following is allowed transition	a.singlet to singlet	b.singlet to triplet	c.triplet to singlet	d.none	a.singlet to singlet
The time taken for an electronic transition is very small compared to time taken for one vibration.This principle is known as	a.Paulis principle	b.Frank-condon principle	c.predissociation	d.Hunds principle	b.Frank-condon principle
In predissociation, some molecules dissociation occur at ------ energy	a.Higher	b.lower	c.zero	d.without	b.lower
Radiation source used in UV instrumentation is	a.Hydrogen	b.deuterium lamp	c. xenon discharge lamp	d.Hydrogen, deutrium and xenon lamp	d.Hydrogen, deutrium and xenon lamp

Question	a	b	c	d	Answer
Which of the energy not accounted in total energy state of electronic absorption by Born-oppenhiemer approximation?	a.E_{elec}	b. E_{rot}	c. E_{trans}	d. E_{vib}	c. E_{trans}
The relative intensity of molecular spectra both in absorption and emission may be interpreted in terms of	a.Frank-condom principle	b.Hiesenberg principle	c.Paulis principle	d.Hooks law.	a.Frank-condom principle
Beer-Lamberts law implies the fractional change in light intensity is proportional to	a.concentration of solution and thickness of solution	b.concentration only	c.thickness of the solution only	d.intensity of emitted light.	a.concentration of solution and thickness of solution
Bathochromic shift also called	a.blue shift	b.red shift	c.yellow shift	d.orange shift	b.red shift
Water has the electronic transition	a. .n-π*	b.π- π*	c. .σ- σ*	d. n-σ*	d. n-σ*
If a molecule exists in two tautomeric form,the preference of one form to another can be detected by ------- spectroscopy	a.UV	b.IR	c,NMR	d.ESR	a.UV
Addition in unsaturation with the increase in the number of double bonds shifts the absorption to------- wavelength	a.shorter	b.longer	c.no change	d.maximum	b.longer

Question	a	b	c	d	Answer
Which of the following is an electromagnetic radiation	a.alpha rays	b.beta rays	c.gammarays	d. anode rays	c.gammarays
Which of the following statements is true	a. X-rays are affected by electric field	b. X-rays are affectedby magnetic field	c. gamma rays are more energetic than X-rays	d.gamma rays are a stream of position	c. gamma rays are more energetic than X-rays
The wave length of x-rays is of the order of	a.10^{-8}m	b.10^{-8} cm	c. 10^{-23} cm	d. 40000A°	b.10^{-8} cm
The wave length of 1000 A° is in the ------ region	a. far UV	b.Visible	c.near UV	d. IR	a. far UV
Of the following radiations, which represents the visible region?	a. 0-100 nm	b. 100-200 nm	c.200-400 nm	d.400-800 nm	d.400-800 nm
Among the following electromagnetic radiations, which has the maximum wavelength?	a. IR	b.UV	c.radio wave	d. X-ray	c.radio wave
Which of the following radiation has the maximum energy	a.UV	b. far IR	c.visible	d. near IR	a.UV
Which of the following colours of visible light is bent most as it passes through a prism?	a. Yellow	b. Red	c. Blue	d. Green	c. Blue
A frequencyof 1000 cm^{-1} is in the ----- region	a.UV	b. IR	c.visible	d. microwave	b. IR

Question	a	b	c	d	Answer
One electron- volt of energy is equivalent to a photon with a wave lengthof about	a. 300 A°	b. 30 A°	c. 3000A°	d.12000A°	d.12000A°
Which among the following radiation will not ionise a gas?	a. X-rays	b. α-particles	c.β-particles	d. neutrons	d. neutrons
Radiation which has the least energy (among the following)	a.alpha rays	b.beta rays	c.gammarays	d. electrica; waves	d. electrica; waves
One nm is equal to	a. 10A°	b. 0.1 A°	c. 10^{-9} cm	d. 10^{-8} cm	a. 10A°
Which of the following transition require the least energy?	a. .n-π*	b.π- π*	c. .σ- σ*	d. n-σ*	a. .n-π*
Which of the following molecule has the shortest wavelength absorption band?	a. H_2O	b.CH_4	c. CH_3Cl	d. CH_3CHO	b.CH_4
Which compound does not involve the π-π* transition in UV spectroscopy	a. alkenes	b. azo compound	c. alcohols	c. cyanides	c. alcohols
Which one is acidic auxochromic group?	a. -OH	b. -NO_2	c. -OR	d.NH_2	b. -NO_2
What will be the theoritical number of vibrational degrees of freedom in benzene,CO_2, SO2 respectively	a. 12,4,3	b. 3,4,12	c. 30,4,3	d. 30,3,3	c. 30,4,3
The number of vibrational degrees of freedom in $C_6H_5CH_3$	a. 39	b. 15	c. 18	d. 40	a. 39

Which one is the correctbasic value of λ_{max} for a homoanular ddiene--	a.214	b.217	c.253	d.215	c.253

UNIT II

SYLLABUS

IR Spectroscopy: Fundamental and non-fundamental molecular vibrations; IR absorption positions of O, N and S containing functional groups; Effect of H-bonding, conjugation, resonance and ring size on IR absorptions; Fingerprint region and its significance; application in functional group analysis.

Infrared spectroscopy

Infrared spectroscopy (IR spectroscopy) is the spectroscopy that deals with the infrared region of the electromagnetic spectrum, that is light with a longer wavelength and lower frequency than visible light. It covers a range of techniques, mostly based on absorption spectroscopy. As with all spectroscopic techniques, it can be used to identify and study chemicals. A common laboratory instrument that uses this technique is a Fourier transform infrared (FTIR) spectrometer.

The infrared portion of the electromagnetic spectrum is usually divided into three regions; the near-, mid- and far- infrared, named for their relation to the visible spectrum. The higher energy near-IR, approximately $14000–4000 \text{ cm}^{-1}$ (0.8–2.5 μm wavelength) can excite overtone or harmonic vibrations. The mid-infrared, approximately $4000–400 \text{ cm}^{-1}$ (2.5–25 μm) may be used to study the fundamental vibrations and associated rotational-vibrational structure. The far-infrared, approximately $400–10 \text{ cm}^{-1}$ (25–1000 μm), lying adjacent to the microwave region, has low energy and may be used for rotational spectroscopy. The names and classifications of these subregions are conventions, and are only loosely based on the relative molecular or electromagnetic properties.

Theory

Infrared spectroscopy exploits the fact that molecules absorb specific frequencies that are characteristic of their structure. These absorptions are resonant frequencies, i.e. the frequency of the absorbed radiation matches the frequency of the bond or group that vibrates. The energies

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are determined by the shape of the molecular potential energy surfaces, the masses of the atoms, and the associated vibronic coupling.

In particular, in the Born–Oppenheimer and harmonic approximations, i.e. when the molecular Hamiltonian corresponding to the electronic ground state can be approximated by a harmonic oscillator in the neighborhood of the equilibrium molecular geometry, the resonant frequencies are determined by the normal modes corresponding to the molecular electronic ground state potential energy surface. Nevertheless, the resonant frequencies can be in a first approach related to the strength of the bond, and the mass of the atoms at either end of it. Thus, the frequency of the vibrations can be associated with a particular bond type.

Number of vibrational modes

In order for a vibrational mode in a molecule to be "IR active," it must be associated with changes in the permanent dipole.

A molecule can vibrate in many ways, and each way is called a *vibrational mode*. Linear molecules have $3N - 5$ degrees of vibrational modes whereas nonlinear molecules have $3N - 6$ degrees of vibrational modes (also called vibrational degrees of freedom). As an example, H_2O, a non-linear molecule, will have $3 \times 3 - 6 = 3$ degrees of vibrational freedom, or modes.

Simple diatomic molecules have only one bond and only one vibrational band. If the molecule is symmetrical, e.g. N_2, the band is not observed in the IR spectrum, but only in the Raman spectrum. Unsymmetrical diatomic molecules, e.g. CO, absorb in the IR spectrum. More complex molecules have many bonds, and their vibrational spectra are correspondingly more complex, i.e. big molecules have many peaks in their IR spectra.

The atoms in a CH_2 group, commonly found in organic compounds, can vibrate in six different ways: **symmetric and antisymmetric stretching**, **scissoring**, **rocking**, **wagging** and **twisting**:

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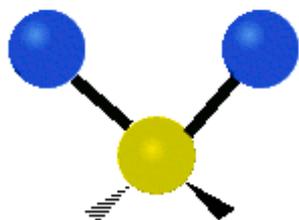
Symmetrical stretching	Antisymmetrical stretching	Scissoring
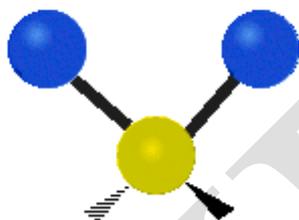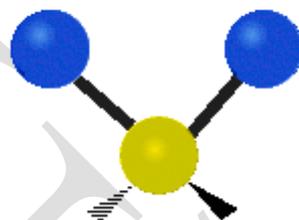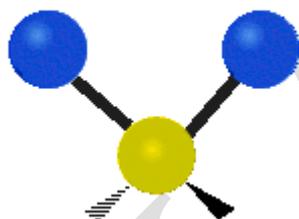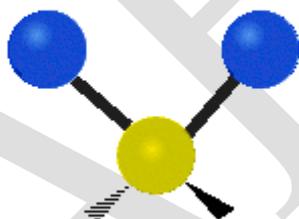
Rocking	Wagging	Twisting
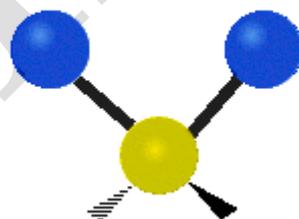
(These figures do not represent the "recoil" of the C atoms, which, though necessarily present to balance the overall movements of the molecule, are much smaller than the movements of the lighter H atoms).

Special effects

The simplest and most important IR bands arise from the "normal modes," the simplest distortions of the molecule. In some cases, "overtone bands" are observed. These bands arise from the absorption of a photon that leads to a doubly excited vibrational state. Such bands appear at approximately twice the energy of the normal mode. Some vibrations, so-called 'combination modes," involve more than one normal mode. The phenomenon of Fermi resonance can arise when two modes are similar in energy, Fermi resonance results in an unexpected shift in energy and intensity of the bands.

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Practical IR spectroscopy

The infrared spectrum of a sample is recorded by passing a beam of infrared light through the sample. Examination of the transmitted light reveals how much energy was absorbed at each wavelength. This can be done with a monochromatic beam, which changes in wavelength over time, or by using a Fourier transform instrument to measure all wavelengths at once. From this, a transmittance or absorbance spectrum can be produced, showing at which IR wavelengths the sample absorbs. Analysis of these absorption characteristics reveals details about the molecular structure of the sample. When the frequency of the IR is the same as the vibrational frequency of a bond, absorption occurs.

This technique works almost exclusively on samples with covalent bonds. Simple spectra are obtained from samples with few IR active bonds and high levels of purity. More complex molecular structures lead to more absorption bands and more complex spectra. The technique has been used for the characterization of very complex mixtures.

Sample preparation

Gaseous samples require a sample cell with a long pathlength (typically 5–10 cm), to compensate for the diluteness.

Liquid samples can be sandwiched between two plates of a salt (commonly sodium chloride, or common salt, although a number of other salts such as potassium bromide or calcium fluoride are also used). The plates are transparent to the infrared light and do not introduce any lines onto the spectra.

Solid samples can be prepared in a variety of ways. One common method is to crush the sample with an oily mulling agent (usually Nujol) in a marble or agate mortar, with a pestle. A thin film of the mull is smeared onto salt plates and measured. The second method is to grind a quantity of the sample with a specially purified salt (usually potassium bromide) finely (to remove scattering effects from large crystals). This powder mixture is then pressed in a mechanical press to form a translucent pellet through which the beam of the spectrometer can

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pass. A third technique is the "cast film" technique, which is used mainly for polymeric materials. The sample is first dissolved in a suitable, non hygroscopic solvent. A drop of this solution is deposited on surface of KBr or NaCl cell. The solution is then evaporated to dryness and the film formed on the cell is analysed directly. Care is important to ensure that the film is not too thick otherwise light cannot pass through. This technique is suitable for qualitative analysis. The final method is to use microtomy to cut a thin (20–100 µm) film from a solid sample. This is one of the most important ways of analysing failed plastic products for example because the integrity of the solid is preserved.

It is important to note that spectra obtained from different sample preparation methods will look slightly different from each other due to differences in the samples' physical states.

Comparing to a reference
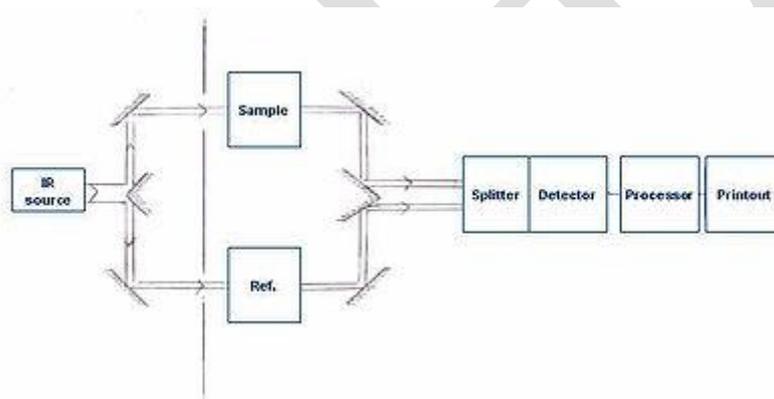
Schematics of a two-beam absorption spectrometer. A beam of infrared light is produced, passed through an interferometer (not shown), and then split into two separate beams. One is passed through the sample, the other passed through a reference. The beams are both reflected back towards a detector, however first they pass through a splitter, which quickly alternates which of the two beams enters the detector. The two signals are then compared and a printout is obtained. This "two-beam" setup gives accurate spectra even if the intensity of the light source drifts over time.

To take the infrared spectrum of a sample, it is necessary to measure both the sample and a "reference" (or "control"). This is because each measurement is affected by not only the light-absorption properties of the sample, but also the properties of the instrument (for example,

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what light source is used, what detector is used, etc.). The reference measurement makes it possible to eliminate the instrument influence. Mathematically, the sample transmission spectrum is divided by the reference transmission spectrum.

The appropriate "reference" depends on the measurement and its goal. The simplest reference measurement is to simply remove the sample (replacing it by air). However, sometimes a different reference is more useful. For example, if the sample is a dilute solute dissolved in water in a beaker, then a good reference measurement might be to measure pure water in the same beaker. Then the reference measurement would cancel out not only all the instrumental properties (like what light source is used), but also the light-absorbing and light-reflecting properties of the water and beaker, and the final result would just show the properties of the solute (at least approximately).

A common way to compare to a reference is sequentially: First measure the reference, then replace the reference by the sample, then measure the sample. This technique is not perfectly reliable: If the infrared lamp is a bit brighter during the reference measurement, then a bit dimmer during the sample measurement, the measurement will be distorted. More elaborate methods, such as a "two-beam" setup (see figure), can correct for these types of effects to give very accurate results.

 FTIR

Fourier transform infrared spectroscopy

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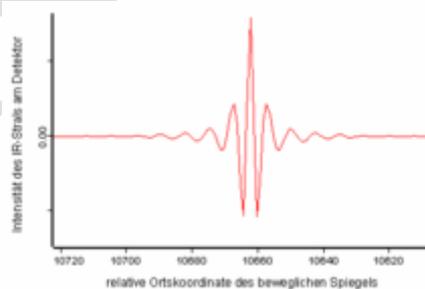
An interferogram from an FTIR measurement. The horizontal axis is the position of the mirror, and the vertical axis is the amount of light detected. This is the "raw data" which can be Fourier transformed to get the actual spectrum.

Fourier transform infrared (FTIR) spectroscopy is a measurement technique that allows one to record infrared spectra. Infrared light is guided through an interferometer and then through the sample (or vice versa). A moving mirror inside the apparatus alters the distribution of infrared light that passes through the interferometer. The signal directly recorded, called an "interferogram", represents light output as a function of mirror position. A data-processing technique called Fourier transform turns this raw data into the desired result (the sample's spectrum): Light output as a function of infrared wavelength (or equivalently, wavenumber). As described above, the sample's spectrum is always compared to a reference.

There is an alternate method for taking spectra (the "dispersive" or "scanning monochromator" method), where one wavelength at a time passes through the sample. The dispersive method is more common in UV-Vis spectroscopy, but is less practical in the infrared than the FTIR method. One reason that FTIR is favored is called "Fellgett's advantage" or the "multiplex advantage": The information at all frequencies is collected simultaneously, improving both speed and signal-to-noise ratio. Another is called "Jacquinot's Throughput Advantage": A dispersive measurement requires detecting much lower light levels than an FTIR measurement. There are other advantages, as well as some disadvantages, but virtually all modern infrared spectrometers are FTIR instruments.

Absorption bands

Infrared Spectroscopy Correlation Table

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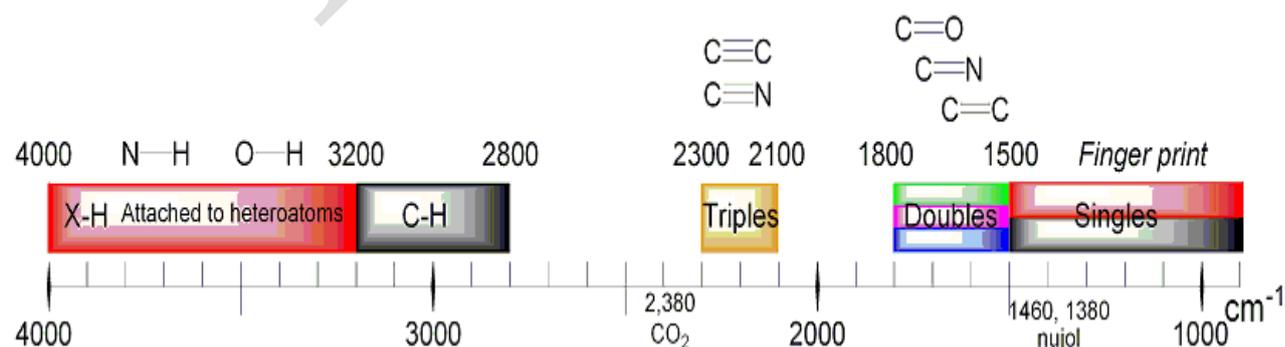
Wavenumbers listed in cm^{-1}.

Uses and applications

Infrared spectroscopy is widely used in both research and industry as a simple and reliable technique for measurement, quality control and dynamic measurement. It is also used in forensic analysis in both criminal and civil cases, enabling identification of polymer degradation for example.

The instruments are now small, and can be transported, even for use in field trials. With increasing technology in computer filtering and manipulation of the results, samples in solution can now be measured accurately (water produces a broad absorbance across the range of interest, and thus renders the spectra unreadable without this computer treatment). Some instruments will also automatically tell you what substance is being measured from a store of thousands of reference spectra held in storage.

By measuring at a specific frequency over time, changes in the character or quantity of a particular bond can be measured. This is especially useful in measuring the degree of polymerization in polymer manufacture. Modern research instruments can take infrared measurements across the whole range of interest as frequently as 32 times a second. This can be done whilst simultaneous measurements are made using other techniques. This makes the observations of chemical reactions and processes quicker and more accurate.

Infrared spectroscopy has been highly successful for applications in both organic and inorganic chemistry. Infrared spectroscopy has also been successfully utilized in the field of semiconductor microelectronics: for example, infrared spectroscopy can be applied to semiconductors like silicon, gallium arsenide, gallium nitride, zinc selenide, amorphous silicon, silicon nitride, etc.

Isotope effects

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The different isotopes in a particular species may give fine detail in infrared spectroscopy. For example, the O–O stretching frequency (in reciprocal centimeters) of oxyhemocyanin is experimentally determined to be 832 and 788 cm^{-1} for $\nu(^{16}O–^{16}O)$ and $\nu(^{18}O–^{18}O)$, respectively.

By considering the O–O bond as a spring, the wavenumber of absorbance, ν can be calculated:

$$\nu = \frac{1}{2\pi c}\sqrt{\frac{k}{\mu}}$$

where k is the spring constant for the bond, c is the speed of light, and μ is the reduced mass of the A–B system:

$$\mu = \frac{m_A m_B}{m_A + m_B}$$

(m_i is the mass of atom i).

The reduced masses for $^{16}O–^{16}O$ and $^{18}O–^{18}O$ can be approximated as 8 and 9 respectively. Thus

$$\frac{\nu(^{16}O)}{\nu(^{18}O)} = \sqrt{\frac{9}{8}} \approx \frac{832}{788}.$$

Where ν is the wavenumber; [wavenumber = frequency/(speed of light)]

The effect of isotopes, both on the vibration and the decay dynamics, has been found to be stronger than previously thought. In some systems, such as silicon and germanium, the decay of the anti-symmetric stretch mode of interstitial oxygen involves the symmetric stretch mode with a strong isotope dependence. For example, it was shown that for a natural silicon sample, the lifetime of the anti-symmetric vibration is 11.4 ps. When the isotope of one of the silicon atoms is increased to ^{29}Si, the lifetime increases to 19 ps. In similar manner, when the silicon atom is changed to ^{30}Si, the lifetime becomes 27 ps.

Two-dimensional IR

Two-dimensional infrared correlation spectroscopy analysis is the application of 2D correlation analysis on infrared spectra. By extending the spectral information of a perturbed sample, spectral analysis is simplified and resolution is enhanced. The 2D synchronous and 2D asynchronous spectra represent a graphical overview of the spectral changes due to a perturbation (such as a changing concentration or changing temperature) as well as the relationship between the spectral changes at two different wavenumbers.

Two-dimensional infrared spectroscopy
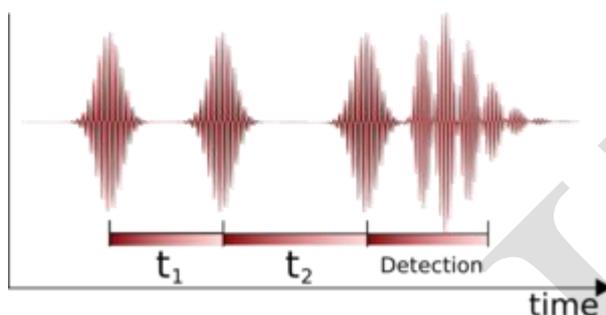
Pulse Sequence used to obtain a two-dimensional Fourier transform infrared spectrum. The time period τ_1 is usually referred to as the coherence time and the second time period τ_2 is known as the waiting time. The excitation frequency is obtained by Fourier transforming along the τ_1 axis.

Nonlinear two-dimensional infrared spectroscopy is the infrared version of correlation spectroscopy. Nonlinear two-dimensional infrared spectroscopy is a technique that has become available with the development of femtosecond infrared laser pulses. In this experiment, first a set of pump pulses are applied to the sample. This is followed by a waiting time, wherein the system is allowed to relax. The typical waiting time lasts from zero to several picoseconds, and the duration can be controlled with a resolution of tens of femtoseconds. A probe pulse is then applied resulting in the emission of a signal from the sample. The nonlinear two-dimensional infrared spectrum is a two-dimensional correlation plot of the frequency ω_1 that was excited by the initial pump pulses and the frequency ω_3 excited by the probe pulse after the waiting time. This allows the observation of coupling between different vibrational modes; because of its extremely high time resolution, it can be used to monitor molecular dynamics on a picosecond

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timescale. It is still a largely unexplored technique and is becoming increasingly popular for fundamental research.

As with two-dimensional nuclear magnetic resonance (2DNMR) spectroscopy, this technique spreads the spectrum in two dimensions and allows for the observation of cross peaks that contain information on the coupling between different modes. In contrast to 2DNMR, nonlinear two-dimensional infrared spectroscopy also involves the excitation to overtones. These excitations result in excited state absorption peaks located below the diagonal and cross peaks. In 2DNMR, two distinct techniques, COSY and NOESY, are frequently used. The cross peaks in the first are related to the scalar coupling, while in the later they are related to the spin transfer between different nuclei. In nonlinear two-dimensional infrared spectroscopy, analogs have been drawn to these 2DNMR techniques. Nonlinear two-dimensional infrared spectroscopy with zero waiting time corresponds to COSY, and nonlinear two-dimensional infrared spectroscopy with finite waiting time allowing vibrational population transfer corresponds to NOESY. The COSY variant of nonlinear two-dimensional infrared spectroscopy has been used for determination of the secondary structure content proteins.

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Organic Compound Identification Using Infrared Spectroscopy

This exercise is intended to familiarize you with the identification of functional groups in organic compounds using infrared spectra. Before you can use this technique, you need to have an introduction to infrared spectroscopy and to what an IR spectrum is.

Infrared spectroscopy deals with the interaction of infrared light with matter. The energy of an infrared photon can be calculated using the Planck energy relation.

$E = hn$

where h = 6.6 x 10^{-34} joule second and n = frequency of the photon. This shows that high energy photons have high frequency.

The frequency, n, and speed of light, c, are related through the relation

$c = ln$

where c = 3.0 x 10^8 meter/second and l = wavelength for the light
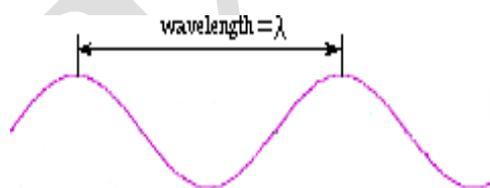
These two equations can be used to identify a common spectroscopic unit called *wavenumber*, $\bar{v}$, which is the reciprocal of the wavelength.

$E = hn = h\, c\left(\frac{1}{\lambda}\right); E = hn = h\, c\, \bar{v};$

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$\bar{v}=$ wavenumber $= \left(\frac{1}{\lambda}\right)$ has units of (cm^{-1})

You can see that both frequency and wavenumber are directly proportional to energy.

Molecules are flexible, moving collections of atoms. The atoms in a molecule are constantly oscillating around average positions. Bond lengths and bond angles are continuously changing due to this vibration. A molecule absorbs infrared radiation when the vibration of the atoms in the molecule produces an oscillating electric field with the same frequency as the frequency of incident IR "light".
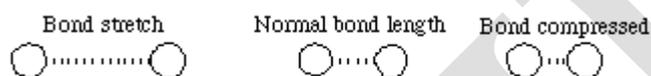
All of the motions can be described in terms of two types of molecular vibrations. One type of vibration, a stretch, produces a change of bond length. A stretch is a rhythmic movement along the line between the atoms so that the interatomic distance is either increasing or decreasing.

The second type of vibration, a bend, results in a change in bond angle. These are also sometimes called scissoring, rocking, or "wig wag" motions.
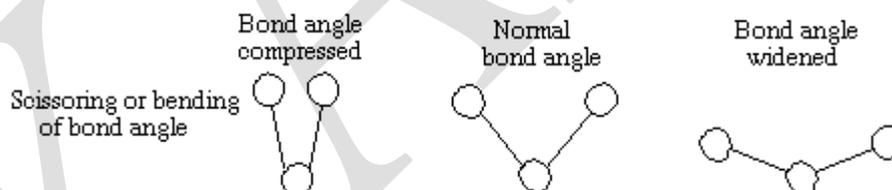
Each of these two main types of vibration can have variations. A stretch can be symmetric or asymmetric. Bending can occur in the plane of the molecule or out of plane; it can be scissoring, like blades of a pair of scissors, or rocking, where two atoms move in the same direction.

Different stretching and bending vibrations can be visualized by considering the CH$_2$ group in hydrocarbons. The arrows indicate the direction of motion. The stretching motions require more energy than the bending ones.

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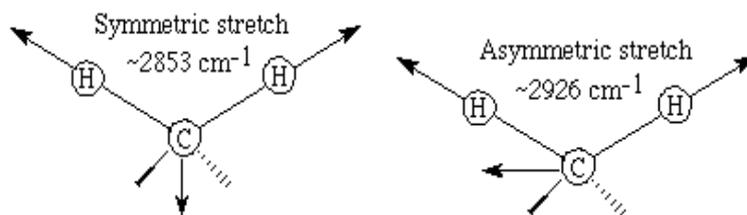
Note the high wavenumber (high energy) required to produce these motions.

The bending motions are sometimes described as wagging or scissoring motions.
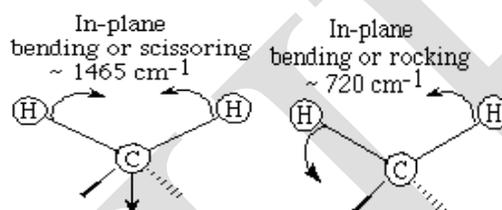
You can see that the lower wavenumber values are consistent with lower energy to cause these vibrations.

A molecule absorbs a unique set of IR light frequencies. Its IR spectrum is often likened to a person's fingerprints. These frequencies match the natural vibrational modes of the molecule. A molecule absorbs only those frequencies of IR light that match vibrations that cause a change in the dipole moment of the molecule. Bonds in symmetric N2 and H2 molecules do not absorb IR because stretching does not change the dipole moment, and bending cannot occur with only 2 atoms in the molecule. Any individual bond in an organic molecule with symmetric structures and identical groups at each end of the bond will not absorb in the IR range. For example, in ethane, the bond between the carbon atoms does not absorb IR because there is a methyl group at each end of the bond. The C-H bonds within the methyl groups do absorb.

In a complicated molecule many fundamental vibrations are possible, but not all are observed. Some motions do not change the dipole moment for the molecule; some are so much alike that they coalesce into one band.

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Even though an IR spectrum is characteristic for an entire molecule, there are certain groups of atoms in a molecule that give rise to absorption bands at or near the same wavenumber, $\bar{v}$,

(frequency) regardless of the rest of the structure of the molecule. These persistent characteristic bands enable you to identify major structural features of the molecule after a quick inspection of the spectrum and the use of a correlation table. The correlation table is a listing of functional groups and their characteristic absorption frequencies.

The infrared spectrum for a molecule is a graphical display. It shows the frequencies of IR radiation absorbed and the % of the incident light that passes through the molecule without being absorbed. The spectrum has two regions. The *fingerprint* region is unique for a molecule and the *functional group* region is similar for molecules with the same functional groups.
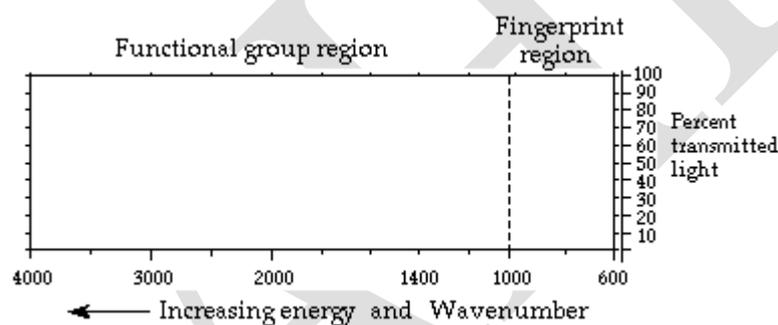
The nonlinear horizontal axis has units of wavenumbers. Each wavenumber value matches a particular frequency of infrared light. The vertical axis shows % transmitted light. At each frequency the % transmitted light is 100% for light that passes through the molecule with no interactions; it has a low value when the IR radiation interacts and excites the vibrations in the molecule.

A portion of the spectrum where % transmittance drops to a low value then rises back to near 100% is called a "band". A band is associated with a particular vibration within the molecule. The width of a band is described as broad or narrow based on how large a range of frequencies it covers. The efficiencies for the different vibrations determine how "intense" or strong the absorption bands are. A band is described as strong, medium, or weak depending on its depth.

In the hexane spectrum below the band for the CH stretch is strong and that for the CH bend is medium. The alkane, hexane (C_6H_{14}) gives an IR spectrum that has relatively few bands because

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there are only CH bonds that can stretch or bend. There are bands for CH stretches at about 3000 cm^{-1}. The CH$_2$ bend band appears at approximately 1450 cm^{-1} and the CH$_3$ bend at about 1400 cm^{-1}. The spectrum also shows that shapes of bands can differ.
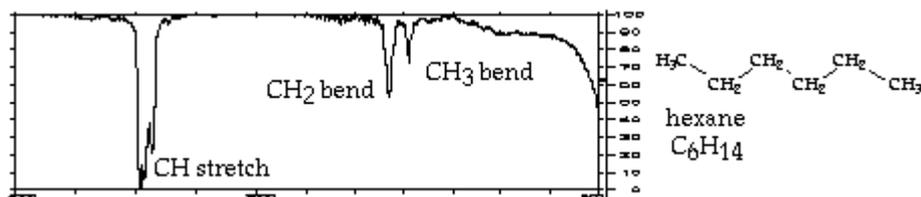
Every molecule will have its own characteristic spectrum. The bands that appear depend on the types of bonds and the structure of the molecule. Study the sample spectra below, noting similarities and differences, and relate these to structure and bonding within the molecules.

The spectrum for the alkene, 1-hexene, C$_6$H$_{12}$, has few strong absorption bands. The spectrum has the various CH stretch bands that all hydrocarbons show near 3000 cm^{-1}. There is a weak alkene CH stretch above 3000 cm^{-1} . The strong CH stretch bands below 3000 cm^{-1} come from carbon-hydrogen bonds in the CH$_2$ and CH$_3$ groups. There is an out-of-plane CH bend for the alkene in the range 1000-650 cm^{-1}. There is also an alkene CC double bond stretch at about 1650 cm^{-1} .
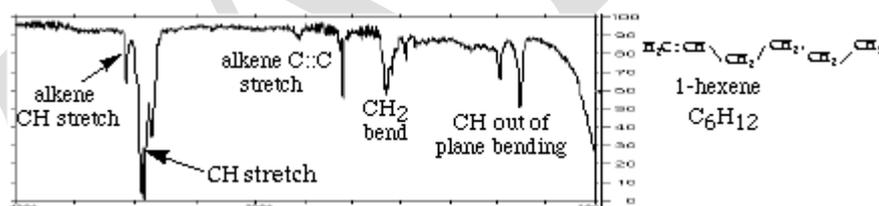
The spectrum for cyclohexene, (C$_6$H$_{10}$) also has few strong bands. The main band is a strong CH stretch from the CH$_2$ groups at about 3000 cm^{-1}. The CH stretch for the alkene CH is, as always, to the left of 3000 cm^{-1}. The CH$_2$ bend appears at about 1450 cm^{-1}. The other weaker bands in the range 1000-650 cm^{-1} are for the out of plane CH bending. There is a very weak alkene CC double bond stretch at about 1650 cm^{-1}.

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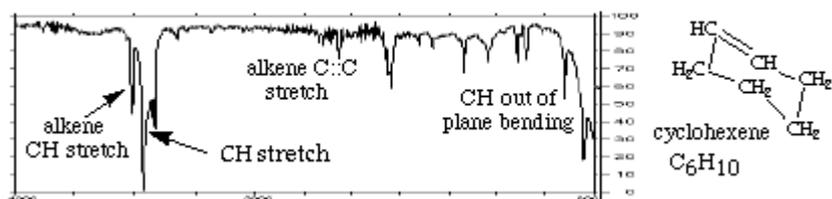
The IR spectrum for benzene, C_6H_6, has only four prominent bands because it is a very symmetric molecule. Every carbon has a single bond to a hydrogen. Each carbon is bonded to two other carbons and the carbon-carbon bonds are alike for all six carbons. The molecule is planar. The aromatic CH stretch appears at 3100-3000 cm^{-1} There are aromatic CC stretch bands (for the carbon-carbon bonds in the aromatic ring) at about 1500 cm^{-1}. Two bands are caused by bending motions involving carbon-hydrogen bonds. The bands for CH bends appear at approximately 1000 cm^{-1} for the in-plane bends and at about 675 cm^{-1} for the out-of-plane bend.
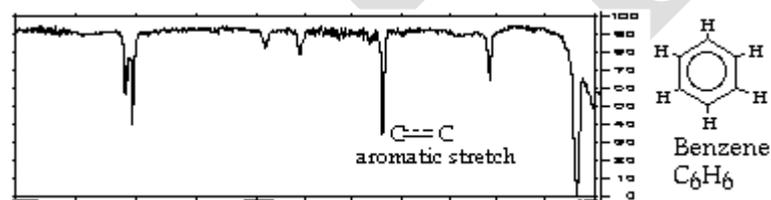
The IR spectrum for the alcohol, ethanol (CH_3CH_2OH), is more complicated. It has a CH stretch, an OH stretch, a CO stretch and various bending vibrations. The important point to learn here is that no matter what alcohol molecule you deal with, the OH stretch will appear as a broad band at approximately 3300-3500 cm^{-1}. Likewise the CH stretch still appears at about 3000 cm^{-1}.

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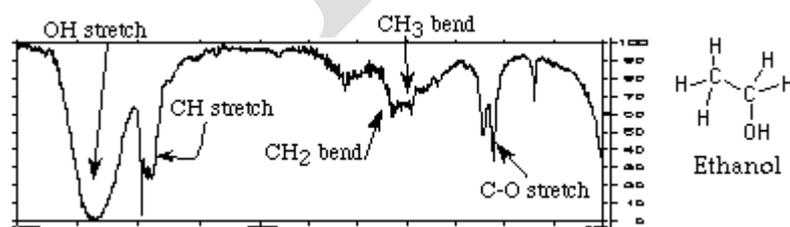
The spectrum for the aldehyde, octanal ($CH_3(CH_2)_6CHO$), is shown here. The most important features of the spectrum are carbonyl CO stretch near 1700 cm^{-1} and the CH stretch at about 3000 cm^{-1}. If you see an IR spectrum with an intense strong band near 1700 cm-1 and the compound contains oxygen, the molecule most likely contains a carbonyl group,
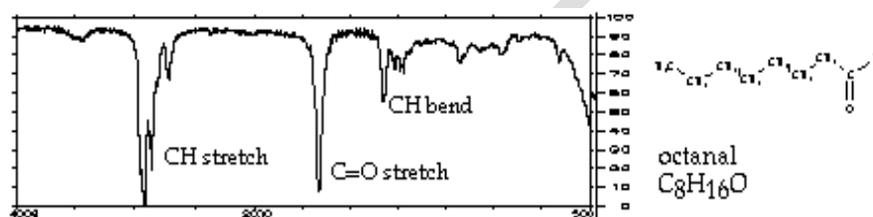
The spectrum for the ketone, 2-pentanone, appears below. It also has a characteristic carbonyl band at 1700 cm^{-1}. The CH stretch still appears at about 3000 cm^{-1}, and the CH2 bend shows up at approximately 1400 cm^{-1}. You can see the strong carbonyl CO stretch at approximately 1700 cm^{-1}. You can also see that this spectrum is different from the spectrum for octanal. At this point in your study of IR spectroscopy, you can't tell which compound is an aldehyde and which is a ketone. You can tell that both octanal and a 2-pentanone contain C-H bonds and a carbonyl group.
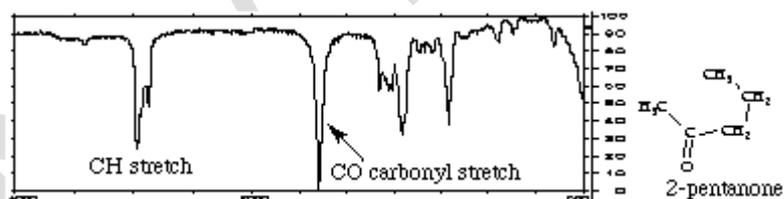
Carboxylic acids have spectra that are even more involved. They typically have three bands caused by bonds in the COOH functional group. The band near 1700 cm^{-1} is due to the CO double bond. The broad band centered in the range 2700-3300 cm^{-1} is caused by the presence of the OH and a band near 1400 cm^{-1} comes from the CO single bond. The spectrum for the carboxylic acid, diphenylacetic acid, appears below. Although the aromatic CH bands complicate the spectrum, you can still see the broad OH stretch between 2700-3300 cm^{-1}. It overlaps the CH stretch which appears

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near 3000 cm^{-1}. A strong carbonyl CO stretch band exists near 1700 cm^{-1}. The CO single bond stretch shows up near 1200 cm^{-1}.

diphenylacetic acid
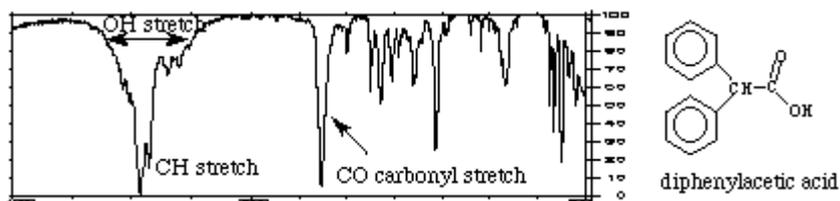
The spectrum for 1-bromobutane, C$_4$H$_9$Br, is shown here. This is relatively simple because there are only CH single bonds and the CBr bond. The CH stretch still appears at about 3000 cm-1. The CH$_2$ bend shows up near 1400 cm^{-1}, and you can see the CBr stretch band at approximately 700 cm^{-1}.

1-bromobutane
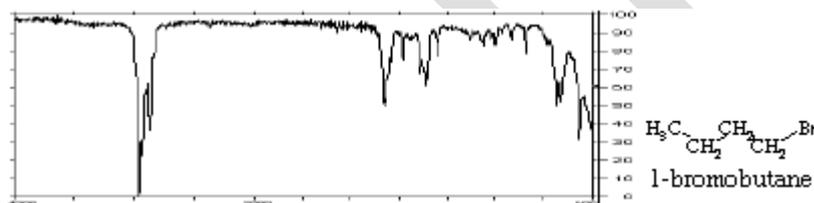
IR spectra can be used to identify molecules by recording the spectrum for an unknown and comparing this to a library or data base of spectra of known compounds. Computerized spectra data bases and digitized spectra are used routinely in this way in research, medicine, criminology, and a number of other fields.

In this exercise you will try to identify the outstanding bands characteristic of certain bonds and functional groups in the spectra you examine. You are certainly not expected to identify all the absorption bands in each IR spectrum at this point in your work.

Table 1. A summary of the principle infrared bands and their assignments.

R is an aliphatic group.

Functional Group	Type		Frequencies cm-1	Peak Intensity

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C-H	sp3 hybridized	R3C-H	2850-3000	M(sh)
	sp2 hybridized	=CR-H	3000-3250	M(sh)
	sp hybridized	C-H	3300	M-S(sh)
	aldehyde C-H	H-(C=O)R	2750, 2850	M(sh)
N-H	primary amine, amide	RN-H2, RCON-H2	3300, 3340	S,S(br)
	secondary amine, amide	RNR-H, RCON-HR	3300-3500	S(br)
	tertiary amine, amide	RN(R3), RCONR2	none	
O-H	alcohols, phenols	free O-H	3620-3580	W(sh)
		hydrogen bonded	3600-3650	S(br)
	carboxylic acids	R(C=O)O-H	3500-2400	S(br)
CN	nitriles	RCN	2280-2200	S(sh)

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CC	acetylenes	R-CC-R	2260-2180	W(sh)
		R-CC-H	2160-2100	M(sh)
C=O	aldehydes	R(C=O)H	1740-1720	S(sh)
	ketones	R(C=O)R	1730-1710	S(sh)
	esters	R(CO2)R	1750-1735	S(sh)
	anhydrides	R(CO2CO)R	1820, 1750	S, S(sh)
	carboxylates	R(CO2)H	1600, 1400	S,S(sh)
C=C	olefins	R2C=CR2	1680-1640	W(sh)
		R2C=CH2	1600-1675	M(sh)
		R2C=C(OR)R	1600-1630	S(sh)
-NO2	nitro groups	RNO2	1550, 1370	S,S(sh)

Effect of resonance and conjugation on infrared frequencies

Let's continue our discussion of the importance of resonance but shift from the nitro group to the carboxylate anion. The carboxylate anion is represented as a resonance hybrid by the following figure:

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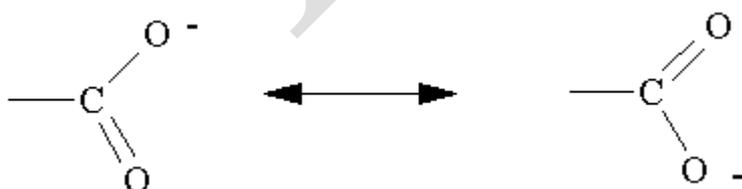
Unlike the nitro group which contained functional groups we will not be discussing, the carboxyl group is made up of a resonance hybrid between a carbon oxygen single bond and a carbon oxygen double bond. According to resonance, we would expect the C-O bond to be an average between a single and double bond or approximately equal to a bond and a half. We can use the carbonyl frequency of an ester of 1735 cm-1 to describe the force constant of the double bond. We have not discussed the stretching frequency of a C-O single bond for the simple reason that it is quite variable and because it falls in the fingerprint region. However, the band is known to vary from 1000 to 1400 cm-1. For purposes of this discussion, we will use an average value of 1200 cm-1. The carbonyl frequency for a bond and a half would be expected to fall halfway between 1735 and 1200 or at approximately 1465 cm-1. The carboxyl group has the same symmetry as the nitro and CH2 groups. Both a symmetric and asymmetric stretch should be observed. The infrared spectrum of sodium benzoate is given in Figure 42. An asymmetric and symmetric stretch at 1410 and 1560 cm-1 is observed that averages to 1480 cm-1, in good agreement with the average frequency predicted for a carbon oxygen bond with a bond order of 1.5. While this is a qualitative argument, it is important to realize that the carboxylate anion does not show the normal carbonyl and normal C-O single bond stretches (at approximately 1700 and 1200 cm-1) suggested by each of the static structures above.

In the cases of the nitro group and the carboxylate anion, both resonance forms contribute equally to describing the ground state of the molecule. We will now look at instances where two or more resonance forms contribute unequally to describing the ground state and how these resonance forms can effect the various stretching frequencies.

Carbonyl frequencies

Most carbonyl stretching frequencies are found at approximately 1700 cm-1. A notable exception is the amide carbonyl which is observed at approximately 1600 cm-1. This suggests that the following resonance form makes a significant contribution to describing the ground state of amides:

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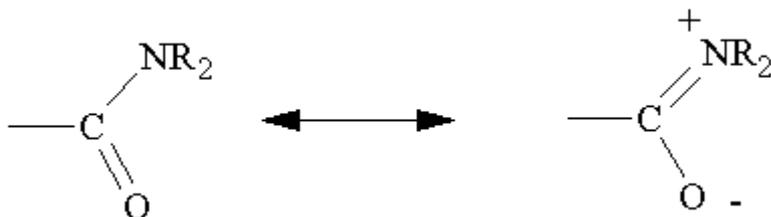
You may recall that resonance forms that lead to charge separation are not considered to be very important. However, the following information support the importance of resonance in amides. X-ray crystal structures of amides show that in the solid state the amide functional group is planar. This suggests sp2 hybridization at nitrogen rather than sp3. In addition, the barrier to rotation about the carbon nitrogen bond has been measured. Unlike the barrier of rotation of most aliphatic C-N bonds which are of the order of a few kcal/mol, the barrier to rotation about the carbon nitrogen bond in dimethyl formamide is approximately 18 kcal/mol. This suggests an important contribution of the dipolar structure to the ground state of the molecule and the observed frequency of 1600 cm-1, according to the arguments given above for the carboxylate anion, is consistent with more C-O single bond character than would be expected otherwise.

Conjugation of a carbonyl with a C=C bond is thought to lead to an increase in resonance interaction. Again, the resonance forms lead to charge separation which clearly de-emphasizes their importance.
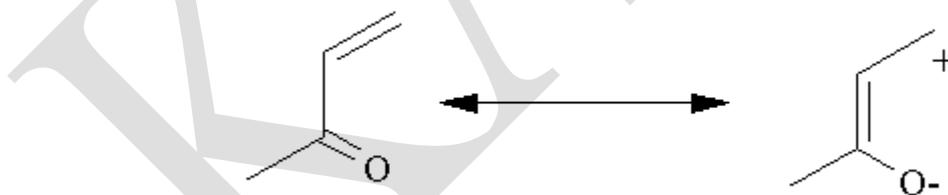
However, this conjugative interaction is useful in interpreting several features of the spectrum. First it predicts the small but consistent shift of approximately 10 cm-1 to lower frequency, observed when carbonyls are conjugated to double bonds or aromatic rings. This feature is summarized in Table 4 for a variety of carbonyl groups. Next, the dipolar resonance form suggests a more polar C=C than that predicted for an unconjugated C=C. In terms of the change in dipole moment, contributions from this structure suggest that the intensity of infrared absorption of a C=C double bond would increase relative to an unconjugated system. Comparison of Figures 9, 10 and 35 with

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Figures 43, and 44-47 shows this to be the case. Conjugation is associated with an increase in intensity of the C=C stretching frequency. Finally, examination of Figures 43-46 reveals an intricacy not previously observed with simple non-conjugated carbonyls. The carbonyls of Figures 43-46 which are all conjugated appear as multiplets while those unconjugated carbonyls such as those in Figures 14 and 35 appear as single frequencies. Note however that not all conjugated carbonyls appear as multiplets (Figures 15 and 47. Resolution of this additional complicating feature can be achieved if we consider that conjugation requires a fixed conformation. For most conjugated carbonyls, two or more conformations are possible. The *s-cis* form is shown above and the *s-trans* form is shown below.
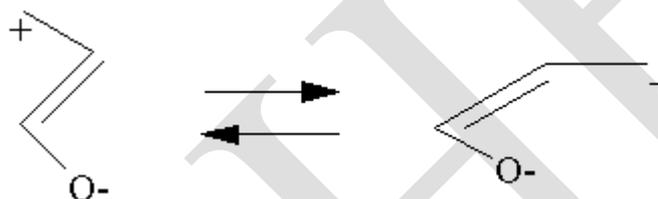
If the resonance interaction in these two forms differ, the effect of resonance on the carbonyl will differ leading to similar but different frequencies. The presence of multiple carbonyl frequencies is a good indication of a conjugated carbonyl. In some conjugated systems such as benzaldehyde

Table 4. The effect of conjugation on carbonyl frequencies.

Non-conjugated Compound	Frequency cm-1	Conjugated Compound	Frequency cm-1		Frequency cm-1
butanal	1725	2-butenal	1691	benzaldehyde	1702
2-butanone	1717	methyl vinyl ketone	1700, 1681	acetophenone	1685
propanoic acid	1715	propenoic acid	1702	benzoic acid	1688
ethyl propionate	1740	ethyl acrylate	1727	ethyl benzoate	1718

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butanoic anhydride	1819, 1750	2-butenoic anhydride	1782, 1722	benzoic anhydride	1786, 1726
cis-cyclohexane-1,2-dicarboxylic anhydride	1857, 1786	1-cyclohexene-1,2-dicarboxylic anhydride	1844, 1767	phthalic anhydride	1852, 1762

and benzyl 4-hydroxyphenylketone (Figures 15 and 47), only one conformation by symmetry is possible and conjugation does not lead to any additional carbonyl frequencies. It should also be noted that in many of the examples given above, *cis-trans* isomerization about the carbon-carbon double bond is also possible. Some of the observed bands may also be due to the presence of these additonal isomers. Since the intensity of the peak is determined by the change in dipole moment, the presence of a small amount of geometric isomer can still lead to a detectable peak.

Fingerprint Region of the Molecule:

Fingerprint Region of the Molecule Whole-molecule vibrations and bending vibrations are also quantitized. No two molecules will give exactly the same IR spectrum (except enantiomers). Simple stretching: 1600-3500 cm-1. Complex vibrations: 600-1400 cm-1, called the "fingerprint region."

 POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. Write a short note on fermi resonance.
2. Define Infra-red spectroscopy.
3. What are the wavenumber ranges for the fingerprint region and functional group regions of the spectrum?
4. How will you distinguish an aliphatic aldehyde from an aromatic ketone?
5. How will you distinguish between an aliphatic and an aromatic compound?
6. Name the various types of bending vibrations.

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7. What do you mean by coupled vibrations.

8. What are the major requirement for Infra-red spectroscopy?

9. What is Hooke's law?

PART C (6 Mark Questions)

1. Explain the following effects on vibrational frequency shift in IR spectrum.

   (i)   Coupled vibration

   (ii)   Field effect and Bond angle

2. What is the effect of ring size on carbonyl absorption incase of cycloketones?

3. Explain the applications of IR spectroscopy in organic compounds?

4. Explain the electronic factors which influence the absorption frequency.

5. Write a note on finger print region.

6. Define Infra-red spectroscopy. What are the major requirement for Infra-red spectroscopy?

7. Describe the effect of intramolecular and intermolecular hydrogen bonding on the position of absorption frequency of a compound. Give an example.

SUBJECT : Organic Chemistry -IV (Organic Spectroscopy)

Subject Code : **16HCU403**

Class : **II B.Sc Chemistry**

Staff Name : **Dr.M.Makeswari and Mr. R Kumar**

Batch : **2016-2018 Batch**

UNIT-II

QUESTIONS	OPTION-I	OPTION-II	OPTION-III	OPTION-IV	ANSWER
The most important region in IR is	a)15µ-200 µ	b) 2.5 µ-15 µ	c) 0.8 µ-2.5µ	d) 20µ–50µ	b) 2.5 µ-15 µ
Stretching Vibration require ---------- energy than bending vibration	a)less	b) more	c) same	d) equal	b) more
The vibrational frequency is given by	a)$\upsilon = 1/2\pi c\sqrt{k/\mu}$	b) $\upsilon = 1/4\pi c\sqrt{\mu}/R$	c) $\upsilon/c = 1/2\pi c\sqrt{\mu}/R$	d) $\upsilon = 1/2\pi c * \mu/R$	a)$\upsilon = 1/2\pi c\sqrt{k/\mu}$
The vibrational energy of a chemical bond is given by	a.)Evib=[v+1\2]hv	b)Evib=[v+1]hv	c)Evib=[v+1\2]3\2hv	d)Evib=[v_1\2]v	a.)Evib=[v+1\2]hv
The energy of fundamental band is	a)ΔEvib= hυ	b) ΔEvib=(hυ+3\2)	c) ΔEvib=3 hυ	d) ΔEvib= hυ\2	a)ΔEvib= hυ
The energy of first overtone is	a)ΔEvib= 2hυ	b) ΔEvib= hυ+3\2	c) ΔEvib= 3hυ	d) ΔEvib= hυ\2	a)ΔEvib= 2hυ
The number of vibrational degree of freedom for C_6H_6 is	a)40	b)60	c)30	d)10	c)30
The spectra caused in the IR region by the transition in vibrational levels in different modes of vibrations are called	a)rotational spectra	b)electronic spectra	c)vibrational spectra	d)absorption spectra	c)vibrational spectra
The IRspectra of a comgpound helps in	a)proving the identity of compounds	b)showing the presence of certain functional groups in the molecule	c)neither of the above	d)both (a) and (b)	d)both (a) and (b)
The wave numbers are expressed in	a)sec	b)cmsec	c)cm	d)cmsec^1	c)cm
The internal energy of a molecule is its	a)rotational energy	b) vibrational energy	c)translational energy	d)all of these	d)all of these
The frequency and wavelength are related to each other by the formula	a) ν = c ν	b) ν=cv	c) ν=h ν	d) ν=h c/λ	d) ν=h c/λ
The molecule which is IR inactive but Raman active is	a)Hcl	b)N_2	c)SO_2	d)protein	d)protein
Number of translationa; rotational and vibrational degree of freedom in CO2 are respectively	a)3,2,4	b)3,4,2	c)3,3,3	d)4,3,2	a)3,2,4
Zero point energy of diatomic S.H.O. of vibrational frequency ν is	a)h ν	b) 1\2h ν	c)1\4h ν	d)0	a)h ν
The relation between De and Do the diossociation energies, of an S.H.O.is	a)De=Do+h ν\2	b)Do=De+h ν\2	c)De=Do+h ν	d)De=Do+2h ν	a)De=Do+h ν\2
The selection rule for a vibrational transition in S.H.O.is	a)Δv = +1	b) Δv=+0	c) Δv=+or-2	d) Δn= 0	a)Δv = +1
Very important requirement for a molecule to show an I.R.spectrum is that	a)change in dipolemoment	b)change in force constant	c)change in electronic energy	d)change in wave number	a)change in dipolemoment
The rotational energy of a rigid rotar is	a)Erot =$h^2 / 4\pi^2 IJ(J+1)$	b.E_{rot}-=$h^2/8 \pi^2 IJ(J+1)$	c. E_{rot}=h/8 лIJ(J+1)	d.h/2I(J+1)	b.E_{rot}-=$h^2/8 \pi^2 IJ(J+1)$
The IR spectrum od rigid rotator consist of ------- equally spaced lines with a spacing of each side of band origin	a)B	b)2B	c)4B	d)3B	a)B
The ΔJ=0 transition gives rise to a new group of lines called	a)R branch	b)S branch	c)Qbranch	d)Pbranch	c)Qbranch
To get parallel band in IR forCO2,the oscillating dipole moment is ----- to the molecular axis is	a)parallel	b)perpendicular	c)angular	d)linear	a)parallel

Question	a	b	c	d	Answer
To get parallel band in IR the selection rule is	a)ΔV=+1, ΔJ=+1	b) ΔV= 1, ΔJ =+1	c) ΔV=+1, ΔJ =_1	d) ΔV=+2, ΔJ=+3	a)ΔV=+1, ΔJ=+1
The selection rule to get the perpendicular band in spectrum is	a) ΔV=+1, ΔJ = - 1	b) ΔV=+1, ΔJ = - 1,O	c) ΔV=O, ΔJ =+ - 1	d) ΔV=+2 ΔJ =_1^2	b) ΔV=+1, ΔJ = - 1,O
Due to the +I effect of methyl group absorbtion takes place at ------- wave number in IR spectrum	a)higher	b)lower	c)same	d)none of above	b)lower
Introduction of electronegative atoms (or)groups-------the wave number absorption	a)increases	b)decreases	c)same	d)none of the above	a)increases
In IR C—H s tretching vibration occur at the region	a)1470—1430cm^{-1}	b)2960-2850cm^{-1-}	c)1300-1800cm^{-1}	d)1000-1300cm^{-1}	b)2960-2850cm^{-1-}
In IR,C=C stretching has the frequency in the region	a)970—980cm^{-1}	b)650-610cm^{-1}	c)1680-1620cm^{-1}	d)995-985cm^{-1}	c)1680-1620cm^{-1}
Absorbance is defined as	a)A=log10(1\T)	b)A=e$^-$1\T	c)A=1\T	d)A=2\T	a)A=log10(1\T)
For a non linear molecule there are ------degrees of vibrational degree of freedom	a)3n-2	b)3n-6	c)3n-3	d)3n-4	b)3n-6
Position of C—O stretching band for primary alcohol occur at ----in IR	a)1050cm^{-1}	b)1500cm^{-1}	c)1800cm^{-1}	d)200cm^{-1}	a)1050cm^{-1}
The O-H stretching of Phenol exibit a strong broad band in the range in IR	a)3600-3200cm^{-1}	b)1600-1700cm^{-1}	c)2300-2500cm^{-1}	d)900-100cm^{-1}	a)3600-3200cm^{-1}
The potential energy of an anhormonic oscillator is	a)Vr=De[1-expa(r-re)]^2	b)Vr=De[1-a(ro-r)]^2	c)Vr=De[1\ro-r]^2	d)Vr=a[Do-(r-ro)]^2	a)Vr=De[1-expa(r-re)]^2
μ/For a molecule to be IR active	a)dμ/dr=o	b) dr/dμ =o	c) dμ/dr not equal to 0	d) d¥/dc not equal to 0	c) dμ/dr not equal to 0
>C=O stretching of aldehudes occur in the region in the IR region.	a)2770-2700 cm^{-1}	b)1740-1720cm^{-1}	c)700-970cm^{-1}	d)3300-3400^{-1}cm	b)1740-1720cm^{-1}
The type of H-bonding which give rise to broad lines in IR Techinque is -----	a)Intermolecular	b)Intramolecular	c)C-H stretching	d)C-H bending	b)Intramolecular
The type of H-bonding which give rise to sharp lines in IR Techinque is ------	a)Sym.stretching	b)Anti.sym.stretching	c)Intramoleclulear	d)Intercular	a)Sym.stretching
In which region we get absorbtiion bands and shoulders	a)Far infradredf	b)near infrared	c)mid-infrared	d)finger print region	d)finger print region
N-H bending vibration for primary amines occurs in the region	a)700-900cm^{-1}	b)800-700cm^{-1}	c)1600-1500cm^{-1}	d)800-700cm^{-1}	c)1600-1500cm^{-1}
In a double beam instrument ,the beamspilts into-----parts	a)one	b)three	c)two	d)none of the above	c)two
The radiation used to study the vibrational spectra of a molecule is	a. microwave	b.radiowave	c.UV	d.IR	d.IR
The number of vibrational degrees of freedom of watermolecule is	a. 4	b.9	c.2	d. 3	d. 3
Which of the following molecules has the smallest spacing in thefine structureof Irspectrum?	a. HCl	b.HBr	c.CO	d.HI	d.HI
Carbonyl group shows a characteristic intenseband in the IR. This high intensity is due to	a. high reactivity of the carbonyl group	b. the presence of lone pair of electrons which areeasily excited	c. high polarity of the group	d. largeforce constant of thegroup	c. high polarity of the group
The vibrational frequency of HD is less than that of H$_2$becausce	a. H$_2$ has a higher force constant	b. H$_2$has a lower force constant	c. HD has a higher mass	d. HD has a higher mass and lower force constant	c. HD has a higher mass
Which one of the following spectroscopy is known as magnetic radiation absorption spectroscopy?	a. MS	b.NMR	c. IR	d. UV	c. IR

Question	a	b	c	d	Answer
Which one of thefollowing region in IR is known as functional group region	a. 1300-4000 cm^{-1}	b. 900-1300 cm^{-1}	c. 650-900 cm^{-1}	d)1000-1300cm^{-1}	a. 1300-4000 cm^{-1}
Whatwill be the C=O stretching band in IR of CH_2=CHCOCH$_3$	a. 1700 cm^{-1}	b. 1710 cm^{-1}	c. 1680 cm^{-1}	d. 1780 cm^{-1}	c. 1680 cm^{-1}
Which one of thefollowing statement is false for IR spectroscopy	a. Conjugation decreases the C=O stretching frequency	b. higher the frequency if more strained the alicyclic ring containig C=O group	c. Electron releasing substituents decreases the frequency of C=O band	d. Electran withdrawing subtituents decreases thefrequencyof C=O band	d. Electran withdrawing subtituents decreases thefrequencyof C=O band
An alcohol having mol-formula C_4H10O gives C-O stretching band at1120 cm^{-1} will be	a. 1-butanol	b.2.butanol	c. 2-methyl-2-propanol	d. isobutanol	b.2.butanol
Pedict thenumber of translational ,rotational and vibrational degree offreedom in neon--	a. 3,0,0	b. 3,1,0	c.3,0,1	d.3,1,1	a. 3,0,0
Which one of the following is microwave inactive?	a. HCl	b.HBr	c.Cl$_2$	d. NO	c.Cl$_2$
The rotational constant (B) of a diatomicmolecule is	a. h/4π^2I	b.h^2/4π^2I	c. h^2/8π^2I	d. h/8π^2I	d. h/8π^2I
The degree of degeneracy for a rid rotor in energy level with quantum number J is--	a.J	b.2J	c.2J-1	d.2J+1	d.2J+1
From the pure rotation spectrum of HF information can beobtained about	a. the force constant	b. The proton spin	c. The hydrogen bonding	d. the internuclear distance	d. the internuclear distance
The characteristic bond stretching frequency for C-Ois about---	a.10^4 cm^{-1}	b. 10^5 cm^{-1}	c. 10^3 cm^{-1}	d.10^{2}cm^{-1}	c. 10^3 cm^{-1}
In practical organic chemistry tetramethyl silane is used mainly for--	a. Making volatile derivatives of alcohols	b. A spectroscopic standard	c. A solvent for IR spectra	d. An antinock in gasolines	b. A spectroscopic standard
The spectra resulting from changes in vibrational energy levels for the same electronic state fall in which region of thespectrum	a. microwave	b.Visible	c. UV	d.IR	d.IR
Which of the following isboth IR and microwave active?	a.Br$_2$	b.HBr	c.CS$_2$	d.CO$_2$	b.HBr
The symmetric C=C stretching ibration of €-2- butene is mesuredby which one of thefollowing spectroscopic methods	a. microwave	b.Visible	c. Raman	d.IR	c. Raman

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CLASS: II B SC CHEMISTRY   COURSE NAME: ORGANIC CHEMISTRY- IV
(Organic Spectroscopy)
COURSE CODE: 16CHU403   UNIT: III (NMR Spectroscopy)   BATCH-2016-2019

UNIT III

SYLLABUS

NMR Spectroscopy: Basic principles of Proton Magnetic Resonance, chemical shift and factors influencing it; Spin – Spin coupling and coupling constant; Anisotropic effects in alkene, alkyne, aldehydes and aromatics, Interpetation of NMR spectra of simple compounds. Applications of IR, UV and NMR for identification of simple organic molecules.

NMR spectroscopy

Nuclear magnetic resonance spectroscopy, most commonly known as NMR spectroscopy, is the name given to a technique that exploits the magnetic properties of certain nuclei. For details regarding this phenomenon and its origins, refer to the nuclear magnetic resonance article. The most important applications for the organic chemist are proton NMR and carbon-13 NMR spectroscopy. In principle, NMR is applicable to any nucleus possessing spin.

Many types of information can be obtained from an NMR spectrum. Much like using infrared spectroscopy (IR) to identify functional groups, analysis of a NMR spectrum provides information on the number and type of chemical entities in a molecule. However, NMR provides much more information than IR.

The impact of NMR spectroscopy on the natural sciences has been substantial. It can, among other things, be used to study mixtures of analytes, to understand dynamic effects such as change in temperature and reaction mechanisms, and is an invaluable tool in understanding protein and nucleic acid structure and function. It can be applied to a wide variety of samples, both in the solution and the solid state.

Theory of nuclear magnetic resonance

Nuclear spin and the splitting of energy levels in a magnetic field

Subatomic particles (electrons, protons and neutrons) can be imagined as spinning on their axes. In many atoms (such as ^{12}C) these spins are paired against each other, such that the nucleus

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of the atom has no overall spin. However, in some atoms (such as ^{1}H and ^{13}C) the nucleus does possess an overall spin. The rules for determining the net spin of a nucleus are as follows;

1. If the number of neutrons **and** the number of protons are both even, then the nucleus has **NO** spin.

2. If the number of neutrons **plus** the number of protons is odd, then the nucleus has a half-integer spin (i.e. 1/2, 3/2, 5/2)

3. If the number of neutrons **and** the number of protons are both odd, then the nucleus has an integer spin (i.e. 1, 2, 3)

The overall spin, *I*, is important. Quantum mechanics tells us that a nucleus of spin *I* will have $2I + 1$ possible orientations. A nucleus with spin 1/2 will have 2 possible orientations. In the absence of an external magnetic field, these orientations are of equal energy. If a magnetic field is applied, then the energy levels split. Each level is given a *magnetic quantum number, m.*

Energy levels for a nucleus with spin quantum number 1/2
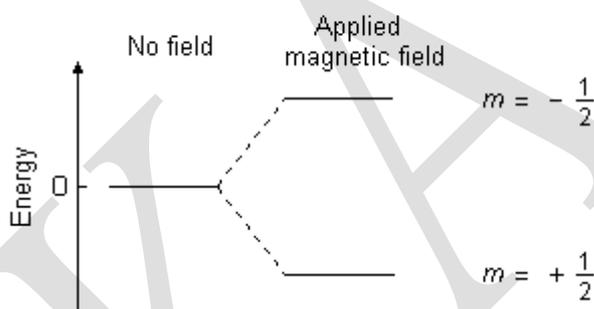
When the nucleus is in a magnetic field, the initial populations of the energy levels are determined by thermodynamics, as described by the Boltzmann distribution. This is very important, and it means that **the lower energy level will contain slightly more nuclei than the higher leve**l. It is possible to excite these nuclei into the higher level with electromagnetic radiation. The frequency of radiation needed is determined by the difference in energy between the energy levels

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Nuclear spin and magnets

All nucleons, that is neutrons and protons, composing any atomic nucleus, have the intrinsic quantum property of spin. The overall spin of the nucleus is determined by the spin quantum number S. If the number of both the protons and neutrons in a given nuclide are even then $S =$ 0, i.e. there is no overall spin; just as electrons pair up in atomic orbitals, so do even numbers of protons or even numbers of neutrons (which are also spin-$\frac{1}{2}$ particles and hence fermions) pair up giving zero overall spin.

However, a proton and neutron will have lower energy when their spins are parallel, **not anti-parallel**, as this parallel spin alignment does not infringe upon the Pauli principle, but instead has to do with the quark structure of these two nucleons. Therefore, the spin ground state for the deuteron (the deuterium nucleus, or the ^{2}H isotope of hydrogen)—that has only a proton and a neutron—corresponds to a spin value of **1**, *not of zero*; the single, isolated deuteron is therefore exhibiting an NMR absorption spectrum characteristic of a quadrupolar nucleus of spin **1**, which in the 'rigid' state at very low temperatures is a characteristic ('Pake') *doublet*, (not a singlet as for a single, isolated ^{1}H, or any other isolated fermion or dipolar nucleus of spin 1/2). On the other hand, because of the Pauli principle, the (radioactive) tritium isotope has to have a pair of anti-parallel spin neutrons (of total spin zero for the neutron spin couple), plus a proton of spin 1/2; therefore, the character of the tritium nucleus ('triton') is again magnetic dipolar, *not quadrupolar*—like its non-radioactive deuteron neighbor—and the tritium nucleus total spin value is again 1/2, just like for the simpler, abundant hydrogen isotope, ^{1}H nucleus (the *proton*). The NMR absorption (radio) frequency for tritium is however slightly higher than that of ^{1}H because the tritium nucleus has a slightly higher gyromagnetic ratio than ^{1}H. In many other cases of *non-radioactive* nuclei, the overall spin is also non-zero. For example, the Al nucleus has an overall spin value $S = \frac{5}{2}$.

A non-zero spin is thus always associated with a non-zero magnetic moment (μ) via the relation $\mu = \gamma S$, where γ is the gyromagnetic ratio. It is this magnetic moment that allows the observation of NMR absorption spectra caused by transitions between nuclear spin levels. Most nuclides (with some rare exceptions) that have both even numbers of protons and even numbers of neutrons, also have zero nuclear magnetic moments-and also have zero magnetic dipole and

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quadrupole moments; therefore, such nuclides do not exhibit any NMR absorption spectra. Thus, 18O is an example of a nuclide that has no NMR absorption, whereas 13C, 31P, 35Cl and 37Cl are nuclides that do exhibit NMR absorption spectra; the last two nuclei are quadrupolar nuclei whereas the preceding two nuclei (13 C and 31P) are dipolar ones.

Electron spin resonance (ESR) is a related technique which detects transitions between electron spin levels instead of nuclear ones. The basic principles are similar; however, the instrumentation, data analysis and detailed theory are significantly different. Moreover, there is a much smaller number of molecules and materials with unpaired electron spins that exhibit ESR (or electron paramagnetic resonance (EPR)) absorption than those that have NMR absorption spectra. Significantly also, is the much greater sensitivity of ESR and EPR in comparison with NMR. Furthermore, ferromagnetic materials and thin films may exhibit 'very unusual', highly resolved ferromagnetic resonance (FMR) spectra, or ferromagnetic spin wave resonance (FSWR) excitations in non-crystalline solids such as ferromagnetic metallic glasses, well beyond the common single-transitions of most routine NMR, FMR and EPR studies.

Values of spin angular momentum

The angular momentum associated with nuclear spin is quantized. This means both that the magnitude of angular momentum is quantized (i.e. S can only take on a restricted range of values), and also that the orientation of the associated angular momentum is quantized. The associated quantum number is known as the magnetic quantum number, m, and can take values from $+S$ to $-S$, in integer steps. Hence for any given nucleus, there is a total of $2S + 1$ angular momentum states.

The z-component of the angular momentum vector (**S**) is therefore $S_z = m\hbar$, where $\hbar$ is the reduced Planck constant. The z-component of the magnetic moment is simply:

$$\mu_z = \gamma S_z = \gamma m\hbar$$

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Spin behavior in a magnetic field
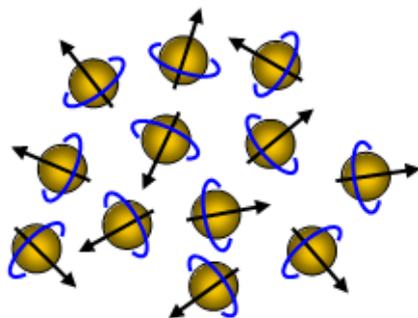
Figure 1
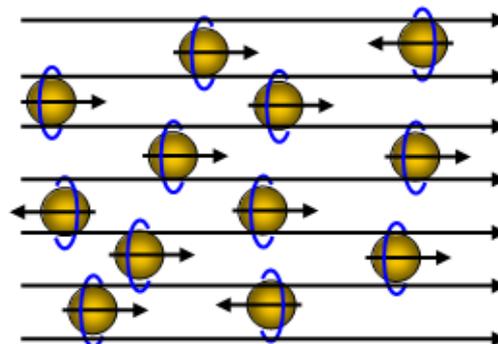
Figure 2

If these spinning nuclei are subjected to an external magnetic field they will align themselves with the filed, just like iron filings do on a larger scale. Most will be parallel to the field (low energy state) but a few will be anti-parallel (high energy state).
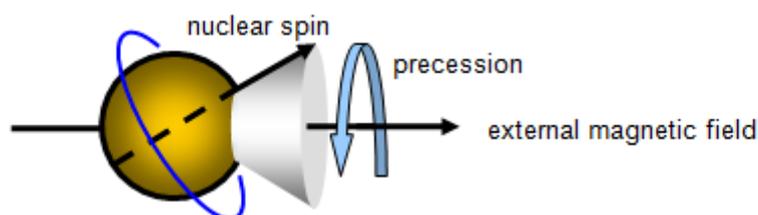
Figure 3

Splitting of nuclei spin states in an external magnetic field

Consider nuclei which have a spin of one-half, like 1H, 13C or 19F. The nucleus has two possible spin states: $m = \frac{1}{2}$ or $m = -\frac{1}{2}$ (also referred to as spin-up and spin-down, or sometimes α and β spin states, respectively). These states are degenerate, that is they have the same energy. Hence the number of atoms in these two states will be approximately equal at thermal equilibrium.

As a result the different nuclear spin states have different energies in a non-zero magnetic field. In hand-waving terms, we can talk about the two spin states of a spin $\frac{1}{2}$ as being *aligned* either

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with or against the magnetic field. If γ is positive (true for most isotopes) then $m = \frac{1}{2}$ is the lower energy state.

The magnetic moment of the nucleus forces the nucleus to behave as a tiny bar magnet. In the absence of an external magnetic field, each magnet is randomly oriented. During the NMR experiment the sample is placed in an external magnetic field, B_0B_0, which forces the bar magnets to align with (low energy) or against (high energy) the B_0B_0. During the NMR experiment, a spin flip of the magnets occurs, requiring an exact quanta of energy. To understand this rather abstract concept it is useful to consider the NMR experiment using the nuclear energy levels.

The energy difference between the two states is:
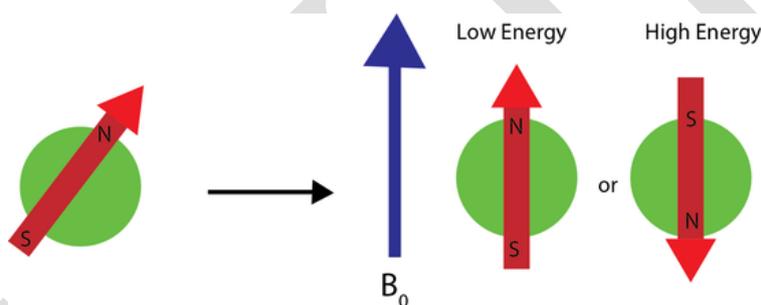
and this difference results in a small population bi as toward the lower energy state.

Magnetic resonance by nuclei

Resonant absorption by nuclear spins will occur only when electromagnetic radiation of the correct frequency (e.g., equaling the Larmor precession rate) is being applied to match the energy difference between the nuclear spin levels in a constant magnetic field of the appropriate strength. The energy of an absorbed photon is then $E = hv_0$, where v_0 is the resonance radiofrequency that has to match (that is, it has to be equal to) the Larmor precession frequency v_L of the nuclear magnetization in the constant magnetic field $\mathbf{B}_0$. Hence, a magnetic resonance absorption will only occur when $\Delta E = hv_0$, which is when $v_0 = \gamma B_0/(2\pi)$. Such magnetic resonance frequencies typically correspond to the radio frequency (or RF) range of the electromagnetic spectrum for magnetic fields up to ~20 T.

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It is this magnetic resonant absorption which is detected in NMR
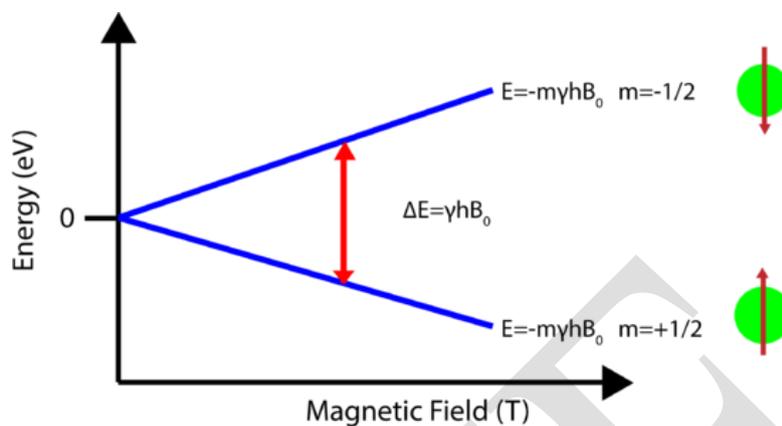
Nuclear shielding

It might appear from the above that all nuclei of the same nuclide (and hence the same *g*) would resonate at the same frequency. This is not the case. The most important perturbation of the NMR frequency for applications of NMR is the 'shielding' effect of the surrounding electrons. In general, this electronic shielding reduces the magnetic field *at the nucleus* (which is what determines the NMR frequency).

As a result the energy gap is reduced, and the frequency required to achieve resonance is also reduced. This shift in the NMR frequency due to the electrons' molecular orbital coupling to the external magnetic field is called chemical shift, and it explains why NMR is able to probe the chemical structure of molecules which depends on the electron density distribution in the corresponding molecular orbitals. If a nucleus in a specific chemical group is shielded to a higher degree by a higher electron density of its surrounding molecular orbital, then its NMR frequency will be shifted "upfield" (that is, a lower chemical shift), whereas if it is less shielded by such surrounding electron density, then its NMR frequency will be shifted "downfield" (that is, a higher chemical shift).

Unless the local symmetry of such molecular orbitals is very high (leading to "isotropic" shift), the shielding effect will depend on the orientation of the molecule with respect to the external field (B_0). In solid-state NMR spectroscopy, magic angle spinning is required to average out this orientation dependence in order to obtain values close to the average chemical shifts. This

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is unnecessary in conventional NMR investigations of molecules, since rapid molecular tumbling averages out the chemical shift anisotropy (CSA). In this case, the term "average" chemical shift (ACS) is used.

Relaxation

Relaxation refers to the phenomenon of nuclei returning to their thermodynamically stable states after being excited to higher energy levels. The energy absorbed when a transition from a lower energy level to a high energy level occurs is released when the opposite happens. This can be a fairly complex process based on different timescales of the relaxation. The two most common types of relaxation are spin lattice relaxation (T_1) and spin spin relaxation (T_2). A more complex treatment of relaxation is given elsewhere.
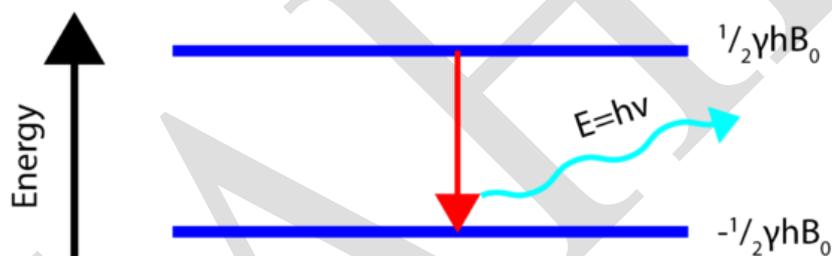
There are two major relaxation processes;

- Spin - lattice (longitudinal) relaxation
- Spin - spin (transverse) relaxation

Spin - lattice relaxation

Nuclei in an NMR experiment are in a sample. The sample in which the nuclei are held is called the *lattice*. Nuclei in the lattice are in vibrational and rotational motion, which creates a complex magnetic field. The magnetic field caused by motion of nuclei within the lattice is called the *lattice field*. This lattice field has many components. Some of these components will be equal in frequency and phase to the Larmor frequency of the nuclei of interest. These components of the lattice field can interact with nuclei in the higher energy state, and cause them to lose energy (returning to the lower state). The energy

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that a nucleus loses increases the amount of vibration and rotation within the lattice (resulting in a tiny rise in the temperature of the sample).

The relaxation time, T_1 (the average lifetime of nuclei in the higher energy state) is dependant on the magnetogyric ratio of the nucleus and the mobility of the lattice. As mobility increases, the vibrational and rotational frequencies increase, making it more likely for a component of the lattice field to be able to interact with excited nuclei. However, at extremely high mobilities, the probability of a component of the lattice field being able to interact with excited nuclei decreases.

Spin - spin relaxation

Spin - spin relaxation describes the interaction between neighbouring nuclei with identical precessional frequencies but differing magnetic quantum states. In this situation, the nuclei can exchange quantum states; a nucleus in the lower energy level will be excited, while the excited nucleus relaxes to the lower energy state. There is no **net** change in the populations of the energy states, but the average lifetime of a nucleus in the excited state will decrease. This can result in line-broadening.

Chemical shift

Depending on the local chemical environment, different protons in a molecule resonate at slightly different frequencies. Since both this frequency shift and the fundamental resonant frequency are directly proportional to the strength of the magnetic field, the shift is converted into a *field-independent* dimensionless value known as the chemical shift. The chemical shift is reported as a relative measure from some reference resonance frequency. (For the nuclei ^{1}H, ^{13}C, and ^{29}Si, TMS (tetramethylsilane) is commonly used as a reference.) This difference between the frequency of the signal and the frequency of the reference is divided by frequency of the reference signal to give the chemical shift. The frequency shifts are extremely small in comparison to the fundamental NMR frequency. A typical frequency shift might be 100 Hz, compared to a fundamental NMR frequency of 100 MHz, so the chemical shift is generally expressed in parts per million (ppm). To detect such small frequency differences the applied magnetic field must be constant throughout the sample volume. High resolution NMR spectrometers use shims to adjust the homogeneity of the magnetic field to parts per billion (ppb) in a volume of a few cubic centimeters.

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By understanding different chemical environments, the chemical shift can be used to obtain some structural information about the molecule in a sample. The conversion of the raw data to this information is called *assigning* the spectrum. For example, for the ^{1}H-NMR spectrum for ethanol (CH_3CH_2OH), one would expect three specific signals at three specific chemical shifts: one for the C*H_3* group, one for the C*H_2* group and one for the O*H* group. A typical CH_3 group has a shift around 1 ppm, a CH_2 attached to an OH has a shift of around 4 ppm and an OH has a shift around 2–3 ppm depending on the solvent used.

Because of molecular motion at room temperature, the three methyl protons *average* out during the course of the NMR experiment (which typically requires a few ms). These protons become degenerate and form a peak at the same chemical shift.

The shape and size of peaks are indicators of chemical structure too. In the example above—the proton spectrum of ethanol—the CH_3 peak would be three times as large as the OH. Similarly the CH_2 peak would be twice the size of the OH peak but only 2/3 the size of the CH_3 peak.

Modern analysis software allows analysis of the size of peaks to understand how many protons give rise to the peak. This is known as integration—a mathematical process which calculates the area under a curve. The analyst must integrate the peak and not measure its height because the peaks also have *width*—and thus its size is dependent on its area not its height. However, it should be mentioned that the number of protons, or any other observed nucleus, is only proportional to the intensity, or the integral, of the NMR signal, in the very simplest one-dimensional NMR experiments. In more elaborate experiments, for instance, experiments typically used to obtain carbon-13 NMR spectra, the integral of the signals depends on the relaxation rate of the nucleus, and its scalar and dipolar coupling constants. Very often these factors are poorly known - therefore, the integral of the NMR signal is very difficult to interpret in more complicated NMR experiments.

The magnetic field at the nucleus is **not** equal to the applied magnetic field; electrons around the nucleus shield it from the applied field. The difference between the applied magnetic field and the field at the nucleus is termed the *nuclear shielding*.

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Consider the s-electrons in a molecule. They have spherical symmetry and circulate in the applied field, producing a magnetic field which opposes the applied field. This means that the applied field strength must be increased for the nucleus to absorb at its transition frequency. This *upfield shift* is also termed *diamagnetic shift*.

The NMR spectra is displayed as a plot of the applied radio frequency versus the absorption. The applied frequency increases from left to right, thus the left side of the plot is the low field, downfield or deshielded side and the right side of the plot is the high field, upfield or shielded side (see the figure below). The concept of shielding will be explained shortly.
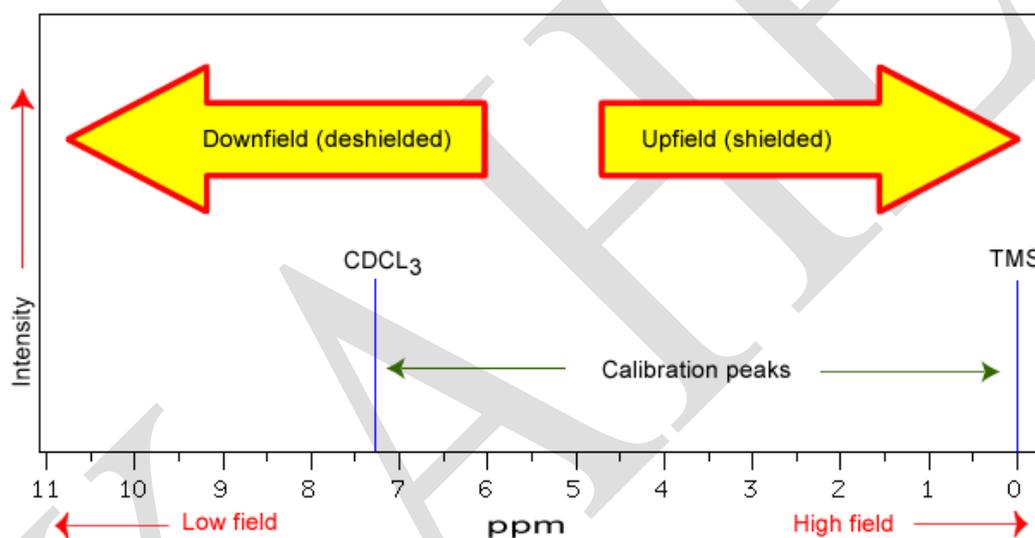
Electrons in p-orbitals have **no** spherical symmetry. They produce comparatively large magnetic fields at the nucleus, which give a *low field shift*. This "deshielding" is termed *paramagnetic shift*.

In proton (^{1}H) NMR, p-orbitals play no part (there aren't any!), which is why only a small range of chemical shift (10 ppm) is observed. We can easily see the effect of s-electrons on the chemical shift by looking at substituted methanes, CH_3X. As X becomes increasingly electronegative, so the electron density around the protons decreases, and they resonate at lower field strengths (increasing $\square_H$ values).

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Chemical shift is defined as *nuclear shielding / applied magnetic field*. Chemical shift is a function of the nucleus and its environment. It is measured relative to a reference compound. For ^1H NMR, the reference is usually tetramethylsilane, $Si(CH_3)_4$.

J-coupling

Some of the most useful information for structure determination in a one-dimensional NMR spectrum comes from **J-coupling** or **scalar coupling** (a special case of spin-spin coupling) between NMR active nuclei. This coupling arises from the interaction of different spin states through the chemical bonds of a molecule and results in the splitting of NMR signals. These splitting patterns can be complex or simple and, likewise, can be straightforwardly interpretable or deceptive. This coupling provides detailed insight into the connectivity of atoms in a molecule.

Multiplicity	Intensity Ratio
Singlet (s)	1
Doublet (d)	1:1
Triplet (t)	1:2:1
Quartet (q)	1:3:3:1
Quintet	1:4:6:4:1
Sextet	1:5:10:10:5:1
Septet	1:6:15:20:15:6:1

Coupling to *n* equivalent (spin ½) nuclei splits the signal into a *n*+1 **multiplet** with intensity ratios following Pascal's triangle as described on the right. Coupling to additional spins will lead to further splittings of each component of the multiplet e.g. coupling to two different spin ½ nuclei with significantly different coupling constants will lead to a *doublet of doublets* (abbreviation: dd). Note that coupling between nuclei that are chemically equivalent (that is, have the same chemical shift) has no effect of the NMR spectra and couplings between nuclei that are distant (usually more than 3 bonds apart for protons in flexible molecules) are usually too small to cause observable splittings. *Long-range* couplings over more than three bonds can often be observed in cyclic and aromatic compounds, leading to more complex splitting patterns.

For example, in the proton spectrum for ethanol described above, the CH_3 group is split into a *triplet* with an intensity ratio of 1:2:1 by the two neighboring CH_2 protons. Similarly, the CH_2 is split into a *quartet* with an intensity ratio of 1:3:3:1 by the three neighboring CH_3 protons. In principle, the two CH_2 protons would also be split again into a *doublet* to form a *doublet of quartets* by the hydroxyl proton, but intermolecular exchange of the acidic hydroxyl proton often results in a loss of coupling information.

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Coupling to any spin ½ nuclei such as phosphorus-31 or fluorine-19 works in this fashion (although the magnitudes of the coupling constants may be very different). But the splitting patterns differ from those described above for nuclei with spin greater than ½ because the spin quantum number has more than two possible values. For instance, coupling to deuterium (a spin 1 nucleus) splits the signal into a *1:1:1 triplet* because the spin 1 has three spin states. Similarly, a spin 3/2 nucleus splits a signal into a *1:1:1:1 quartet* and so on.

Coupling combined with the chemical shift (and the integration for protons) tells us not only about the chemical environment of the nuclei, but also the number of *neighboring* NMR active nuclei within the molecule. In more complex spectra with multiple peaks at similar chemical shifts or in spectra of nuclei other than hydrogen, coupling is often the only way to distinguish different nuclei.

Spin - spin coupling

The ^{1}H-NMR spectra that we have seen so far (of methyl acetate and *para*-xylene) are somewhat unusual in the sense that in both of these molecules, each set of protons generates a single NMR signal. In fact, the ^{1}H-NMR spectra of most organic molecules contain proton signals that are 'split' into two or more sub-peaks. Rather than being a complication, however, this splitting behavior actually provides us with more information about our sample molecule.

Consider the spectrum for 1,1,2-trichloroethane. In this and in many spectra to follow, we show enlargements of individual signals so that the signal splitting patterns are recognizable

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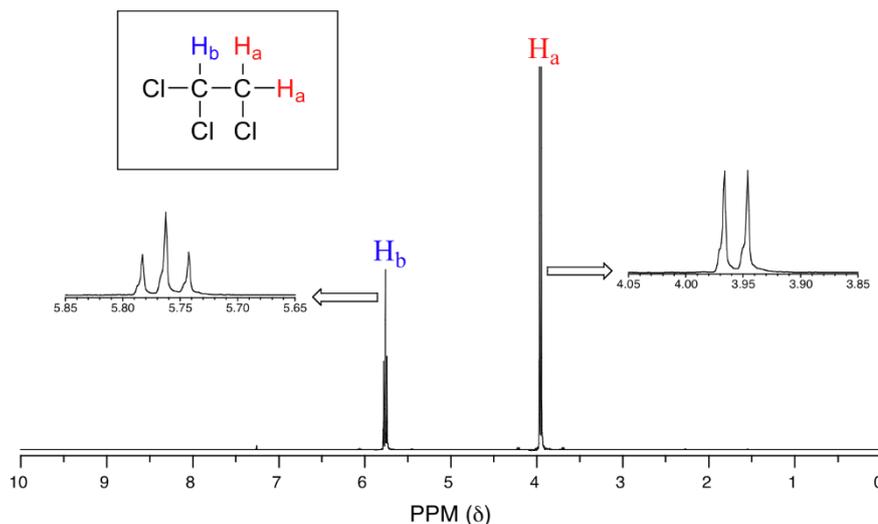
The signal at 3.96 ppm, corresponding to the two H_a protons, is split into two subpeaks of equal height (and area) – this is referred to as a **doublet**. The H_b signal at 5.76 ppm, on the other hand, is split into three sub-peaks, with the middle peak higher than the two outside peaks - if we were to integrate each subpeak, we would see that the area under the middle peak is twice that of each of the outside peaks. This is called a **triplet**.

The source of signal splitting is a phenomenon called **spin-spin coupling**, a term that describes the magnetic interactions between neighboring, non-equivalent NMR-active nuclei. In our 1,1,2 trichloromethane example, the H_a and H_b protons are spin-coupled to each other. Here's how it works, looking first at the H_a signal: in addition to being shielded by nearby valence electrons, each of the H_a protons is also influenced by the small magnetic field generated by H_b next door (remember, each spinning proton is like a tiny magnet). The magnetic moment of H_b will be aligned *with* B_0 in (slightly more than) half of the molecules in the sample, while in the remaining half of the molecules it will be opposed to B_0. The B_{eff} 'felt' by H_a is a slightly weaker if H_b is aligned against B_0, or slightly stronger if H_b is aligned with B_0. In other words, in half of the molecules H_a is *shielded* by H_b (thus the NMR signal is shifted slightly upfield) and in the other half H_a is *deshielded* by H_b (and the NMR signal shifted slightly downfield). What would otherwise be a single H_a peak has been split into two sub-peaks (a doublet), one upfield and one downfield of the original signal. These ideas an be illustrated by a **splitting diagram**, as shown below.

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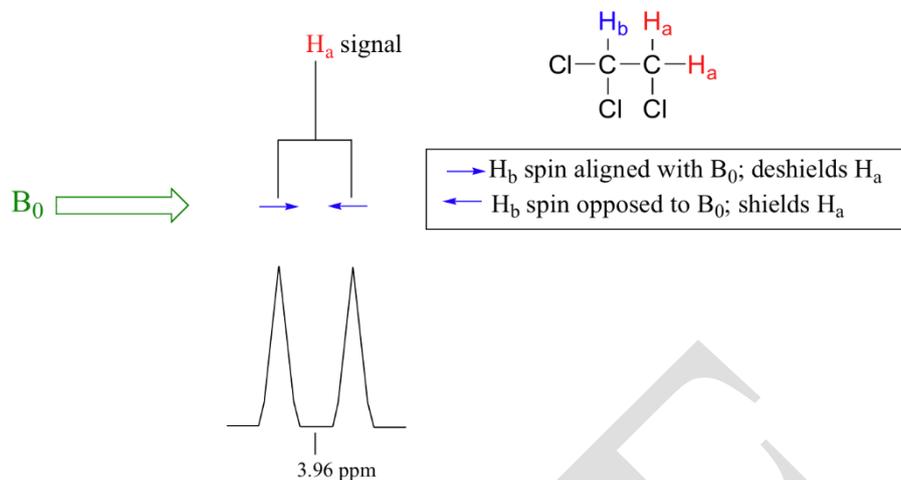
- The multiplicity of a multiplet is given by the number of equivalent **protons** in **neighbouring** atoms plus one, i.e. *the n + 1 rule*
- Equivalent nuclei do not interact with each other. The three methyl protons in ethanol cause splitting of the neighbouring methylene protons; they do not cause splitting among themselves
- The coupling constant is not dependant on the applied field. Multiplets can be easily distinguished from closely spaced chemical shift peaks.

Magnetic Anisotropy: π Electron Effects

The π electrons in a compound, when placed in a magnetic field, will move and generate their own magnetic field. The new magnetic field will have an effect on the shielding of atoms within the field. The best example of this is benzene (see the figure below).

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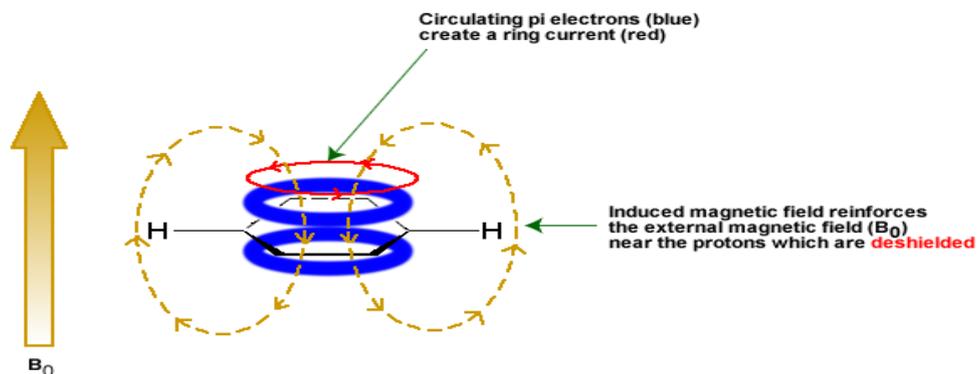
Hydrogen Bonding

Protons that are involved in hydrogen bonding (*i.e.*-OH or -NH) are usually observed over a wide range of chemical shifts. This is due to the deshielding that occurs in the hydrogen bond. Since hydrogen bonds are dynamic, constantly forming, breaking and forming again, there will be a wide range of hydrogen bonds strengths and consequently a wide range of deshielding. This as well as solvation effects, acidity, concentration and temperature make it very difficult to predict the chemical shifts for these atoms.

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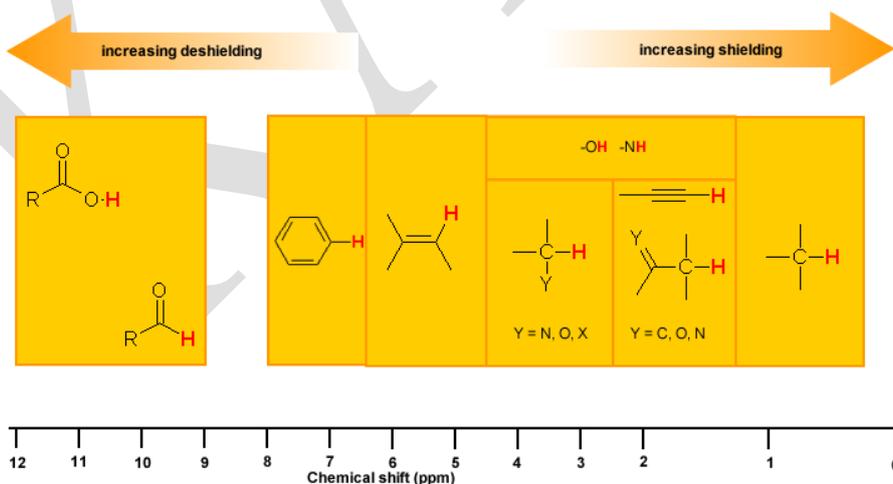
Experimentally -OH and -NH can be identified by carrying out a simple D_2O exchange experiment since these protons are exchangeable.

- run the normal H-NMR experiment on your sample

- add a few drops of D_2O

- re-run the H-NMR experiment

- compare the two spectra and look for peaks that have "disappeared"
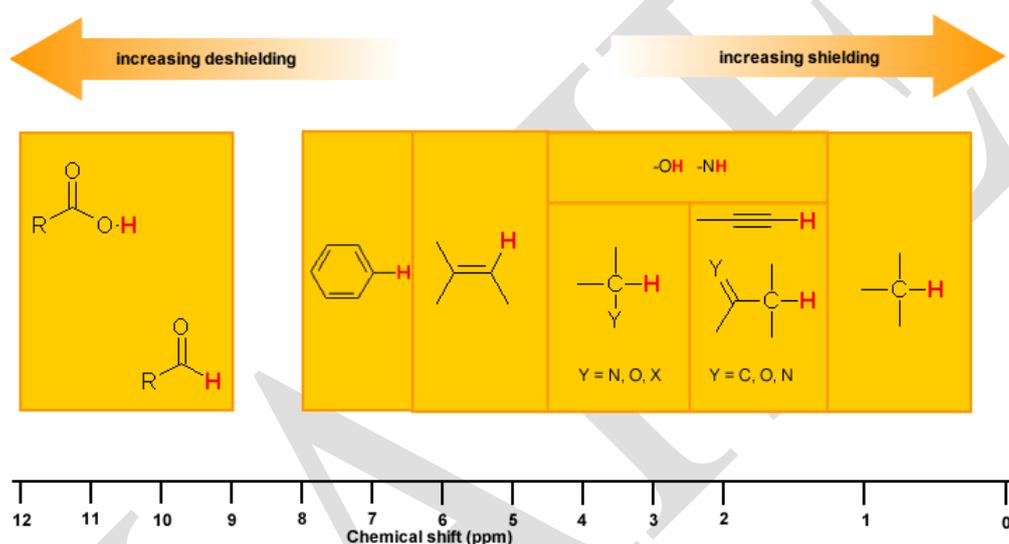
Carbon-13 NMR

Many of the molecules studied by NMR contain carbon. Unfortunately, the carbon-12 nucleus does not have a nuclear spin, but the carbon-13 (C-13) nucleus does due to the presence of an unpaired neutron. Carbon-13 nuclei make up approximately one percent of the carbon nuclei on earth. Therefore, carbon-13 NMR spectroscopy will be less sensitive (have a poorer SNR) than hydrogen NMR spectroscopy. With the appropriate concentration, field strength, and pulse sequences, however, carbon-13 NMR spectroscopy can be used to supplement the previously described hydrogen NMR information. Advances in superconducting magnet design and RF sample coil efficiency have helped make carbon-13 spectroscopy routine on most NMR spectrometers.

The *sensitivity* of an NMR spectrometer is a measure of the minimum number of spins detectable by the spectrometer. Since the NMR signal increases as the population difference between the energy levels increases, the sensitivity improves as the field strength increases.

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The sensitivity of carbon-13 spectroscopy can be increased by any technique which increases the population difference between the lower and upper energy levels, or increases the density of spins in the sample. The population difference can be increased by decreasing the sample temperature or by increasing the field strength. Several techniques for increasing the carbon-13 signal have been reported in the NMR literature.

Unfortunately, or fortunately, depending on your perspective, the presence of spin-spin coupling between a carbon-13 nucleus and the nuclei of the hydrogen atoms bonded to the carbon-13, splits the carbon-13 peaks and causes an even poorer signal-to-noise ratio. This problem can be addressed by the use of a technique known as decoupling, addressed in the next section.

Carbon-13 NMR (^{13}**C NMR** or sometimes simply referred to as carbon NMR) is the application of nuclear magnetic resonance (NMR) spectroscopy to carbon. It is analogous to proton NMR (1H NMR) and allows the identification of carbon atoms in an organic molecule just as proton NMR identifies hydrogen atoms. As such ^{13}C NMR is an important tool in chemical structure elucidation in organic chemistry. ^{13}C NMR detects only the 13C isotope of carbon, whose natural abundance is only 1.1%, because the main carbon isotope, 12C, is not detectable by NMR since it has zero net spin.

Decoupling

The signal-to-noise ratio in an NMR spectrometer is related to the population difference between the lower and upper spin state. The larger this difference the larger the signal. We know from chapter 3 that this difference is proportional to the strength of the B_o magnetic field.

To understand decoupling, consider the familiar hydrogen NMR spectrum of HC-$(CH_2CH_3)_3$. The HC hydrogen peaks are difficult to see in the spectrum due to the splitting from the 6 -CH$_2$- hydrogens. If the effect of the 6 -CH$_2$- hydrogens could be removed, we would lose the 1:6:15:20:15:6:1 splitting for the HC hydrogen and get one peak. We would also lose the 1:3:1 splitting for the CH$_3$ hydrogens and get one peak. The process of removing the spin-spin splitting between spins is called decoupling. Decoupling is achieved with the aid of a saturation

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pulse. If the effect of the HC hydrogen is removed, we see the following spectrum. Similarly, if the effect of the -CH_3 hydrogens is removed, we see this spectrum.

A saturation pulse is a relatively low power B_1 field left on long enough for all magnetization to disappear. A saturation pulse applied along X' rotates magnetization clockwise about X' several times. As the magnetization is rotating, T_2 processes cause the magnetization to dephase. At the end of the pulse there is no net Z, X, or Y magnetization. It is easier to see this behavior with the use of plots of M_Z, $M_{X'}$, and $M_{Y'}$ as a function of time. Since the B_1 pulse is long, its frequency content is small. It therefore can be set to coincide with the location of the -CH_2- quartet and saturate the -CH_2- spin system. By saturating the -CH_2- spins, the -CH_2- peaks and the splittings disappear, causing the height of the now unsplit HC- and -CH_3 peaks to be enhanced.

Now that the concept of decoupling has been introduced, consider the carbon-13 spectrum from CH_3I. The NMR spectrum from the carbon-13 nucleus will yield one absorption peak in the spectrum. Adding the nuclear spin from one hydrogen will split the carbon-13 peak into two peaks. Adding one more hydrogen will split each of the two carbon-13 peaks into two, giving a 1:2:1 ratio. The final hydrogen will split each of the previous peaks, giving a 1:3:3:1 ratio. If the hydrogen spin system is saturated, the four lines collapse into a single line having an intensity which is eight times greater than the outer peak in the 1:3:3:1 quartet since $1+3+3+1=8$. In reality, we see a single line with a relative intensity of 24. Where did the extra factor of three come from?

1-D C-13 Spectra

The following table of compounds contains links to their corresponding one-dimensional carbon-13 NMR spectra. The spectra were recorded on a 300 MHz NMR spectrometer with a delay time between successive scans of two seconds. This relatively short delay time may cause differences in the peak heights due to variations in T_1 values. Other differences may be caused by variations in the nuclear Overhauser effect. In spectra recorded with deuterated chloroform ($CDCl_3$) as the lock solvent, the three peaks at = 75 are due to splitting of the $CDCl_3$ carbon-13 peak by the nuclear spin = 1 deuterium nucleus.

Molecule	Formula	Solvent

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cyclohexane	C_6H_{12}	$CDCl_3$
benzene	C_6H_6	$CDCl_3$
toluene	$C_6H_5CH_3$	$CDCl_3$
ethyl benzene	$C_6H_5CH_2CH_3$	$CDCl_3$
acetone	$CH_3(C=O)CH_3$	$CDCl_3$
methyl ethyl ketone	$CH_3(C=O)CH_2CH_3$	$CDCl_3$
ethanol	CH_3CH_2OH	$CDCl_3$
ethanol	CH_3CH_2OH	D_2O
1-propanol	$CH_3CH_2CH_2OH$	$CDCl_3$
2-propanol	$(CH_3)_2CHOH$	$CDCl_3$
t-butnol	$(CH_3)_3COH$	$CDCl_3$
2-butanol	$CH_3CH_2CH(OH)CH_3$	$CDCl_3$
pyridine	C_5H_5N	$CDCl_3$

Applications of NMR Spectroscopy

NMR spectroscopy can provide an enormous amount of information—including physical, chemical, structural, and electronic—about samples under analysis. NMR spectroscopy has applications in medicine, chemistry and other fields of scientific research, industry,

Determining molecular structure and conformation of a sample and examining interactions between molecules can often only be achieved via NMR spectroscopy in conjunction with mass spectroscopy. Very often this type of research is critical to further or complete a given project

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(and determining structure and conformation is also important in obtaining intellectual property rights).

NMR spectroscopy is also vital for **studying cell metabolism**, due to the fact that metabolism is based on interactions between molecules and cells. NMR allows these types of studies to be carried out non-invasively, as it can be used to detect the presence of metabolites and chemical energy produced by cells.

Industrial processes such as reaction and process monitoring, and content and purity checks, often involve NMR spectroscopy. The specificity of NMR makes it highly suitable for monitoring and optimizing dynamic reactions and processes. Content and purity checks use NMR spectroscopy to monitor the quality and purity of batches of certain types of manufactured products, and to determine the composition of mixtures. NMR-based monitoring and testing is particularly useful because it can be done non-destructively—that is, without destroying the item being examined.

The ability of NMR spectroscopy to provide non-destructive analysis is actually highly useful in biological research because samples can be studied for extended periods using NMR, whereas biochemical experiments might destroy the samples.

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POSSIBLE QUESTIONS

PART B (2 Mark Questions)

1. which type of nuclei show magnetic properties for the purpose of NMR spectroscopy?

2. Which property of certain atomic nuclei is involved in NMR spectroscopy?

3. Which spin state has higher energy?

4. ^{13}C NMR active while ^{12}C is not explain.

5. What is the strength of the earth's magnetic field?

6. Why TMS is used as a reference standard in NMR spectroscopy?

7. Do you need any solvent for determining the NMR of an organic compound?

8. Define the term chemical shift.

9. What is meant by induced magnetic field?

10. What is spin-spin splitting?

11. Define coupling constant (J)

PART C (8 Mark Questions)

1. Describe with examples the various factors which affect the magnitude of the chemical shift in NMR spectra.

2. What is double resonance and spin tickling? How these are helpful in simplifying the spectra?

3. Describe ^{13}C NMR spectroscopy. What are the advantages of it over proton magnetic resonance spectroscopy?

4. Explain (i) Qualitative analysis

   (ii)Quantitative analysis using NMR spectra

5. Explain heteronuclear coupling with examples

6. Explain first order and non-first order NMR spectra with example

7. What are the factors that influencing geminal coupling (b) vicinal coupling (c) Long range coupling?

8. What are lathaninde shift reagents and chemical shift reagents?

9. Explain spin-spin coupling and spin-spin splitting are resonance phenomenon

SUBJECT : Organic Chemistry -IV (Organic Spectroscopy)

Subject Code : 16HCU403

Class : II B.Sc Chemistry

Staff Name : Dr.M.Makeswari and Mr. R Kumar

Batch : 2016-2018 Batch

UNIT-III

QUESTIONS	OPTION-I	OPTION-II	OPTION-III	OPTION-IV	ANSWER
What is precessional motion	a.top moves around the vertical	b.top moves away the vertical	c.top moves away from the vertical	d.none of the above	a.top moves around the vertical
The gyromagnetic ratio is	a.2 pi M/Hi	b.2C pi M/hI	c.hI/2 pi M	d.hI/ 2C pi M.	a.2 pi M/Hi
What is flipping	a.energy transfer within the molecule	b.energy transfer outside the molecule	c. .energy transfer from one energy	d.none of the above	a.energy transfer within the molecule
Acetone gives	a.one signal NMR	b. two signal NMR	c. three signal NMR	d. four signal NMR	a.one signal NMR
Methyl cyclo propane gives	a.one signal NMR	b. two signal NMR	c. three signal NMR	d. four signal NMR	c. three signal NMR
For non viscous system NMR gives	a.splitting signal	b.sharp signal	c.broad signal	d.none of the above	b.sharp signal
The relationship between delta value in ppm and frequency in hertz is fundamental	a.$\delta x = v_x - v_{TMS/V0}$	b. $\delta x = v_{TMS} - v_{x/V0}$	C.$v_0/ v_x - v_{TMS}$	d. $v_0/ v_{TMS} - v_x$	a.$\delta x = v_x - v_{TMS/V0}$
What is the rule of spectral multiplicity	a.I(n+1)	b.n(I+1)	C.n+1	d.n-1	C.n+1
Which compound gives AMX spectrum	a.poly styrene compound	b.poly ehylene compound	c.vinyl compound	d. polyvinyl compound	c.vinyl compound
What is karplus equation	a. Ø between 0° and 90° Jvic = $8.5COS^2$ Ǿ-0.28	b. Ø between 0° and 90° Jvic = $9.5COS^2$ Ǿ-0.28	c. Ø between 0° and 180° Jvic = $8.5COS^2$ Ǿ-0.28	d. None of the above	a. Ø between 0° and 90° Jvic = $8.5COS^2$ Ǿ-0.28
What is double resonance	a.At a time use of two radio frequency source	b.alternate use of two radio frequency source	c.simultaneous use of two radio frequency source	d.combined use of two radio frequency source	a.At a time use of two radio frequency source
What is NOE signal	a.nucleous oriented energy level	b.nucleous over effect	c.nuclear over hauser effect	d.nucleous opposite energy level	c.nuclear over hauser effect
How many double bond present in norborene	a.single	b.double	c.triple	d.multiplet	b.double
How many nitrogen present in imidazole	a.1	b. 2	c.3	d.5	b. 2
What is SPI	a.spin permittive intense peak	b.selective population inversion	c.selective possible interaction	d.spin pulse energy intensive peak.	b.selective population inversion

Question	a	b	c	d	Answer
(i)Magnetically equivalent protons are chemically equivalent (ii)each signal corresponds to a set of equivalent protons	a.(i) and (ii) are true	b.(i) true	c.(ii) true	d.(i) and (ii) false	a.(i) and (ii) are true
Propanal gives	a.1 NMR signal	b.2 NMR signal	c.3 NMR signal	d.4 NMR signal	b.2 NMR signal
The DMSO is a	a.highly polar solvent	b.highly non polar solvent	c.weakly polar solvent	d.weakly non polar solvent	a.highly polar solvent
NMR spectrum obtained in	a.microwave region	b.radiofrequency region	c.IR region	d.none of the above	b.radiofrequency region
For NMR, (a) downfield due to deshielding (b)upfield due to shielding	a.both are true	b. a true b false	c.b true a false	d.both are false	a.both are true
What is Geminal coupling a.protons attached as the same carbon having different chemical environment b. protons attached as the same carbon having same chemical environment	a. a and b are true	b. a and d are flase	c. b and a flase	d. both are flase	a. a and b are true
I=0	a. NMR signals observed	b. NMR signals not observed	c. half NMR signals	d. none of the above	b. NMR signals not observed
How many gem methyl group present in $\propto$-pinene	a) one	b) two	c) three	d) zero	b) two
For NMR the aromatic character relates to cyclic delocalization of	a. (4n+2) π electrons	b. (2n+4) π electrons	c. (4n+π) 2 electrons	d. (2n+π) 4 electrons	a. (4n+2) π electrons
What is magnetic equivalence	a)chemical shift equivalence	b)coupling equivalence	c)chemical equivalence	d)magnetic equivalence	c)chemical equivalence
What is accidental equivalence	a.chemical shift of 2 proton are equal	b)environment of 2 protons are equal	c)coupling constants are equal	d)magnetic field of 2 protons are equal	a.chemical shift of 2 proton are equal
For NMR the number of orientatins is	a) (2m+I)	b) (2I+1)	c) (2n+1)	d) (2n+1)	b) (2I+1)
Oppose orientation most stable and alligned orientation least stable a)most stable b)least stale	a) both are true	b) a true b flase	c) both are flase	d) a flase b true	a) both are true
How many methyl group present I methanol	a) 2	b) 3	c) 4	d) 0	b) 3
Which is used as a lanthanide shift reagent	a) Europium	b) Tms	c) 6-methyl quinoline	d) combination of europium and TMS	c) 6-methyl quinoline
What is the natural abundance of ^{13C} NMR	a) 1%	b) 0.1%	c) 1.1%	d) 11%	c) 1.1%
What is the chemical shift range of ^{1}H spectrum	a) 4ppm	b) 40 ppm	c) 80 ppm	d) none	c) 80 ppm
What is the chemical shift range of	a) 4ppm	b) 40 ppm	c) 80 ppm	d) 120 ppm	a) 4ppm

Question	a	b	c	d	Answer
What is "CI DNP"	a. Chemically induced dynamic nuclear polymerization	b. Chemically induced dinuclear polarisation	c. Chemically induced dynamic number polarisation	d. magentically indued	a. Chemically induced dynamic nuclear polymerization
What is MRI	a)magnetic radio frequency imagine	b)magnetic resolution imagine	c)magnetic resonance imagine	d)none	c)magnetic resonance imagine
What is "COSY"	a)2D NMR-Shift correlation spectra	b)2D NMR-Shift corrected spectra	c)NMR shift corrected spectra	d)NMR shift correction spectra	a)2D NMR-Shift correlation spectra
The energy of free spin is related to give their envirnment is called as	a. spin-spin relaxation	b. spin-spin coupling	c. spin-lattice relaxation	d. spin-lattice coupling	c. spin-lattice relaxation
How many number of hydrogen present in annulene	a) 12H	b) 14H	c) 16 H	d) 18 H	d) 18 H
What is shielding	a. spin oppose to magnetic field	b. spin allign to magnetic field	c. spin lateral to magnetic field	d. spin oppose lateral to magnetic field	b. spin allign to magnetic field
What is anisotropic effect	a. δ for protons attached to C=C in alkenes	b. δ for protons attached to C=C in alkynes	c. δ for protons attached to cyclo hexanes	d. δ for protons attached to para hexanes	a. δ for protons attached to C=C in alkenes
The resultant spin of ^1_1H is	a. 0-100 nm	b. 1	c. 1/2	d.3/2	c. 1/2
The nucleus which gives NMR spectrum is	a. $^{16}_8O$	b. $^{10}_5B$	c.^{12}O	d. ^4_2He	b. $^{10}_5B$
The ^1_1H spectrum CH_2 (Cl)CH(Cl)OCH_3 would show	a. a 3 proton singlet,I proton triplet and 2 proton doublet	b. a 3 proton doublet 1 proton triplet and 2 proton singlet	c. a 3 proton triplet 1 proton doublet 2 proton doublet	d. a3 proton singlet 1 proton singlet 2 proton doublet	a. a 3 proton singlet,I proton triplet and 2 proton doublet
The chemical shift of ^1_1H on the δ scale is 2.56. The value on Υ scale is	a. 12.56	b. 7.44	c.2.56	d. 1.44	b. 7.44
The bond length on NO is 0.116 nm. Its rotational constant is	a. 5.0^{30} x 10^{10} sec	b. 1.23x 10^{10} sec	c. 5.030x10^{10} sec^{-1}	d. 1.23x 10^{10} sec-1	c. 5.030x10^{10} sec^{-1}
Among the following which does not give NMR spectra	a. $^{16}_8O$	b. $^{10}_5B$	c. $^{15}_7N$	d.^1_1H	a. $^{16}_8O$
The NMR spectroscopy is based on the magnetic momentby the spinning of a	a. Atom	b. Charged nucleus	c. Electron	d. neutrons	b. Charged nucleus
In the PMR spectrum FCH_2 CHF_2 would give	a. 4 signals	b. 3 signals	c. 2 signals	d.1 signals	c. 2 signals
In a NMR spectrum number of protons of each kind in a molecule is indicated by the	a. number of signals	b. Intensity of signals	c.Splitting of a signals	d. Charged nucleus	b. Intensity of signals

Question	a	b	c	d	Answer
In a low resolution NMR spectrum of ethanol, the area under the peak corresponding to OH, CH$_2$ and CH$_3$ protons respectively will be in the ratio	a. 3:2:1	b. 1:3:2	c.3:1:2	d.1:2:3	a. 3:2:1
What is the spin number of thefollowing nuclei ^{11}B, ^{35}Cl, ^{79}Br, ^{81}Br?	a. 3/2	b. 1/2	c. 1	d. 5/2	a. 3/2
The spin angular momentum of thenucleus, H is ---	a. root of 1/2x h/2π	b.root of 1/2x11/2	c. rootof 1/2x1 1/2xh/2π	d.root of 1/2	c. rootof 1/2x1 1/2xh/2π
The Bohr magneton is aunit of--- and it is nearly--- times the nuclear magneton	a. Magnetic field 1850	b. Magnetic moment,1850	c. Magnetic field 1/1850	d. Magnetic moment, 1/1850	b. Magnetic moment,1850
The proton magnetic resonance is studied in---	a. Radiofrequency	b. microwave region	c.IR region	d.Visible region	a. Radiofrequency
Underhigh resolution, ethanol containing acid inpurity gives--- PMR signals and the hydroxyl proton appears as a	a.3 triplet	b.3.singlet	c.2 singlet	d. 3 quintet	a.3 triplet
The chemical shift of a proton on the δ scale is 4. The value of the τ scale is---	a. 14	b.6	c. 2.5	d.4	b.6
The fine structure and intensity ratios expected in the proton NMRspetrum of NH$_4^+$ ion (for ^{14}N,I=1) are	a. singlet	b. Doublet 1:1	c. Trplet 1:1:1	d.triplet1:2:1	c. Trplet 1:1:1
In the proton NMR spectrum of toluene,the resonancedue to CH$_3$, group is expected to	a. δ 0.5	b.δ 1.25	c.δ2.5	d. δ 3.5	c.δ2.5
How many NMR signals are found in cis dimethyl cyclopropane and transdimethyl cyclopropane?	a. 2,3	b.3,4	c. 1,2	d. 8,10	b.3,4
In NMR spectroscopy the value of coupling constant(5)	a. Changes with ield strength	b. Changes with temperature	c.Changeswith solvent	d. Is independent to field strength, temperature and solvent	d. Is independent to field strength, temperature and solvent

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UNIT-IV
SYLLABUS

Occurrence, classification and their biological importance.

Monosaccharides: Constitution and absolute configuration of glucose and fructose, epimers and anomers, mutarotation, determination of ring size of glucose and fructose, Haworth projections and conformational structures; Interconversions of aldoses and ketoses; Killiani- Fischer synthesis and Ruff degradation;

Disaccharides – Structure elucidation of maltose, lactose and sucrose.

Polysaccharides – Elementary treatment of starch, cellulose and glycogen.

CARBOHYDRATES

Introduction

The term "carbohydrates'' is used to identify a rather diverse group of materials found in nature. They are known to have important functions as constituents of both plants and animals. Carbohydrates provide a structural frame work for plants and serve as a source of energy for both plants and animals. Many industries nowadays depend on carbohydrates.

Carbohydrates, as the name implies, are composed mainly of carbon, hydrogen and oxygen, although other elements have been found in few compounds. For example *chitin, glucosamine* contain nitrogen. Although many of the simpler compounds have the empirical formula CH_2O as that of carbohydrates, are polyfunctional compounds. They have two kinds of functional groups- the alcoholic (hydroxyl) group and the carbonyl group. Thus, they are *polyhydroxy ketones or aldehydes.*

Classification

The behavior of carbohydrates materials towards acid hydrolysis provides the basis for an initial separation into groups.

1) The simplest of these which do not hydrolysis into smaller unit are known as "*monosaccharides*".
   Examples: Glucose, fructose, mannose and galactose.

2) Compounds which undergo hydrolysis to liberate two or more, but fewer than eleven monosaccharide molecules are designed as *"oligosaccharide"*

3) If the oligosaccharide, upon hydrolysis yields two monosaccharide units, then it is termed as *disaccharide* (with molecular formula ($C_{12}H_{22}O_{11}$).
   Examples: Maltose and lactose.

4) If more than ten molecules of monosaccharides result during hydrolysis, the compound is referred to as a *polysaccharide.*

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Examples: Starch and cellulose.

5) Generally the monosaccharides and oligosaccharides are crystalline solids, soluble in water and sweet to taste. They are known as *sugars.*

6) Polysaccharides are non-sugars which are amorphous, tasteless and insoluble in water.

7) The carbohydrates may further be classified as either *reducing* or *non-reducing* sugar. All those carbohydrates which reduce *Fehling's solution* and *Tollen's reagent* are reducing sugars while others are non-reducing sugar. All monosaccharides and disaccharides (expect sucrose) are reducing sugar.

8) Then term *tetrose, pentose* and *hexose* are used to indicate those carbohydrates having four, five and six carbon atoms respectively.
    Example: Glucose has six carbon atoms and is a hexose.

9) If the monosaccharide posseses an aldehyde group, it is an *aldose* and that with a keto group, is a *ketose*.

10) The number of carbon atoms in conjugation with the type of carbonyl group in a sugar is indicated as *aldopentose* and *ketohexose.* The glucose, mannose and galactose are aldohexoses and fructose is a ketohexose.

1. GLUCOSE

Glucose, *dextrose* (grape sugar) is the central carbohydrate of living organisms of all types, the major source of energy. It is widely distributed in nature as the monosaccharides in ripe grapes. Honey,sweet fruit and as a component of disaccharides-lactose, maltose, sucrose and cellobiose. It is the building unit from which the polysaccharides like starch, cellulose and glycogen are formed. It is also normal constituent of blood and occurs in urine of diabetics.

1) Commercially pure D(+) glucose is manufactured by heating starch with dilute hydrochloric acid under pressure:

$$(C_6H_{10}O_5)_n + n\ H_2O \xrightarrow{dil.HCl} n\ C_6H_{12}O_6$$
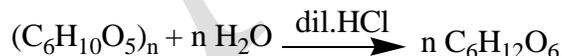
2) It is formed as an intermediate product in the fermentation of starch for the manufacture of ethyl alcohol.

3) Glucose is made by the hydrolysis of sucrose by boiling with dilute hydrochloric acid in alcoholic solution. Glucose and fructose are obtained in equal amounts. On cooling the resulting solution, glucose being less soluble than fructose, separates out.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{dil.HCl} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$
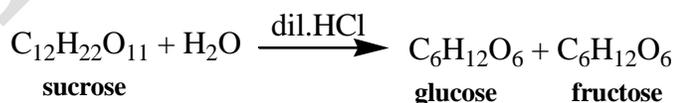
Properties

Glucose is a white crystalline solid (m.p 419 K), sweet to taste. It is readily soluble in water. Naturally occurring glucose is *dextro-rotatory* (hence, the name Dextrose) and it has four asymmetric carbon atom (marked by *).

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$$H_2C - \overset{*}{C}H - \overset{*}{C}H - \overset{*}{C}H - \overset{*}{C}H - \overset{O}{\overset{\|}{C}} - H$$
$$\quad\;\; |\qquad |\qquad |\qquad |\qquad |$$
$$\quad\;\; OH\;OH\quad OH\quad OH\quad OH$$
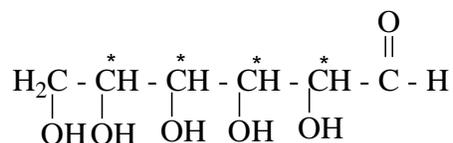
Structural formula of glucose indicates the presence of one aldehydic group, one primary alcoholic group and four secondary alcoholic groups. Chemical properties of glucose are, therefore, the properties of the above functional groups. The structural elucidation very easily follows from its reactions:

1) Quantitative analysis establishes the empirical formula as CH_2O.

2) The molecular weight of glucose determined from a study of the depression of freezing point of glucose solution, shows a value of 180. When this is compared with the empirical formula weight, the conclusion reached is that the molecular formula is $(CH_2O)_6$ or $C_6H_{12}O_6$.

3) The presence of the five alcoholic groups is indicated by its reaction with 5 moles of acetyl chloride or acetic anhydride.

$$CH_2OH \qquad\qquad\qquad\qquad CH_2OCOCH_3$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$(CHOH)_4 + 5\,(CH_3CO)_2O \longrightarrow (CHO\text{-}COCH_3)_4 + 5CH_3COOH$$
$$|\qquad\qquad\qquad\qquad\qquad\qquad |$$
$$CHO \qquad\qquad\qquad\qquad\qquad CHO$$
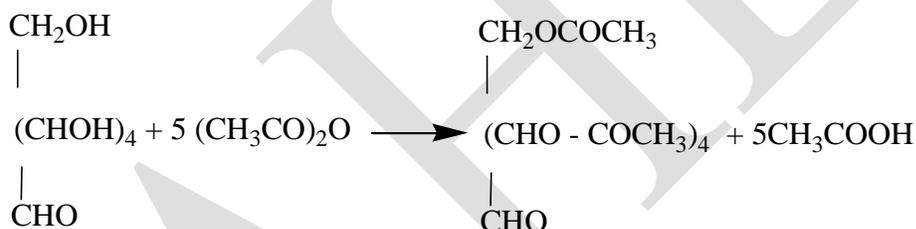
4) Reduction of glucose with concentrated hydriodic acid and red phosphorus at 373 K yields 2-iodohexane. Prolonged heating produces n-hexane. This would mean that glucose is a straight chain compound of six carbon atoms.

$$CHO \qquad\qquad CH_3$$
$$|\qquad\qquad\qquad |$$
$$(CHOH)_4 \longrightarrow (CH_2)_4$$
$$|\qquad\qquad\qquad |$$
$$CH_2OH \qquad\qquad CH_3$$
$$\qquad\qquad\qquad \textbf{n-hexane}$$
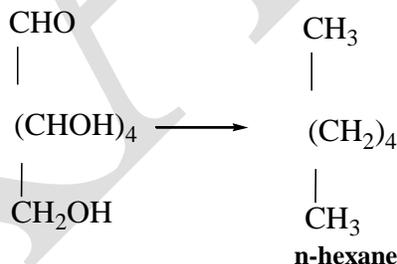
5) The nature of the carbonyl group is indicated by its reaction with mild reducing agent. When reduced with sodium amalgam in aqueous solution, the aldehyde group is reduced to a primary alcoholic group to yield a hexahydric alcohol, called sorbitol.
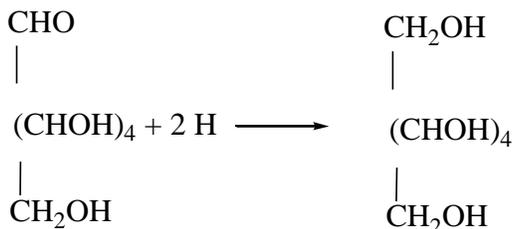
$$CHO \qquad\qquad CH_2OH$$
$$|\qquad\qquad\qquad |$$
$$(CHOH)_4 + 2\,H \longrightarrow (CHOH)_4$$
$$|\qquad\qquad\qquad |$$
$$CH_2OH \qquad\qquad CH_2OH$$

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6) Glucose gives addition product with hydrogen cyanide *(but not with ammonia or sodium bisulphite).* This reaction indicates the presence of a carbonyl group.

$$
\begin{array}{cc}
\text{CHO} & \text{CH(OH) CN} \\
| & | \\
\text{(CHOH)}_4 + \text{HCN} \longrightarrow & \text{(CHOH)}_4 \\
| & | \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH}
\end{array}
$$

glucose cyanohydrin
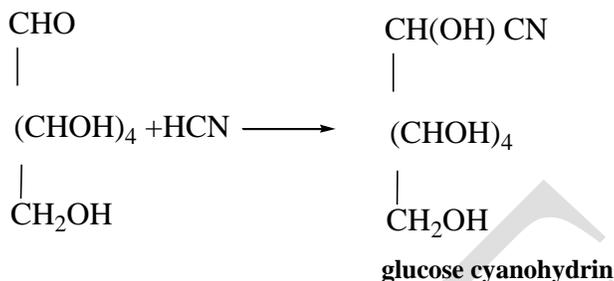
7) Glucose condenses with hydroxylamine to yield the oxime with the elimination of a water molecule.

$$
\begin{array}{cc}
\text{HC} = \text{O} \ + \text{H}_2\text{NOH} & \text{HC} = \text{NOH} \\
| & | \\
\text{(CHOH)}_4 \longrightarrow & \text{(CHOH)}_4 \ + \text{H}_2\text{O} \\
| & | \\
\text{CH}_2\text{OH} & \text{CH}_2\text{OH}
\end{array}
$$
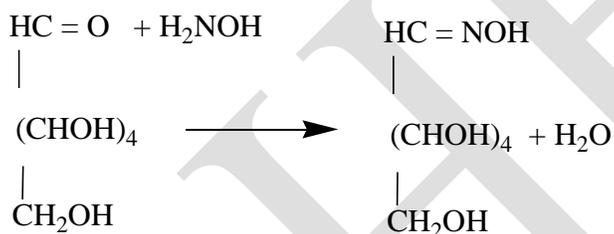
8) Glucose reacts with one molecule of phenylhydrazine in acetic acid which condenses with the aldehyde group to give *phenylhydrazone.* When warmed with excess phenylhydrazine, the secondary alcoholic group, adjacent to the aldehyde group, is next oxidised to a keto group. With this keto group, third molecule of phenylhydrazine condenses to yield *glucosazone:*

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$$
\begin{array}{l}
HC=O + H_2NNHC_6H_5 \\
\quad | \qquad \text{1st molecule} \\
(CHOH) \\
\quad | \\
(CHOH)_3 \\
\quad | \\
CH_2OH
\end{array}
\xrightarrow[-H_2O]{}
\begin{array}{l}
HC=NNHC_6H_5 \\
\quad | \\
CHOH \\
\quad | \\
(CHOH)_3 + C_6H_5NHNH_2 \\
\quad | \qquad \text{2nd molecule} \\
CH_2OH
\end{array}
$$

Glucose phenylhydrazone

$$
\xrightarrow[-NH_3]{-C_6H_5NH_2}
\begin{array}{l}
HC=NNHC_6H_5 \\
\quad | \\
C=O + H_2NNHC_6H_5 \\
\quad | \qquad \text{3rd molecule} \\
(CHOH)_3 \\
\quad | \\
CH_2OH
\end{array}
$$

Glucosone phenylhydrazone

$$\downarrow -H_2O$$

$$
\begin{array}{l}
HC=NNHC_6H_5 \\
\quad | \\
C=NNHC_6H_5 \\
\quad | \\
(CHOH)_3 \\
\quad | \\
CH_2OH
\end{array}
$$

Glucosazone
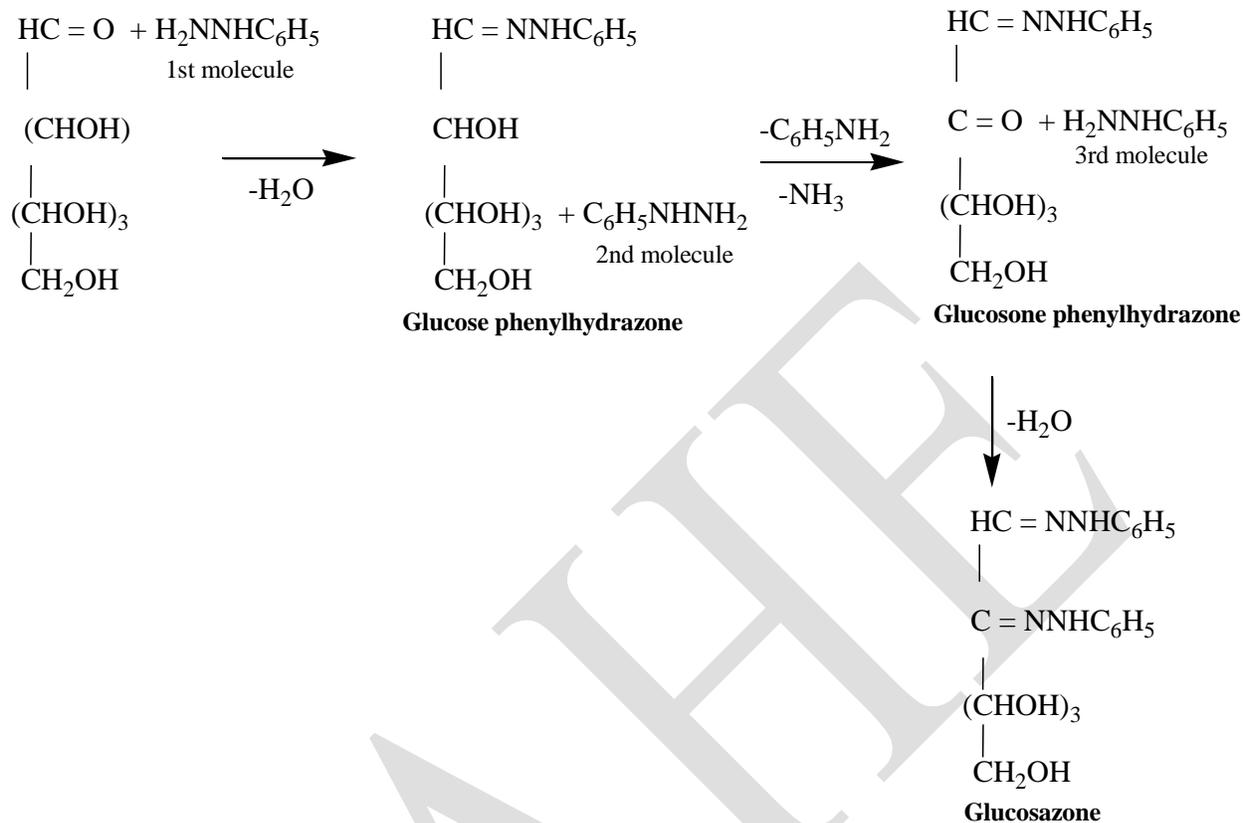
9) With mild oxidising agents like bromine water, glucose is oxidised to gluconic acid, an acid with the same number of carbon atoms. In this reaction, the aldehyde group alone gets oxidised.

$$
\begin{array}{l}
CHO \\
\quad | \\
(CHOH)_4 \\
\quad | \\
CH_2OH
\end{array}
\xrightarrow{Br_2\,/\,H_2O}
\begin{array}{l}
COOH \\
\quad | \\
(CHOH)_4 \\
\quad | \\
CH_2OH
\end{array}
$$

gluconic acid
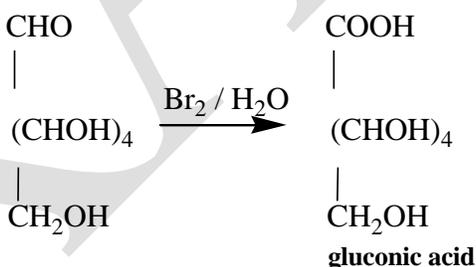
10) With strong oxidising agents like nitric acid, it is oxidised to a dicarboxylic acid, saccharic acid. Nitric acid is able to oxidise the primary alcohol group also to an acid group.

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$$
\begin{array}{ccc}
\text{CHO} & & \text{COOH} \\
| & \xrightarrow{\text{HNO}_3} & | \\
(\text{CHOH})_4 & & (\text{CHOH})_4 \\
| & & | \\
\text{CH}_2\text{OH} & & \text{COOH}
\end{array}
$$

saccharic acid or glucaric acid
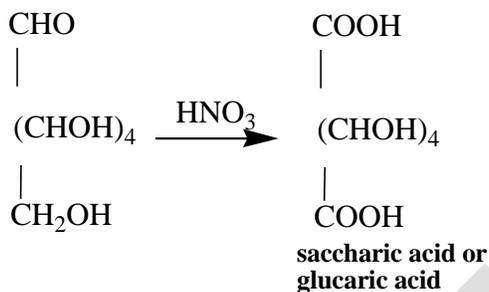
11) Because glucose is readily oxidised, it acts as a strong reducing agent. It reduces both Fehling's solution (I) and Tollen's reagent [ammoniacal silver nitrate, (II)]

$$
\begin{array}{ccccc}
\text{COOH} & & \text{CHO} & & \text{COOH} \\
| & & | & & | \\
\text{Cu}_2\text{O} + (\text{CHOH})_4 & \xleftarrow{\text{(I)}} & (\text{CHOH})_4 & \xrightarrow{\text{(II)}} & (\text{CHOH})_4 + 2\text{Ag} \\
| & & | & & | \\
\text{CH}_2\text{OH} & & \text{CH}_2\text{OH} & & \text{CH}_2\text{OH}
\end{array}
$$
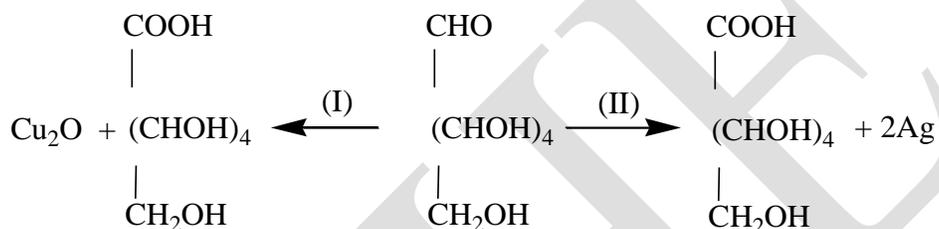
The above reactions (5 to 11) confirm the presence of an aldehyde group in glucose.

Other Reactions of Glucose

12) Glucose on fermentation yields ethyl alcohol.

$$ C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\ CO_2 + 2C_2H_5OH $$

13) A dilute solution of glucose when warmed with dilute alkali solution, gives a mixture of glucose, fructose and mannose.

14) When heated with concentrated hydrochloric acid, it gives laevulic acid and hydroxymethyl furfural.

All the above reactions of glucose indicate that glucose is a polyhydric alcohol with a terminal aldehyde group and that it is a straight chain compound.

As mentioned earlier, glucose does not react with ammonia or sodium bisulphite. Further, it exists in two isomeric forms, α- and β – glucose. The evidence for these forms is *muta rotation.* α – glucose with specific rotation +110º is obtained by crystallizing glucose form alcoholic or acetic acid solution whereas β – glucose with specific rotation +19.7º is obtained by crystallizing glucose form pyridine solution. An aqueous solution of glucose shows muta roration *(meaning, a change of rotation)* i.e., its specific rotation gradually falls from +110º to +52.5º in the case of α – glucose and increases from +19.7º to +52.5º in the case of β – glucose. To account for these facts satisfactorily, Tollen suggested a ring formula with no free aldehyde group. The ring structure for glucose is best representing by a hexagonal formula base on *pyran.*

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α-**D-glucose**

β-**D-glucose**
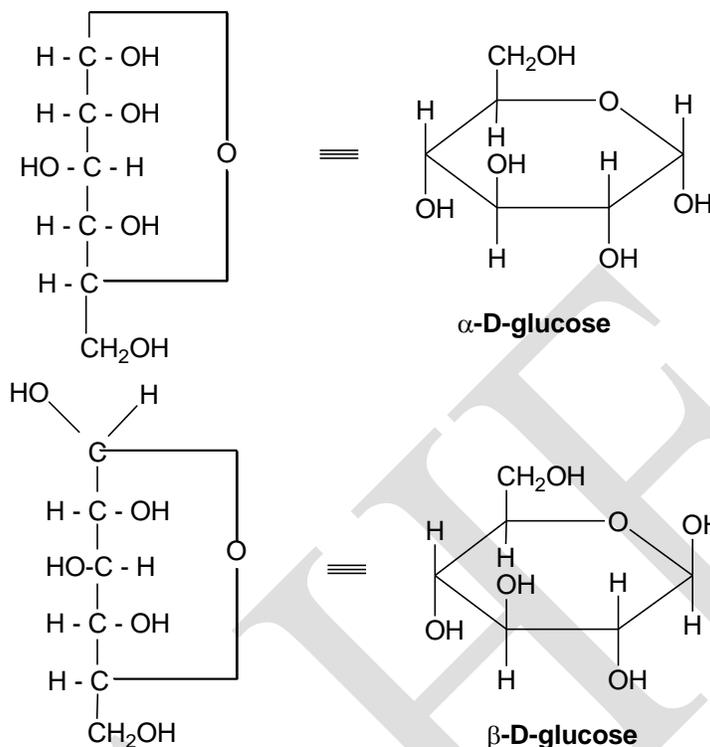
Uses

1) It is used as a sweetening agent in confectionery.
2) It is utilised in the manufacture of ascorbic acid (Vitamin C).
3) It serves as food for invalids and as food preservatives.

2. FRUCTOSE

D (-) Fructose, (Laevulose or Fruit Sugar) $C_6H_{12}O_6$

The only important ketohexose is D (-) fructose, m.p. 368 K. In the course of its degradation in cells and tissues, glucose is converted into fructose derivatives.

Preparation

1) Fructose is prepared in the laboratory by the hydrolysis of sucrose by boiling with dilute acids. It is formed along with glucose.
2) Fructose is obtained commercially by the hydrolysis of *inulin* with oxalic acid or dilutes sulphuric acid.
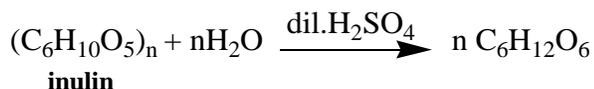
$$(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{dil.}H_2SO_4} n\ C_6H_{12}O_6$$
inulin

Properties

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Fructose is a white crystalline solid. It is the sweetest of all sugars. It is readily soluble in water. It is laevorotatory and therefore called *laevulose.* Structural formula of fructose indicates

$$H_2C - CO - \overset{*}{C}H - \overset{*}{C}H - \overset{*}{C}H - CH_2$$
$$\qquad\quad | \qquad\quad | \qquad | \qquad |$$
$$\qquad\quad OH \qquad OH \; OH \; OH \; OH$$
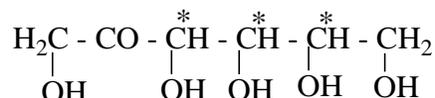
The presence of a keto group, two primary and three secondary (* marked, asymmetric carbons) alcoholic groups. The structure of fructose has been derived from a consideration of facts and conclusion such as the following:

1) Elemental analysis and molecular weight determination show that the molecular formula of fructose is $C_6H_{12}O_6$.

2) Complete reduction of fructose with HI and red phosphorus give n-hexane as the major products, suggesting a straight chain formula.

3) Fructose reacts with 5 moles of acetyl chloride or acetic anhydride to form a penta-acetate. This indicates the presence of five hydroxyl group in a fructose molecule. Since fructose is a stable compound, the five hydroxyl groups must be present on separate carbon atoms.

4) (a) Fructose reacts with hydroxylamine to form an oxime
    (b) It adds with only one mole of HCN to give a cyanohydrin.
    These reactions indicate the presence of a carbonyl group.

5) Fructose condenses with phenylhydrazine and yields fructosazone similar to glucose. Here again the reaction proceeds in stages:
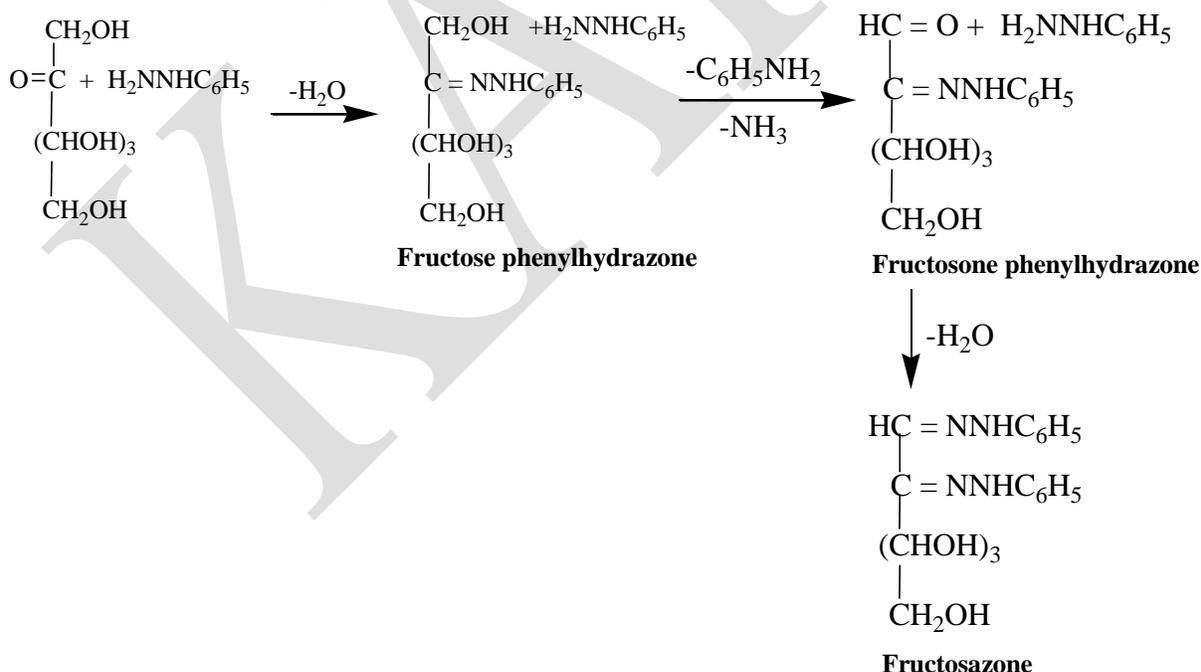
Fructose phenylhydrazone

Fructosone phenylhydrazone

Fructosazone

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6) Reduction of fructose with sodium amalgam and water produces a mixture of two epimeric alcohols, sorbital and mannitol because a new asymmetric carbon has been created at C$_2$. This indicates the presence of keto group.

Mannitol   **Sorbitol**
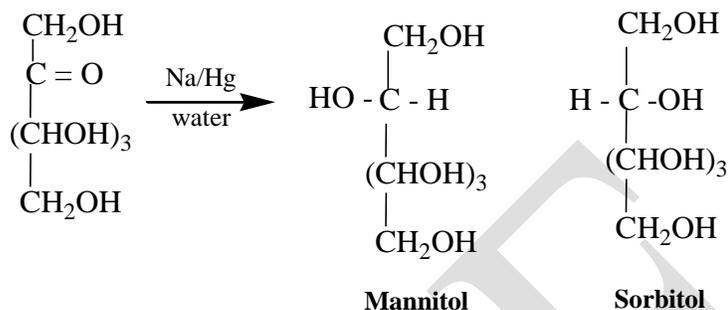
7) Fructose is not affected by mild oxidising agents. But strong oxidising agents, like nitric acid, oxidise fructose to a mixture of trihydroxy glutaric acid, tartaric acid and glycollic acid:

Trihydroxy glutaric acid   **Tartaric acid**   **Glycollic acid**
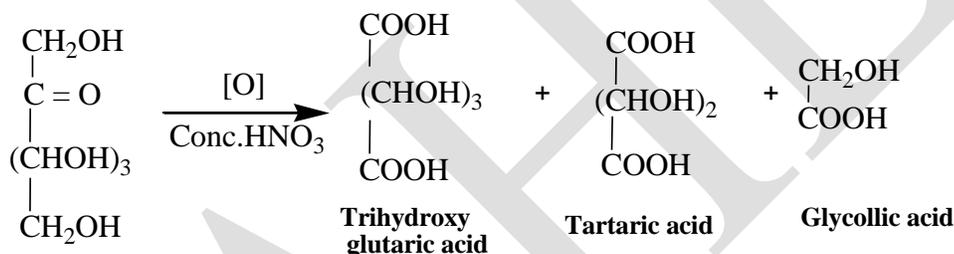
Since this oxidation occurs with the rupture of the carbon chain, the carbonyl group must be present as a keto group in fructose.

8) Fructose is a reducing sugar like glucose. Hence, it reduces both Tollen's reagent and Fehling's solution. Usually ketones do not reduce above reagents but hydroxy ketones possess reducing properties.

9) When fructose is treated with HCN it forms a cyanohydrin which upon hydrolysis and subsequent reduction gives 2-methyl-hexanoic acid. This indicates that the keto group is adjacent to one of the terminal carbon atom.

2-methylhexanoic acid
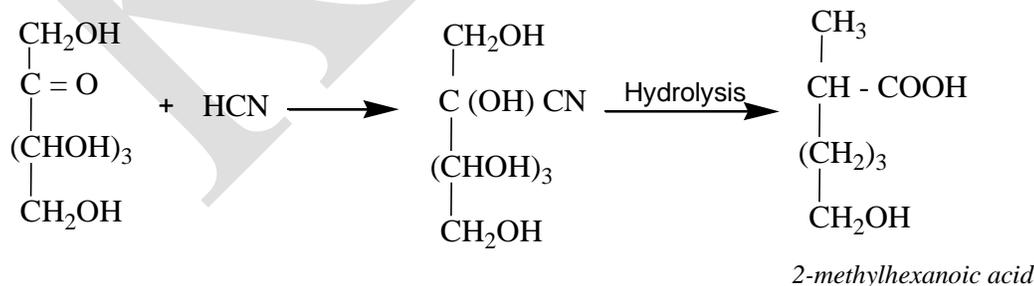
10) Fructose is fermented by yeast to ethyl alcohol.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2\ CO_2 + 2C_2H_5OH$$

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11) Fructose when warmed with dilute alkali forms a mixture of glucose, fructose and mannose like glucose.

12) When heated with Conc. hydrochloric acid, fructose gives laevulic acid. They yield is better than glucose.

13) Fructose does not react with ammonia and sodium bisulphite like glucose. Moreover, it exhibits muta rotation which suggests that it exists in two isomeric forms. So, a cyclic ring formula was suggested for fructose. As in the case of glucose, the hexagonal formula based on pyran is given for fructose.

α-**D-fructose**
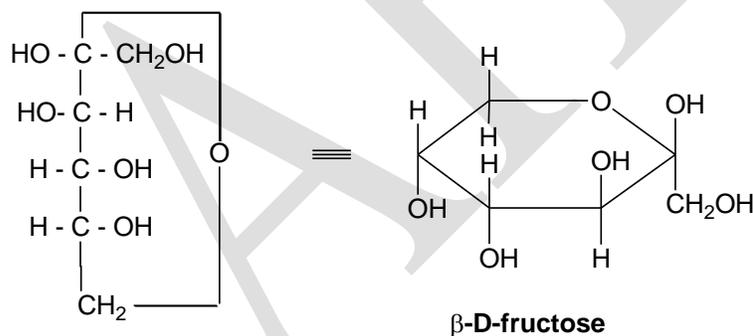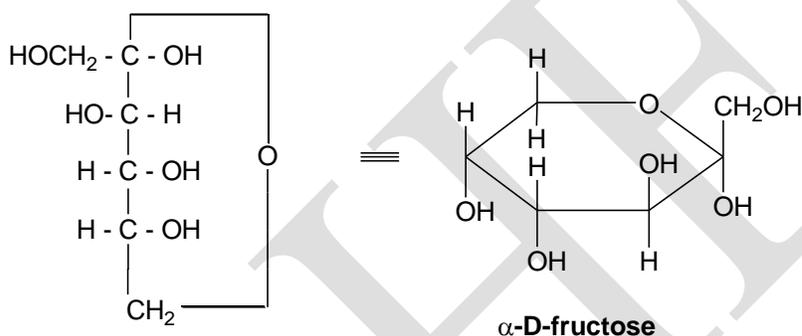
β-**D-fructose**

Γ-fructose is also known which exists in a five membered furan ring structure:
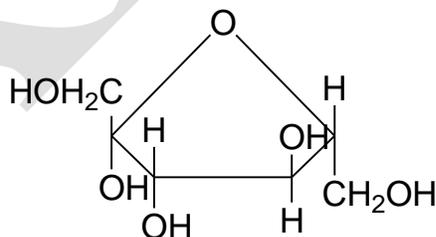
Uses

1) Fructose finds use as sweetening agent.
2) It is used by diabetic patients in the place of cane sugar.

Conversion of Glucose into Fructose

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Glucose is first treated with excess phenylhydrazine in acetic acid to form glucosazone which is next hydrolysed with dil.HCl to give *glucosone.* This is then reduced with zinc and glacial acetic acid to yield fructose:

CHO
|
CHOH + 3H$_2$NNHC$_6$H$_5$ ⟶
|
(CHOH)$_3$
|
CH$_2$OH
Glucose

HC = NNHC$_6$H$_5$
|
C = NNHC$_6$H$_5$
|
(CHOH)$_3$
|
CH$_2$OH
Glucosazone

$\xrightarrow{\text{dil.HCl}}$

CHO
|
CO
|
(CHOH)$_3$
|
CH$_2$OH
Glucosone

$\xrightarrow[\text{Zn/AcOH}]{\text{[H]}}$

CH$_2$OH
|
C = O
|
(CHOH)$_3$
|
CH$_2$OH
Fructose
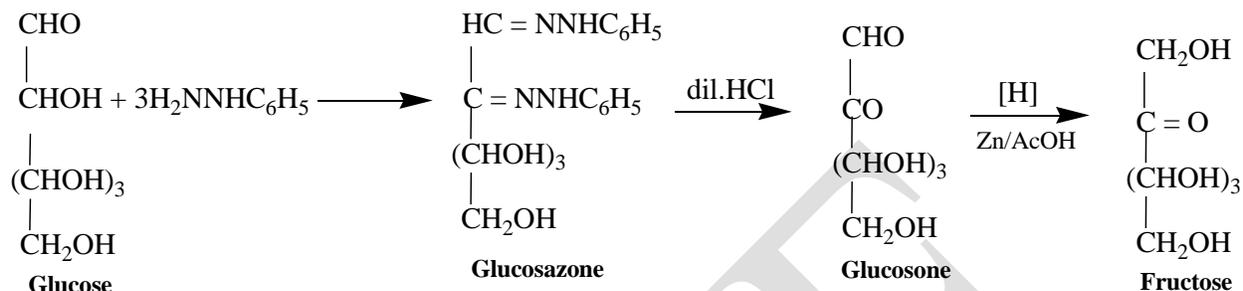
Conversion of Fructose into Glucose

Fructose is first reduced with sodium amalgam to give hexitols. These are next oxidised with nitric acid to yield the corresponding mono-carboxylic acids which on treatment with dil.HCl give *γ*- lactones. The individual lactones are reduced with LiAlH$_4$ to obtain the corresponding aldohexoses. In this conversion, both mannose and glucose are obtained but the route for the conversion of fructose to glucose alone is give below:

CH$_2$OH
|
CO
|
(CHOH)$_3$
|
CH$_2$OH
Fructose

$\xrightarrow{\text{[H]}}$

CH$_2$OH
|
H-C - OH
|
(CHOH)$_3$
|
CH$_2$OH
Sorbitol

$\xrightarrow{\text{HNO}_3}$

COOH
|
(CHOH)$_4$
|
CH$_2$OH
Gluconic acid

$\xrightarrow{\text{-H}_2\text{O}}$

CO —
CHOH
CHOH
CH —
CHOH   O
|
CH$_2$OH

$\xrightarrow{\text{LiAlH}_4}$

CHO
|
(CHOH)$_4$
|
CH$_2$OH
Glucose
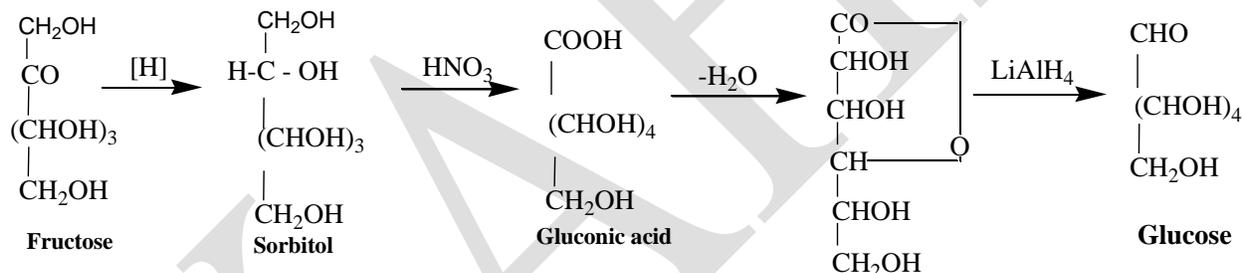
Comparative study of Glucose and Fructose:

No.	Properties	Glucose	Fructose
1.	Nature	(i) Aldohexose (ii) Dextro rotatory	(i) Ketohexose (ii) Laevo rotatory
2.	Osazone	Forms	Forms
3.	Muta rotation	Exhibits	Exhibits
4.	With HNO$_3$	Saccharic acid	Meso tartaric acid, glycollic acid
5.	With Bromine water	Gluconic acid	No reaction
6.	Fehling solution and Tollen's reagent	Reduces	Reduces
7.	With NaOH	Forms epimer	Forms epimer

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8.	In Ether	Insoluble	soluble

3. SUCROSE: $C_{12}H_{22}O_{11}$

Sucrose (common name: **table sugar**, also called **saccharose**) is a disaccharide (glucose + fructose) with the molecular formula $C_{12}H_{22}O_{11}$. Its systematic name is Î±-D-glucopyranosyl-(1â†'2)-Î²-D-fructofuranose. It is best known for its role in human nutrition and is formed by plants but not by higher animals.
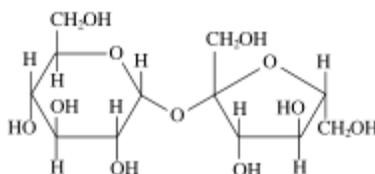

Physical and chemical properties

Pure sucrose is most often prepared as a fine, colorless, odorless crystalline powder with a pleasing, sweet taste. Large crystals are sometimes precipitated from water solutions of sucrose onto a string (or other nucleation surface) to form rock candy, a confection.

Like other carbohydrates, sucrose has a hydrogen to oxygen ratio of 2:1. It consists of two monosaccharides, Î±-glucose and fructose, joined by a glycosidic bond between carbon atom 1 of the glucose unit and carbon atom 2 of the fructose unit. What is notable about sucrose is that unlike most polysaccharides, the glycosidic bond is formed between the reducing ends of both glucose and fructose, and not between the reducing end of one and the nonreducing end of the other. The effect of this inhibits further bonding to other saccharide units. Since it contains no free anomeric carbon atom, it is classified as a nonreducing sugar.

Sucrose melts and decomposes at 186 °C to form caramel, and when combusted produces carbon, carbon dioxide, and water. Water breaks down sucrose by hydrolysis, however the process is so gradual that it could sit in solution for years with negligible change. If the enzyme sucrase is added however, the reaction will proceed rapidly.

Reacting sucrose with sulfuric acid dehydrates the sucrose and forms elemental carbon, as demonstrated in the following equation:

$C_{12}H_{22}O_{11} + H_2SO_4$ catalyst --->12 C + 11 H_2O
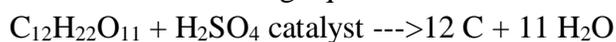
Sugar Manufacture Process

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Juice extraction from cane
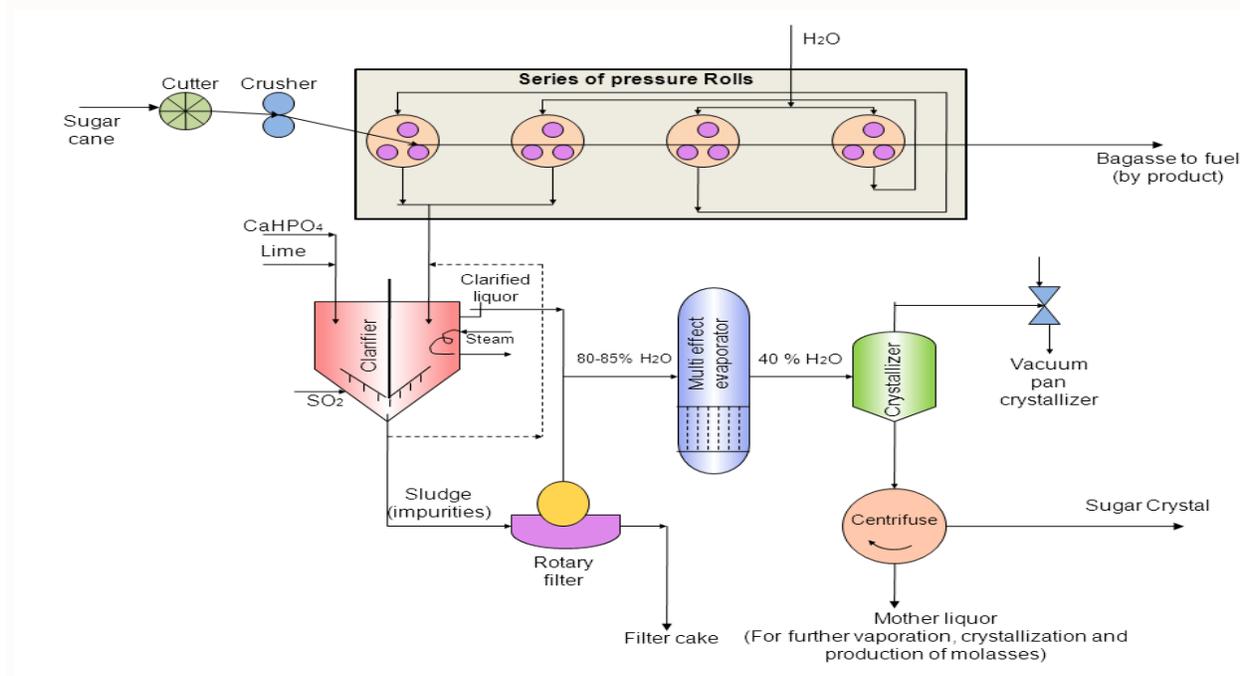
Flow sheet of manufacture of sugar from sugarcane

Sugar cane

The cane plant consists of a stalk, roots, growing leaves, the remains of dead leaves, and a growing leafy top. The typical composition of cane is as follows:

- 15% dissolved matter (13% sucrose; 2% are other sugars -mainly glucose and fructose)
- 15% fibre (insoluble), and
- 70% water.

For every 100 tons cane crushed, 30 tons of fibrous residue (bagasse), and about 12 tons sugar and 4 tons molasses are made.

The farmers transport the cane *stalks* (i.e. cane without roots, without leaves and without tops) to the sugar mill in specially designed vehicles that facilitate easy loading and offloading.

Cane preparation

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Juice can be removed from cane either by repeated crushing and washing (milling) or by washing alone, with a final squeezing simply to dry the spent fibre (diffusion). Better sucrose extraction can be obtained by crushing finely shredded cane rather than intact stalks and "Preparation" refers to that step in which cane is finely shredded before juice is extracted either by milling or diffusion. Cane is prepared by passing it through one or two sets of cane knives and then through a shredder.

Milling

A basic cane mill consists of three grooved rollers. Prepared cane is squeezed between the rollers, thus forcing the juice out of the fibre.

The basic work of a mill is the separation of juice from fibre. Fibre, however, has the natural property of always retaining approximately its own weight of juice regardless of the pressure applied to it. To displace retained juice, water is poured onto the cane fibre before crushing. This is called imbibition.

A single milling unit would give an unacceptably low extraction. Typically, six mills are set in tandem and cane is passed in series from Mill 1 to Mill 6.

Diffusion

A diffuser is an enclosed carrier through which a bed of prepared cane is slowly dragged, while copious quantities of water and juice percolate through the bed to wash out the sucrose -bearing juice.

The fibre leaving the diffuser is saturated with liquid and has to be dewatered in a mill before being sent either to the boilers or to by-product processes.
Purification of juice

Juice from a milling tandem contains a large amount of cane fibre that falls out with the juice between the rollers of the mills. To remove the fibre, juice is poured over a wire-mesh screen, or cascaded over an inclined wedge-wire screen). Diffuser juice, because of the screening effect of the cane bed itself, is generally not screened.

The juice is heated and lime is added to neutralise the natural acidity. It is then placed in a large settling tank called a clarifier The purpose of clarification is to produce a clear juice that is light in colour and free of suspended matter. To improve the precipitate formation, flocculent is added.

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The settled precipitate, referred to as mud, is pumped out of the trays of the clarifier and sent to the filtration station where the juice it contains will be recovered. If a diffuser is used, it is sent to the diffuser and filtered through the bed of bagasse.

Crystal growth

Evaporation

Before crystal growth can take place the clear juice must be concentrated to syrup by the removal of water by evaporation. To improve the efficiency of the water removal step a process known as multiple effect evaporation is used. Multiple effect evaporation is the scheme where juice is boiled in series in several vessels, with steam fed to vessel 1 only. Vapour from vessel 1 boils the juice in vessel 2, vapour from 2 boils the juice in 3, and so on until vapour from the final vessel goes to waste.

Sugar boiling

The syrup produced by the evaporators is concentrated further in specially designed vessels known as pans. As the concentration rises the dissolved sugar crystallises and the work of the pans is to grow sugar crystals (from the sucrose in syrup) in several steps to maximise the amount of sucrose recovered in raw sugar.

This is typically done in three boiling steps; each step producing, after crystal/molasses separation, A-sugar and A-molasses, B-sugar and B-molasses, and C-sugar and C-molasses or final molasses.

Supersaturation is the "driving force" in all sugar boiling. Supersaturation is controlled by adding water or syrup to massecuite (crystal / molasses mixture) and by controlling the temperature.

When the massecuite is discharged from the pans it is retained in stirred tanks called crystallisers, where the sugar crystals continue to grow through cooling rather than boiling. Separation of crystals from molasses

Massecuite leaving the crystallisers has now to be separated into crystals and molasses. The more efficient this separation, the more sucrose will be recovered as sugar and the less sucrose will be lost in molasses. A centrifugal is a machine that separates crystals from molasses. Centrifugation involves spinning massecuite in a perforated basket; centrifugal force acts on the molasses, forcing it through the perforations while the sugar remains on the basket wall. Water and steam may then be sprayed onto the crystals to wash off the remaining molasses.

Sugar drying

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Sugar leaving the centrifugals has excess moisture which has an extremely detrimental effect on the keeping quality of the raw sugar and drying is therefore important. In a drier, the moisture is driven off from the surface of the liquor layer covering the crystal by passing heated air around the sugar crystals.

The product from the process described so far is a raw sugar (Brown sugar) that can be used as is, or sent to a refinery to be converted to a white (refined) sugar.

Sugar refining

The purpose of the refinery is to remove impurities from sugar crystals. The refinery accepts raw sugar as its feed material. The sugar is dissolved (melted) and the colour is removed by various clarification processes.

Re-crystallisation (from a higher purity mother liquor) is alone responsible for a considerable amount of colour removal but other techniques must be employed to obtain the low colour levels of white sugar. Tongaat Hulett uses two colour removal processes before the crystallisation and these are carbonatation and ion exchange.

In carbonatation lime and CO^2 (carbon dioxide) gas are added to the melt to form a calcium carbonate precipitate. This precipitate absorbs colour, is removed by filtration. Further colour is then removed by ion exchange. Resin beads are held in tanks through which the liquor is allowed to percolate under pressure.

The purified melt is evaporated and up to 4 crops of crystals are boiled from this. These crystals are combined to form the refined sugar product.

4. MALTOSE (MALT SUGAR) $C_{12}H_{22}O_{11}$

Preparation:

Maltose does not occur in free state in nature.

$(C_6H_{10}O_5)_n + H_2O \xrightarrow{\text{diastase}} C_{12}H_{22}O_{11}$

Starch   maltose

Structure

Maltose $\xrightarrow[\text{With dilute acids}]{\text{Hydrolysis}}$ D-Glucose
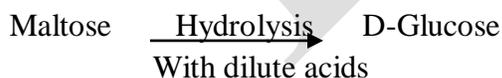
This indicates that the maltose molecule is made up of 2 glucose units.

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Glucose unit   alpha link   Glucose unit   Alpha form
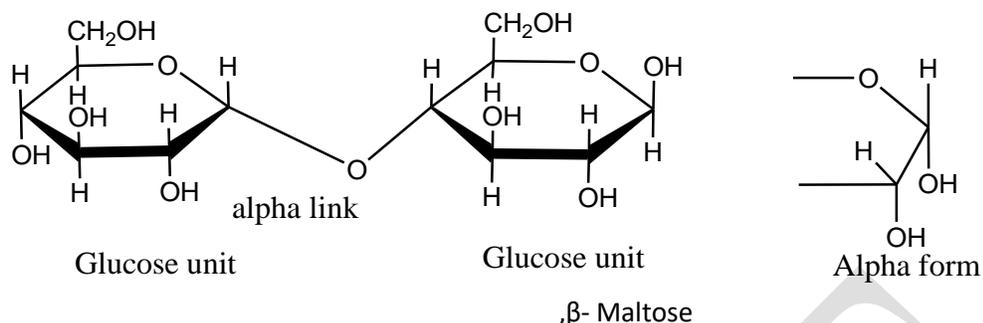
,β- Maltose

Maltose exists in α- and β- forms each of which exhibits mutarotation.

The values specific rotations are +168° for α- maltose and + 136° for the equilibrium mixture.

Properties:- (physical)

Maltose (β-form) is a colourless, odourless crystalline solid, mp : 160°-165°C.

It is soluble in water, but insoluble in alcohol or ether.

An aqueous solution of maltose is dextrorotatory and exhibits mutarotation.

Chemical Properties:-

Maltose is a reducing sugar, Like lactose. Its reactivity is also due mainly to the presence of a free hemiacetal group in one of the glucose units of its reactivity is also due mainly to the presense of a free lemiactel group in one of the glucose units of its molecule.

1. Oxidation

Maltose (aldehyde form)

Maltonic acid

2. Hydrolysis

$$Maltose \xrightarrow[\substack{or \\ enzyme\ maltose}]{hot\ dil.\ acids} D\text{-glucose}$$
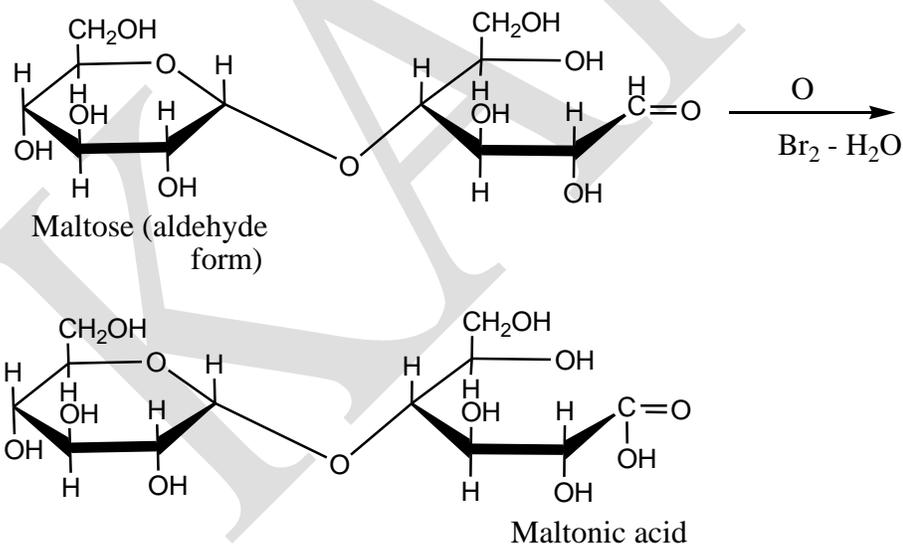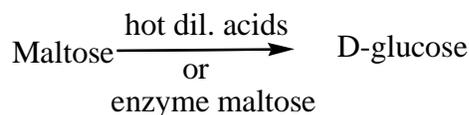
3. Reaction with Phenyl hydrazine (Osazone formation)

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$$\text{Maltose} \xrightarrow[\text{CH}_3\text{COOH}]{\overset{\text{excess}}{\underset{}{\text{C}_6\text{H}_5\text{NHNH}_2}}} \text{Maltosazone}$$
mp 206°C
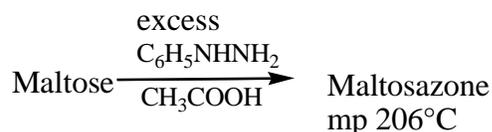
4. Reaction with acetic anhydride (Acetylation)

$$\text{Maltose} \xrightarrow[\substack{\text{ZnCl}_2 \text{ or} \\ \text{CH}_3\text{COONa}}]{\text{acetic anhydride}}$$
alpha- maltose octaacetate
 (mp 125°C)
  and   [alpha]$_D$= +123°
beta- MaltoseOctaacetate
(mp 160°C)

              [α]$_D$= +63°

5. Fermentation :-

$$\text{C}_{11}\text{H}_{22}\text{O}_{11} + \text{H}_2\text{O} \xrightarrow{\text{Maltose}} \text{C}_6\text{H}_{12}\text{O}_6$$
glucose

$$\text{C}_6\text{H}_{12}\text{O}_6 \xrightarrow{\text{Zyma}} 2\text{C}_2\text{H}_5\text{OH} + 2\text{CO}_2$$
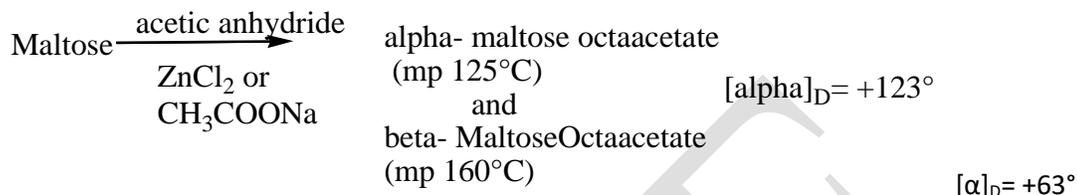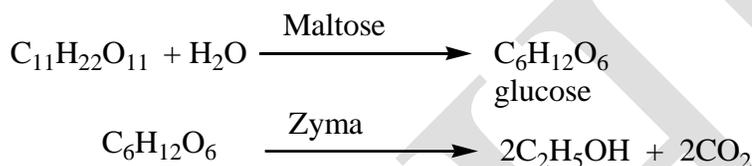
Uses

 Maltose used in infant food and in malted milk.

Polysaccharides are polymers of simple sugars

Many polysaccharides, unlike sugars, are insoluble in water. Dietary fiber includes polysaccharides and oligosaccharides that are resistant to digestion and absorption in the human small intestine but which are completely or partially fermented by microorganisms in the large intestine. The polysaccharides described below play important roles in nutrition, biology, or food preparation.

6. STARCH

Starch is the major form of stored carbohydrate in plants. Starch is composed of a mixture of two substances: *amylose*, an essentially linear polysaccharide, and *amylopectin*, a highly branched polysaccharide. Both forms of starch are polymers of **α-D-Glucose**. Natural starches contain 10-20% amylose and 80-90% amylopectin. Amylose forms a colloidal dispersion in hot water (which helps to thicken gravies) whereas amylopectin is completely insoluble.

Amylose molecules consist typically of 200 to 20,000 glucose units which form a helix as a result of the bond angles between the glucose units.

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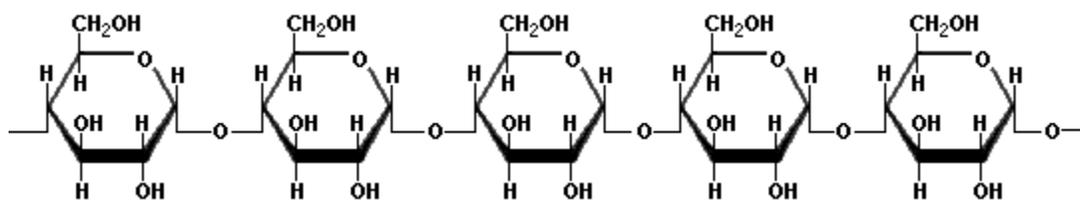
Amylose

Amylopectin differs from amylose in being highly branched. Short side chains of about 30 glucose units are attached with 1α→6 linkages approximately every twenty to thirty glucose units along the chain. Amylopectin molecules may contain up to two million glucose units.
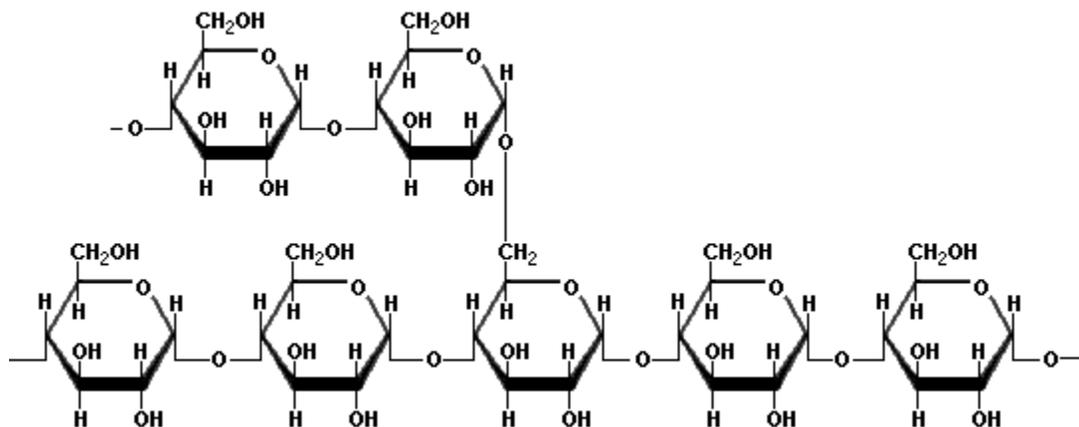
Amylopectin

The side branching chains are clustered together within the amylopectin molecule

Starches are transformed into many commercial products by hydrolysis using acids or enzymes as catalysts. Hydrolysis is a chemical reaction in which water is used to break long polysaccharide chains into smaller chains or into simple carbohydrates. The resulting products are assigned a Dextrose Equivalent (DE) value which is related to the degree of hydrolysis. A DE value of 100 corresponds to completely hydrolyzed starch, which is pure glucose (dextrose). Dextrins are a group of low-molecular-weight carbohydrates produced by the hydrolysis of

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starch. Dextrins are mixtures of polymers of D-glucose units linked by $1\alpha\rightarrow4$ or $1\alpha\rightarrow6$ glycosidic bonds. Maltodextrin is partially hydrolyzed starch that is not sweet and has a DE value less than 20. Syrups, such as corn syrup made from corn starch, have DE values from 20 to 91. Commercial dextrose has DE values from 92 to 99. Corn syrup solids, which may be labeled as soluble corn fiber or resistant maltodextrin, are mildly sweet semi-crystalline or powdery amorphous products with DEs from 20 to 36 made by drying corn syrup in a vacuum or in spray driers. Resistant maltodextrin or soluble corn fiber are not broken down in the digestive system, but they are partially fermented by colonic bacteria thus providing only 2 Calories per gram instead of the 4 Calories per gram in corn syrup. High Fructose Corn Syrup (HFCS), commonly used to sweeten soft drinks, is made by treating corn syrup with enzymes to convert a portion of the glucose into fructose. Commercial HFCS contains from 42% to 55% fructose, with the remaining percentage being mainly glucose. There is an effort underway to rename High Fructose Corn Syrup as Corn Sugar because of the negative public perception that HFCS contributes to obesity. Modified starch is starch that has been changed by mechanical processes or chemical treatments to stabilize starch gels made with hot water. Without modification, gelled starch-water mixtures lose viscosity or become rubbery after a few hours. Hydrogenated glucose syrup (HGS) is produced by hydrolyzing starch, and then hydrogenating the resulting syrup to produce sugar alcohols like maltitol and sorbitol, along with hydrogenated oligo- and polysaccharides. Polydextrose (poly-D-glucose) is a synthetic, highly-branched polymer with many types of glycosidic linkages created by heating dextrose with an acid catalyst and purifying the resulting water-soluble polymer. Polydextrose is used as a bulking agent because it is tasteless and is similar to fiber in terms of its resistance to digestion. The name resistant starch is applied to dietary starch that is not degraded in the stomach and small intestine, but is fermented by microflora in the large intestine.

Relative sweetness of various carbohydrates

Fructose	173
Invert sugar*	120
HFCS (42% fructose)	120
Sucrose	100
Xylitol	100
Tagatose	92
Glucose	74
High-DE corn syrup	70

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Sorbitol	55
Mannitol	50
Trehalose	45
Regular corn syrup	40
Galactose	32
Maltose	32
Lactose	15

* Invert sugar is a mixture of glucose and fructose found in fruits.

7. CELLULOSE

Cellulose is a polymer of β-D-Glucose, which in contrast to starch, is oriented with -CH₂OH groups alternating above and below the plane of the cellulose molecule thus producing long, unbranched chains. The absence of side chains allows cellulose molecules to lie close together and form rigid structures. Cellulose is the major structural material of plants. Wood is largely cellulose, and cotton is almost pure cellulose. Cellulose can be hydrolyzed to its constituent glucose units by microorganisms that inhabit the digestive tract of termites and ruminants. Cellulose may be modified in the laboratory by treating it with nitric acid (HNO₃) to replace all the hydroxyl groups with nitrate groups (-ONO₂) to produce cellulose nitrate (nitrocellulose or guncotton) which is an explosive component of smokeless powder. Partially nitrated cellulose, known as pyroxylin, is used in the manufacture of collodion, plastics, lacquers, and nail polish.
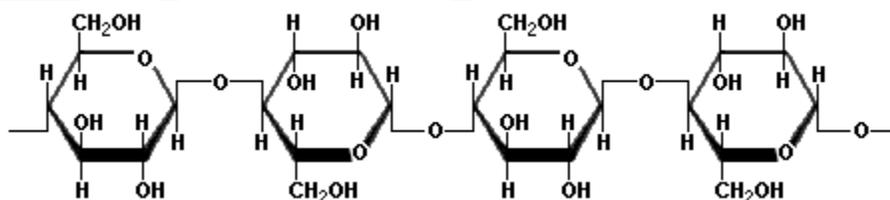
Cellulose

MUTAROTATION

Mutarotation can be defined as the change in optical rotation that is observed when a reducing sugar is dissolved in water, due to the formation of different tautomeric forms. A sugar crystal will consist of molecules having a specific anomeric ring form (furanose or pyranose with _-

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or _-configuration). Upon dissolution, ring opening (hydrolysis) and subsequent ring closure will occur, producing the _- and _-pyranose and _- and _-furanose forms. These forms have different chemical and physical properties (e.g., optical rotation, solubility, chemical reactivity, relative sweetness, etc.). Figure 3.1 shows the five forms of D-glucose that will theoretically exist in solution. For glucose, only the _- and _-pyranose forms exist in significant amounts. _-D-Glucopyranose has an "initial" optical rotation of +112◦, whereas _-D-glucopyranose has an "initial" rotation of free energy. _-D-Glucopyranose has the greatest stability and predominates by being present at 63.6% at equilibrium at 20◦C. Glucose is classified as undergoing "simple" mutarotation since,for practical purposes, only two tautomers are present.

## INTERCONVENTION OF SUGARS:
SYNTHESIS AND INTERCONVERSIONS OF MONOSACCHARIDES:

By means of the following methods it is possible to convert one monosaccharide into another. These interconversions are important for two main reasons.: they are used in determining the relative configurations of monosaccharides, and they also provide routes to compounds which are unknown or very rare in nature.

(1) Conversion of an Aldose in to the next higher Aldose:

(a). Killiani-Fisher Cyanohdrin Synthesis:

The aldose is first allowed to react with HCN. This process introduces a new asymmetric centre and results in the formation of two cyanohydrins (aldononitriles). It should be noted that these cyanohydrins differ only inconfigurationabout the newly introduced asymmetric carbon atom (carbon number 2), and are therefore, epimers. These cyanohydrins are next hydrolysed with dilute acid to give the corresponding aldonic acids. The aldonic acids on heating lose a molecule of water to give γ-lactones (1,4-aldonolactones). These γ-lactones are solids and are separated by fractional crystallization. The individual lactonescan then be reduced with lithium aluminium hydride or sodium amalgam in a weakly acidic solution to give aldoses which contain one more carbon atoms than the original aldose. Thus D-arabinose may be converted into D-glucose and D-mannose as follows.

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D-arabinose
(an aldopentose)

New asymmetric centre

D-gluconitrile   D-mannonitrile H_2O/H^+

D-gluconic acid   D-mannonic acid   Heat -H_2O *Y-D-gluconolactone*   *Y-D-mannanolactone*

Y-D-gluconolactone $LiAlH_4$ or Na-Hg/H^+ D-glucose(aldohexose)

Y-D-mannanolactone $LiAlH_4$ or Na-Hg/H^+ D-mannose(aldohexose)

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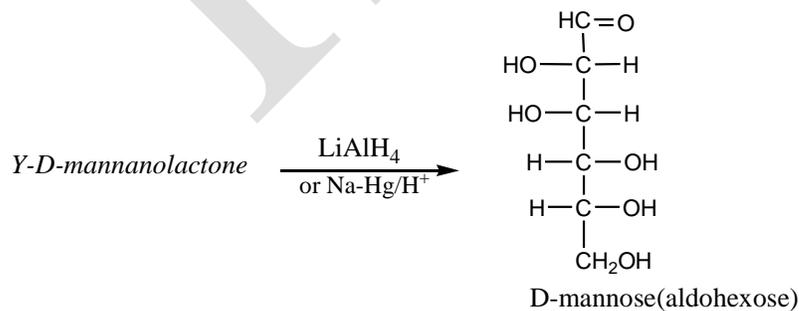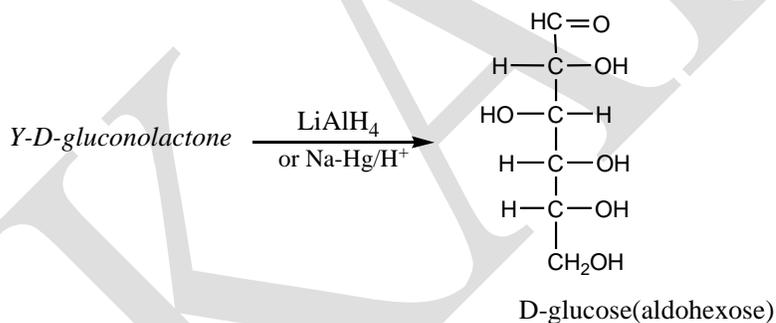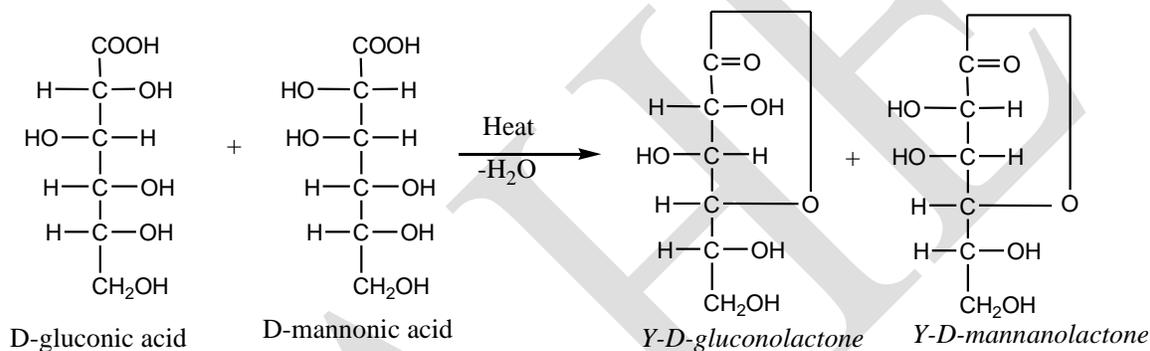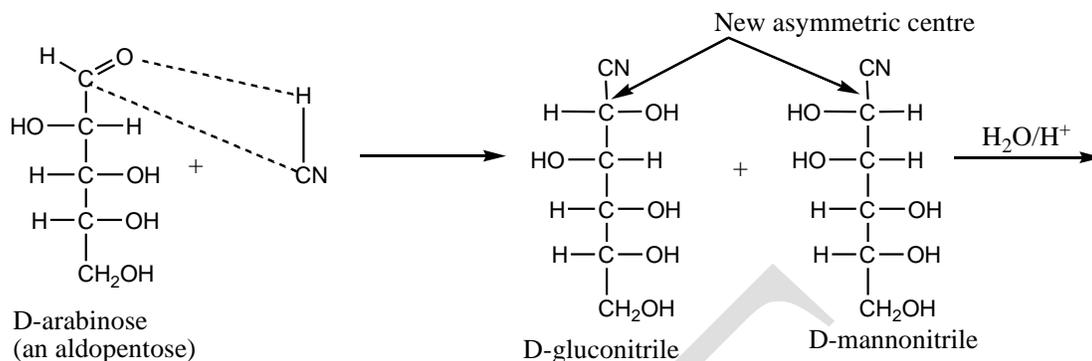
(b). Swoden-Fischer Nitromethane Synthesis:

This is a more recent method and involvesthe reaction of an aldose with nitromethane in the presence of a base. This process introduces a new asymmetric centre and results in the formaton of two different nitroalcohols, which are separated by fractional crystallization. The individual nitroalcohola are next treated with NaOH solution to give the corresponding sodium salts, which may then be decomposed to givethe higher aldoses. Thus , D-glyceraldehyde may be converted in to D-erythrose and D-threose
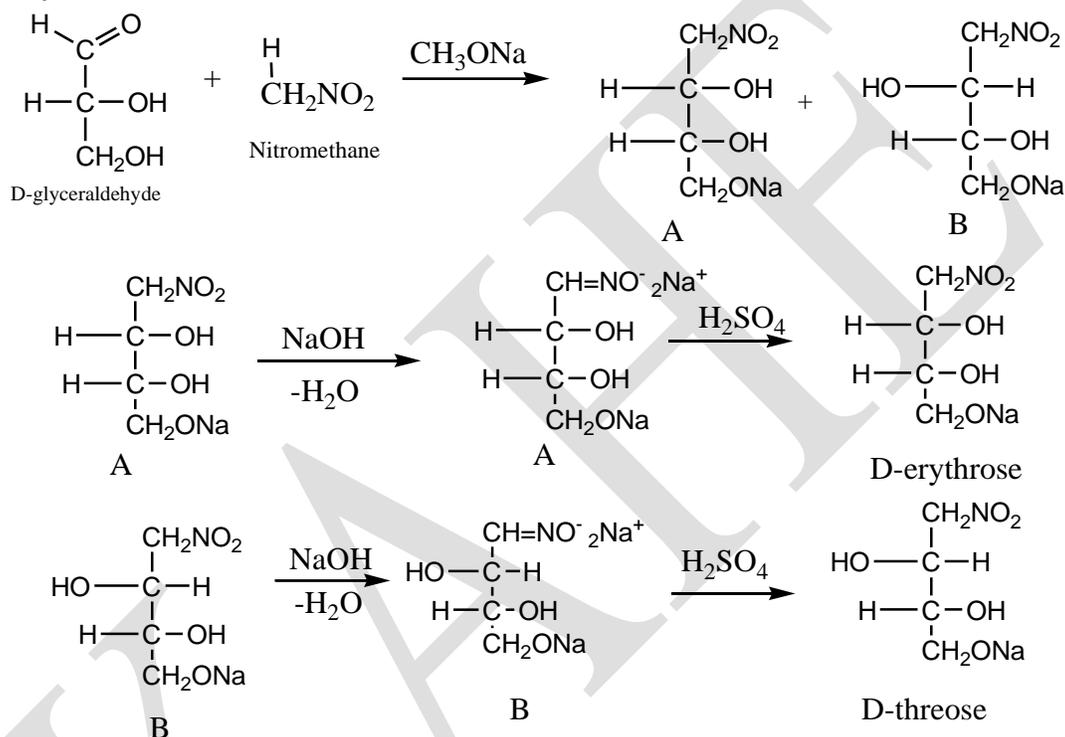
(2).Conversion of the Aldose in to the next lower Aldose:
(a). Wohl's Method:

In this method the aldose is first treated with hydroxylamine to give the corresponding aldoxime. The aldoxime is next warmed with acetic anhydride in the presence of zinc chloride or sodium acetate, so that the oxime group is dehydrated and the hydroxyl groups esterified to give the acetylated aldononitrile. This is next warmed with ammoniacal silver oxide, so that the acetyl groups are removed by hydrolysis and a molecule of hydrogencyanide is eliminated to give an aldose having one carbon atom less than the original aldose. Thus D-glucose may be converted into D-arabinose as indicated below.

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D-glucose → D-glucose oxime → D-gluconitrile pentaacetate

D-arabinose
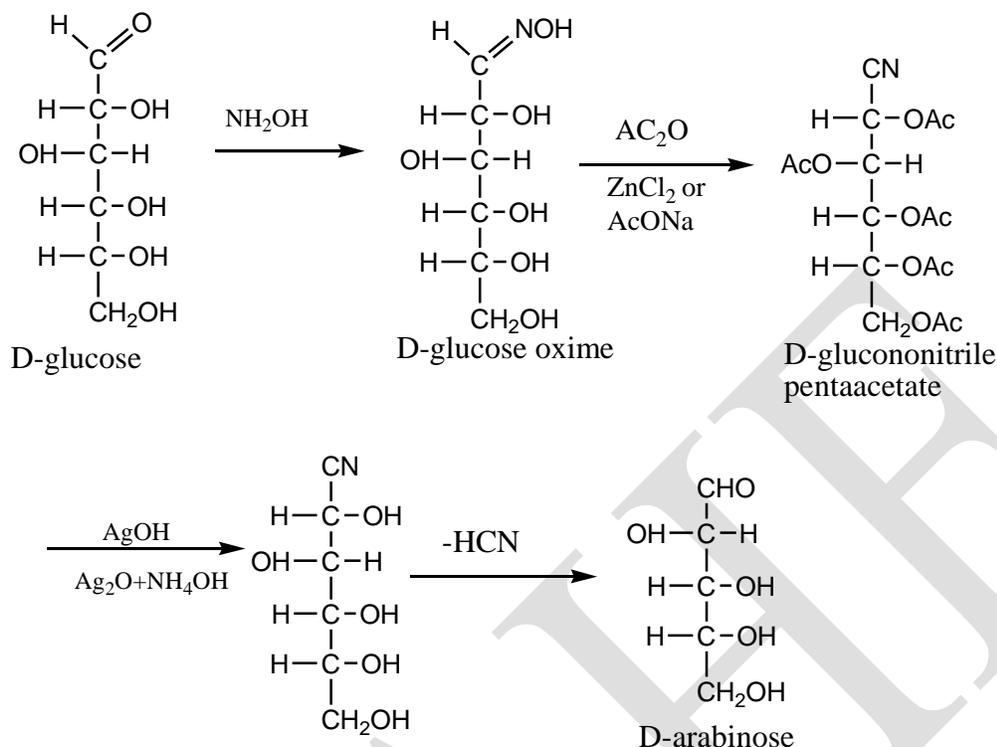
(b). Ruff's Method:

In this method the aldose is first oxidized with bromine water to give the corresponding aldonic acid. The aldonic acid is next treated with calcium carbonate to givethe calcium salt of acid. This is ten treated with hydrogen peroxide and ferric acetate (Fentons's reagent), so that CO_2 and H_2O are eliminated to give the next lower aldose. Thus D-glucose may be converted into D-arabinose as shown below.

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D-glucose → (Br$_2$/H$_2$O) → D-gluconic acid → (Ca^{2+}CO$_3^{2-}$) → Calcium D-gluconate

(H$_2$O$_2$ / Fe(OCOCH$_3$)$_3$) → D-arabinose + CaCO$_3$ + H$_2$O
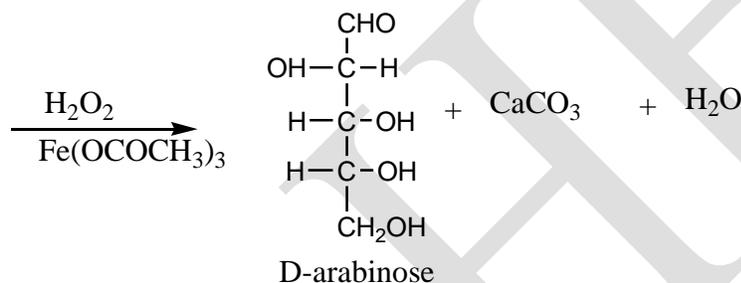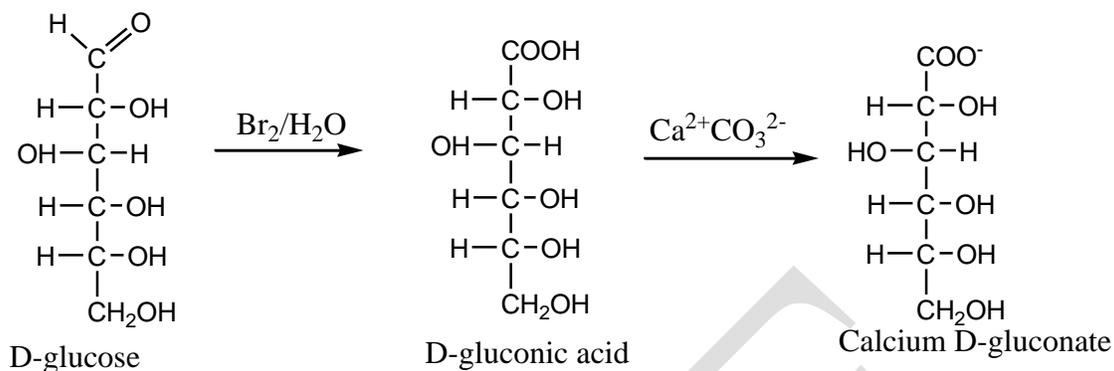
(3). Conversion of Aldose in to next higher Ketose:
Wolfrom's Method:

In this method the aldose is oxidisedto the corresponding aldonic acid, which is acetylated with acetic anhydride. The acetylated aldonic acid is then treated with thionylchloride or PCl$_5$ to give the corresponding acid chloride. Treatment of this with diazomethane followed by heating with aqueous acetic acid and, finally, deacetylation by alkaline hydrolysis to gives next higher ketose. Thus, D-arabinose may be converted in to D-fructose as follows.

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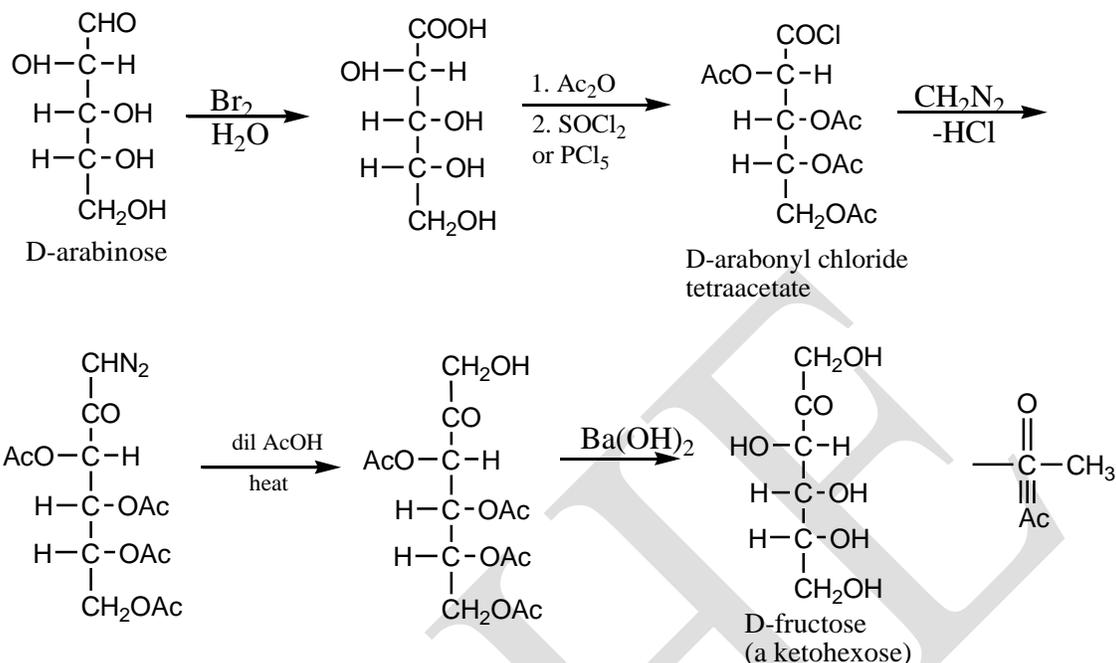
(4). Conversion of Aldose in to corresponding Ketose:

The aldose is first allowed to react with excess phenylhydrazine to give the corresponding osazone. The osazone is next hydrolysed with dilute hydrochloride acid to give the ozone. This is then redused with zinc and glacial acetic acid to give ketose which is isomeric with the original aldose. It should be noted that in glacial acetic acid , zinc reduces the aldehyde group in preference to the ketone group. Thus D-glucose may beconverted into D-fructose as follows.
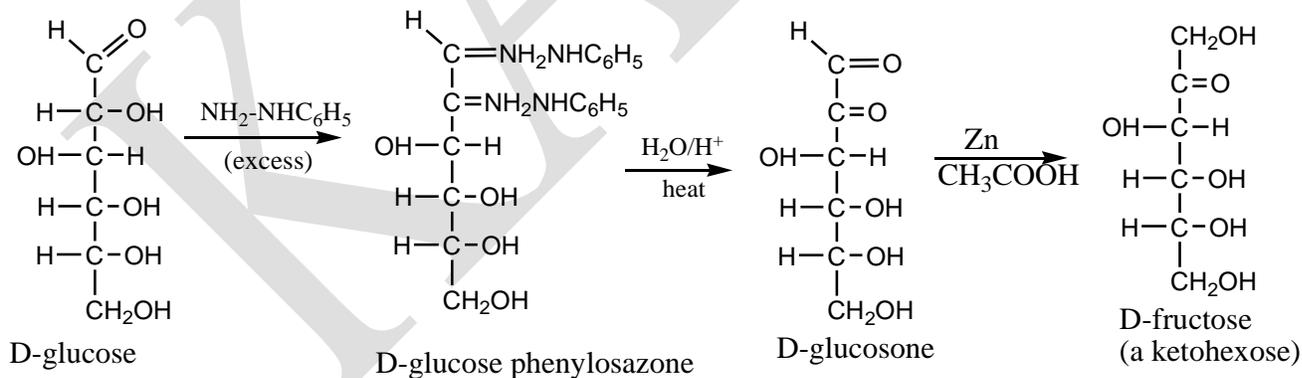

(5). Conversion of Ketose into the corresponding Aldose:

The ketose is first reduced with sodium amalgam in the presence of a trace of acid. This process introduces a new asymmetric centre and results in the formation of two different polyhydric alcohols. These alcohols are next oxidized with nitric acid to give the corresponding monobasic

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aldonic acids. The aldonic acids on treatment with dilute HCl give γ-lactones. These lactones are solids, and are separated by fractional crystallization. The individual lactones are then reduced with lithium aluminium hydride or sodium amalgam in a weakly acidic solution to yield aldoses which are isomeric with original ketose. The D-fructose may be converted in to D-glucose and D-mannose as shown below.
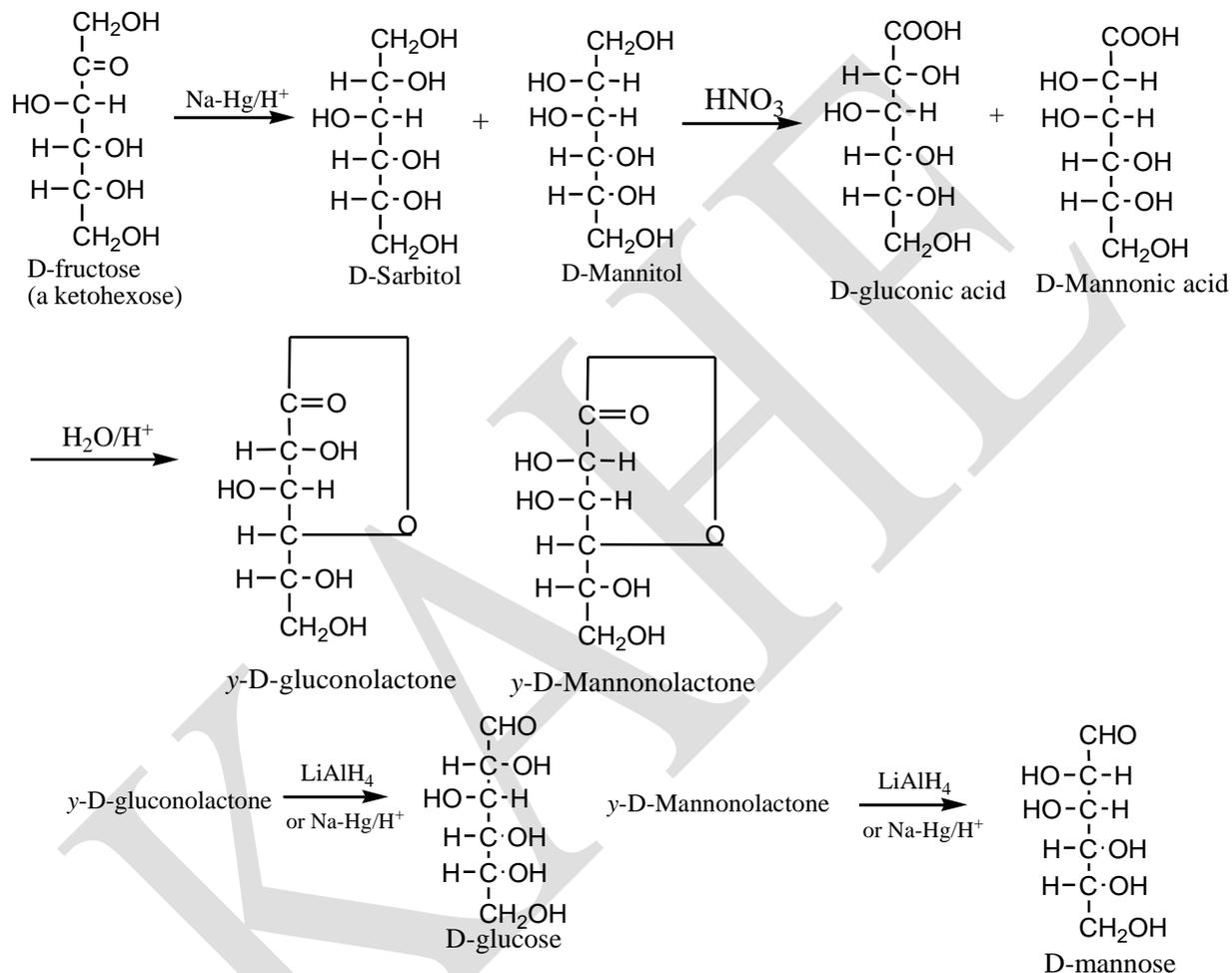
(6). Conversion of Aldose in to its Epimeric Aldose: (Epimerisation)

The aldose is first oxidized with bromine water to give the corresponding aldonic acid, which is then heated in aqueous pyridine or quinoline to give an equilibrium mixture of the original acid and its isomer. These isomeric aldonic acids are identical in all respects expect for the configuration about the asymmetric carbon number 2. They are, therefore, epimers (or more precisely C-2-epimers). These acids are next converted in to lactones. Separated and reduced to the original aldose and its C-2-epimer. Thus D-glucose may be converted into D-mannose as shown below.

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This change of configuration of one asymmetric carbon atom in a compound containing two or more asymmetric carbon atoms is known as epimerization.

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POSSIBLE QUESTIONS

PART-A (One Mark)

(Multiple Choice Questions)
1.On warming with glucose, a silver mirror is formed by
a.Fehling's solution   b.Benedict's solution
c.Barfoed's reagent   d.Tollen's reagent

2. Fehling's solution and Benedict's solution are reduced by glucose to form
a.CuO   **b.Cu_2O**   c.$Cu(OH)_2$ d.CuO_2

3. The sugar which will not reduce Fehling's solution is
a. maltose   b.lactose   **c.sucrose**   d.glucose

4. Glucose on oxidation with bromine ater gives
a.tartaric acid   b.glutaric acid   **c.gluconic acid**   d.glycollic acid

5. The number of asymmetric carbon atom in glucose is
a.2   b.3   **c.4**   d.5

6. Which of the following statement concerning glucose is incorrect
a.it has 4 asymmetric c-atoms   b.it is an aldehyde
c.itisoptically active   **d. it is a disaccharide**

7. The fact that(+) glucose and (+)mannose yield the same osazone shows that
a.they are optical isomers   b. both are aldoses
c.(+) mannose is same as (+) glucose   **d.they are epimers**

8. Sucrose on hydrolysis gives
a.2 molecules of glucose
b.2 molecules of fructose
c. 1molecule each of glucose and fructose

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CLASS   : II B.Sc CHEMISTRY
COURSENAME :ORGANIC CHEMISTRY-IV(ORGANIC SPECTRASCOPY)
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d. 1 molecule each of glucose and mannose

9. Common table sugar is
a. glucose   **b.Sucrose**   c.fructose   d. Maltose

10. An example of a trisaccharide is
a.starch   b.cellulose   **c.raffinose**   d.maltose

PART-B (Two Mark)

1. Define carbohydrates.
2. What are disaccharides? Write the ring structure of lactose.
3. Draw the structures of starch and cellulose indicating their point of difference.
4. Write a short note on mutarotation.
5. How will you convert an aldohexose into a ketohexose?
6. What are reducing and non-reducing sugars? Give an example in each case.
7. Describe Ruff's Degradation.
8. Write note a on anomers and epimers.
9. Write a note on Killiani-Fischer synthesis.
10. Draw the Haworth formulae of Sucrose.
11. What is an anomeric carbon? Give suitable example.
12. Write the uses of cellulose and Starch.

PART-C (6 MARKS)

Either or Type Questions

1. Explain the following:
    (i). Killiani synthesis   (ii) Epimerization
    (iii)Sucrose does not show mutarotation
2.Explain the following:
     (i) Mutarotation   (ii) Epimerization   (iii) Ruff's Degradation in
aldoses.
3. Write notes on   (i) Killiani-Fischer synthesis   (ii) Ruff's Degradation
    (iii) Formation of glycosides.
4. Draw the Haworth formulae of;
    (i) α-D-Glucose   (ii) β-D-Fructose   (iii) Sucrose   (iv) Lactose

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5. Giving suitable examples, write an account of the classification of carbohydrates.

6. Explain the ring size of D-Glucose and fructose.

7. How will you convert an aldohexoses into aldopentose.

8. Describe the manufacture of Sugar beet. How does Sucrose react with (i) lime water (ii) acetic anhydride (iii) yeast (iv) Conc. HNO_3 and (v) Conc. and hot H_2SO_4?

9. Discuss the Structure of Glucose.

10. Discuss the Structure of Maltose

11. Discuss the Structure of Cellulose.

12. Give the conversion of an Aldose into the next lower Aldose by (1) Wohl's Method (2) Ruff's Method.

13. Discuss the structure of D-Fructose.

14. Give the conversion of the Ketose in to the corresponding Aldose.

SUBJECT : Organic Chemistry -IV (Organic Spectroscopy)
Subject Code : **16HCU403**
Class : **II B.Sc Chemistry**
Staff Name : **Dr.M.Makeswari and Mr. R Kumar**
Batch : **2016-2018 Batch**

UNIT-IV
Multiple choice Questions (Each Carry One mark)

Question	Option 1	option 2	Option 3	Option 4	Answer
On warming with glucose, a silver mirror is formed by	a.Fehling's solution	b.Benedict's solution	c.Barfoed's reagent	d.Tollen's reagent	Fehling's solution
Fehling's solution and Benedict's solution are reduced by glucose to form	a.CuO	b.Cu2O	c.Cu(OH)2	d.CuO2	Cu2O
The sugar which will not reduce Fehling's solution is	a. maltose	b.lactose	c.sucrose	d.glucose	sucrose
Glucose on oxidation with bromine ater gives	a.tartaric acid	b.glutaric acid	c.gluconic acid	d.glycollic acid	gluconic acid
The number of asymmetric carbon atom in glucose is	a.2	b.3	c.4	d.5	4
Which of the following statement concerning glucose is incorrect	a.it has 4 asymmetric c-atoms	b.it is an aldehyde	c.itisoptically active	d. it is a disaccharide	it is a disaccharide
The fact that(+) glucose and (+)mannose yield the same osazone shows that	a.they are optical isomers	b. both are aldoses	c.(+) mannose is same as (+) glucose	d.they are epimers	they are epimers
Sucrose on hydrolysis gives	a.2 molecules of glucose	b.2 molecules of fructose	c. 1molecule each of glucose and fructose	d. 1 molecule each of glucose and mannose	one molecule each of glucose and fructose
Common table sugar is	a. glucose	b.Sucrose	c.fructose	d. Maltose	Sucrose
An example of a trisaccharide is	a.starch	b.cellulose	c.raffinose	d.maltose	raffinose
An organic compound insoluble in water is	a.glucose	b.cellulose	c.sucrose	d.fructose	cellulose
The carbohydrate which has an extremely high molecular weight (macomolecule) is	a.cellulose	b.maltose	c.cellobiose	d.lactose	cellulose
Which one of the following is non reducing carbohydrate?	a.lactose	b.maltose	c.sucrose	d.glucose	sucrose
Carbohydrates are characterized by the presence of	a.OH group	b.C=O group	c.Asymmetric carbon	d.all of these	all of these
How many isomeric aldohexoses are possible for the molecular Formula C6H12O6?	a.2	b.4	c.8	d.16	16
Both glucose and mannose can be prepared by Killiani synthesis from	a.D-ribose	b.D-lyxose	c. D-arabinose	d.D-xylose	D-arabinose
Method used to ascend the aldoses series is known as	a.Ruff degradation	b.Wolf's degradation	c.Killiani synthesis	d.Zemplen's modification	Killiani synthesis
Monosaccharides undergo reversible isomerisation in the presence of dilute alkali.This reaction is	a.Mutarotation	b.Lobry de-Bruynand Albedra Van Ekenstein rearrangement	c.Killiani synthesis	d.wood's synthesis	Lobry de-Bruynand Albedra Van Ekenstein rearrangement

Question	a	b	c	d	Answer
Which one of the following is not a polysaccharide?	a.cellulose	b.sucrose	c.Amylose	d.Inulin	Sucrose
Epimers differ in configuration at	a.C-1carbon	b.C-2 carbon	c.C-3 carbon	d.C-3 carbon	C-2 carbon
A freshly prepared solution of glucose has specific rotation of +112 ° but on keeping for some time it changes to +52.7°. This phenomenon is known as	a.Mutarotation	b.Epimerization	c.Racemisation	d.Resolution	Mutarotation
The specific rotation for identification of carbohydrate is	a.Molisch's test	b.Tollen's test	c.Fehling's test	d.Benedicts test	Molisch's test
Glucose does not restore the pink colour of Schiff's reagent. It is due to	a. aldehyde involvedin hemiacetal formation	b.no aldehyde group	c.-I effect of -OH group	d.keto group	aldehyde involvedin hemiacetal formation
The reagent which can be used to distinguish between starch and cellulose is	a.Tollen's test	b.Iodine solution	c.acetic anhydride	d.Fehling's reagent	Iodine solution
Isomers differs in configuration at asymmetric carbon due to hemiacetal ring formation are known as	a.Epimers	b.conformers	c.Anomers	d.Tautomers	Anomers
Fructose is leavorotatory yet it is written as D-fructose. This 'D' indicates	a.specific rotation	b.Generic relationship to D-glyceraldehyde	c.Mutarotation	d.Resolution	Generic relationship to D-glyceraldehyde
Invert sugar is	a.Sucrose	b. Mixture of Glucose+Fructose	c.Mannose	d.D-xylose	Mixture of Glucose+Fructose
Hydrolysis of D-Lactose gives	a.Glucose+Galactose	b.Galactose+Fructose	c.Glucose +Fructose	d.Only glucose	Glucose+Galactose
Synthetic silk known as viscose rayon is	a.Cellulose acetate	b.Regenerated cellulose	c.Cellulose nitrate	d.Nitrated starch	Regenerated cellulose
which one of the following disaccharide on hydrolysis gives only glucose units.	a. maltose	b.sucrose	c.lactose	d.Amylose	maltose
Methylation of sucrose gives	a.Tetramethyl derivative	b.Octamethyl derivative	c.Monomethyl derivative	d.Dimethylderivative	Octamethyl derivative
Acetylation of fructose gives	a.Monoacetyl derivative	b.Diacetyl derivative	c.Triacetyl derivative	d.Pentaacetyl derivative	Pentaacetyl derivative
The conversion of aldohexose into aldopentose is	a.Ruff degradation	b.Wolf's degradation	c.Killiani synthesis	d.wood's synthesis	Wolf's degradation
The molecular formula of sucrose is	a. C10 H22 O11	b.C12 H22 O11	c.C6 H12O6	d.C11 H22 O12	C12 H22 O11
Which one of the following aldopentoses yield a mixture of glucose and mannose in killiani hologation?	a.D-ribose	b.D-lyxose	c.D-xylose	d. D-arabinose	D-xylose
Which one of the following compound is leavorotatory compound?	a.Fructose	b.glucose	c.Mannose	d.cellulose	Fructose
Acetylation of glucose gives	a.Monoacetyl derivative	b.Diacetyl derivative	c.Triacetyl derivative	d.Pentaacetyl derivative	Pentaacetyl derivative
When fructose heated with conc.HCl, it gives	a.Tartaric acid	b.Glycollic acid	c.Trihydroxyglutaric acid	d.Laevulinic acid	Tartaric acid
Which one of the following tests is used to distinguish fructose from glucose?	a.Pinoff's test	b. Selivanoff's test	c.furfural test	d.Xanthoprotic test	Selivanoff's test

The digesion of proteins involves their	a.Tartaric acid	b.Succinic acid	c.Oxalic acid	d.Laevulinic acid Oxalic acid
The disaccharide present in milk is	a.Maltose	b.Lactose	c.sucrose	d.cellbiose Lactose
Glucose react with X number of molecules of phenylhydrazinen to yield osazone. The value of 'X' is	a.Three	b. Two	c.One	d.Four Three
Glucose forms many derivatives.The derivative which will help to prove the furanose structure is	a.Osazone	b.benzoyl	c.acetyl	d. isopropylidine isopropylidine
Which enzyme breaks sucrose into glucose and fructose?	a.Zymase	b.Maltase	c.Diastase	d.Invertase Invertase
A sugar that is not a disaccharide among the following is	a.Lactose	b.Galactose	c.Sucrose	a.Maltose Galactose
α-D(+) glucose and β-D(+) glucose are	a.Enantiomers	b.Geometrical isomers	c.Epimers	d.Anomers Anomers
Mutarotation does not occur in	a.sucrose	b.D-glucose	b.glucose	b.L-glucose sucrose
Complete hydrolysis of cellulose gives	a.L-glucose	b.D-fructose	c.D-ribose	d.D-glucose D-glucose
How many stereoisomers can an aldotetrose have?	a.2	b.4	c.6	d.8 4
How many stereoisomers can an aldopentose have?	a.12	b.8	c.6	d.4 8
In the fischer projection of D-glyceraldehyde,the-OH on thechiral carbon is drawn	a.to the left	b.above	c.below	d.to the right to the right
What is the approximateequilibrium concentration of the open chain formof D-glucose in an aqueous solution?	a. 2%	b.20%	c.90%	d.0.02% 0.02%
What is the structural relationship between the osazones of D-glucose and D-fructose?	a. They are epimers	b.They are enantiomers	c.They are anomers	d.They are identical They are identical
In maltose, the glucose molecules are connected by	a.β-1,4-glycosidic bond	b.α-1,6-glcosidic bond	c.1,2 -glycosidic bond	d.α-1,4-glcosidic bond α-1,4-glcosidic bond
In amylopectin, the glucose molecules are connected by	a.β-1,4-glycosidic bond	b.α-1,6-glcosidic bond	c.α-1,4-glcosidic bond	d.α-1,4-glcosidic bond and α-1,6-glycosidic bonds α-1,4-glcosidic bond and α-1,6-glycosidic bonds
All of the following monosaccharides give the same osazone except	a. Galactose	b.Glucose	c.Fructose	d.Mannose Galactose
Which of the following statement is false about sucrose?	a.It is also called table sugar	b.It may be fermented by yeast to produce alcohol	It reduces Fehling's solution	It doesnot reduce Tollen's reagent It reduces Fehling's solution
α-D-Glucopyranose is a(n)	a.Hemiacetal	b.hemiketal	c.acetal	d.ketal hemiacetal
Starch	a.trisaccharide	b.is also called amylose	c.is also called amlopectin	d.is a mixture of amylose + amylopectin is a mixture of amylose + amylopectin
A reducing sugar will	a.react with Fehling's solutiontb. Not react with Fehling's test	b. not react with Fehling's solution	c.have fewer calories	d.always be a ketone react with Fehling's solutiontb.

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COURSE CODE : 16CHU403
UNIT: V (Dyes and Polymers)   BATCH-2016-2019

UNIT-V

SYLLABUS

Dyes -Classification, Colour and constitution; Mordant and Vat Dyes; Chemistry of dyeing; Synthesis and applications of: Azo dyes – Methyl orange; Triphenyl methane dyes - Malachite green and Rosaniline ; Phthalein Dyes – Phenolphthalein; Natural dyes – structure elucidation and synthesis of Alizarin and Indigotin; Edible Dyes with examples.

Polymers - Introduction and classification including di-block, tri-block and amphiphilic polymers; Polymerisation reactions -Addition and condensation -Mechanism of cationic, anionic and free radical addition polymerization; Metallocene-based Ziegler-Natta polymerisation of alkenes;
Preparation and applications of plastics – thermosetting (phenol-formaldehyde, Polyurethanes) and thermosoftening (PVC, polythene); Fabrics – natural and synthetic (acrylic, polyamido, polyester); Rubbers – natural and synthetic: Buna-S, Chloroprene and Neoprene; Vulcanization; Polymer additives; Introduction to; Biodegradable and conducting polymers with examples.

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 ($-NO_2$),

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P-quinonoid   O-quinonoid
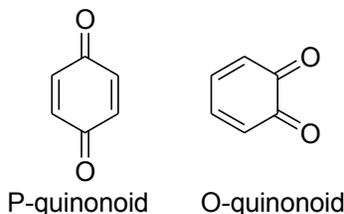
carbonyl (-C=O), thiocarbonyl (-C=S) and dicarbonyl.

Depth of the colour increases with the number of **auxochromes**.

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 colored. 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 $n \rightarrow \pi^*$ 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 ε_{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}.

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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→π*, 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→ π 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 π→π* 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 -NH₂, NR₂ 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.

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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, diazo, triazo – 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 and leather, 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

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1) Methyl orange (anionic dye)

$$(H_3C)_2N \text{—} \bigcirc \text{—} N=N \text{—} \bigcirc \text{—} SO_3Na$$
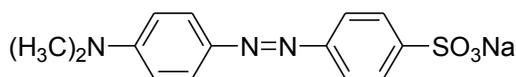
Methyl orange (anionic dye)

2) Chrysoidine (cationic dye)

$$\bigcirc \text{—} N=N \text{—} \bigcirc \text{—} \overset{+}{N}H_3 \ \overset{-}{Cl}$$
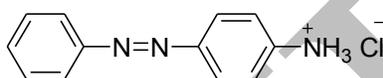
Chrysoidine (cationic dye)

3) Para red (azoic dye)

$$O_2N \text{—} \bigcirc \text{—} N=N \text{—} \text{(naphthalene ring with HO)}$$
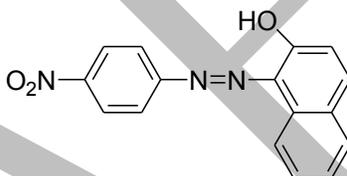
Classification according to application

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:

(structure of indigo)
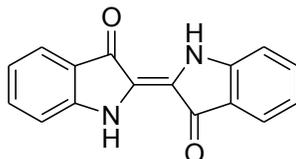
Vat dyes are used to dye cotton and are very fast, because of their insolubility in water.

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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.

Diazotised sulphanilic acid + Dimethylaniline —HCl→ Methyl orange
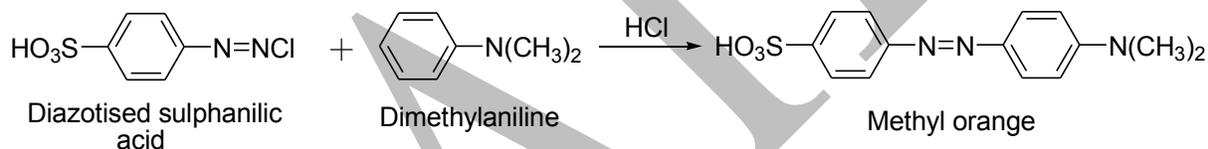
II. TRIPHENYLMETHANE DYES

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.
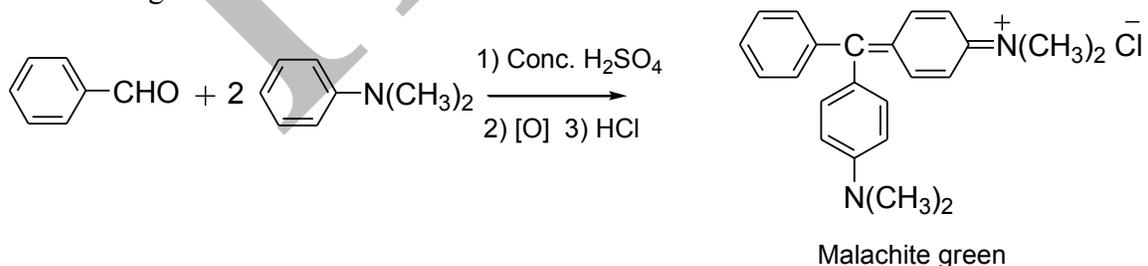
Malachite green

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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.

Aniline   Chloroacetic acid   N-phenylglycine

indoxyl   indigo
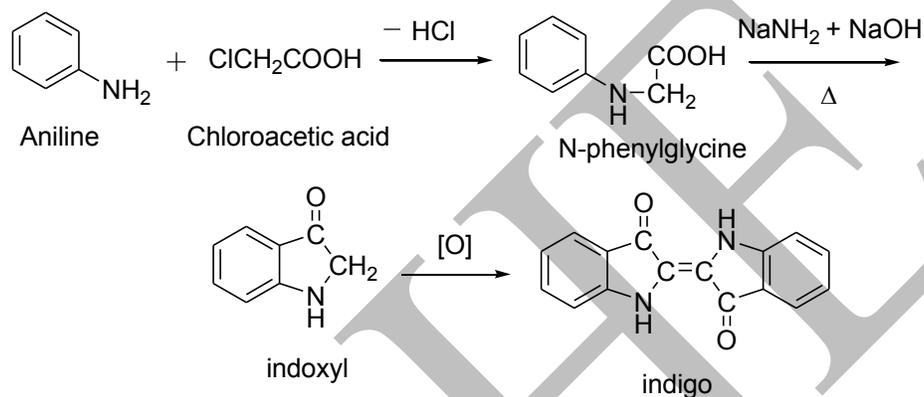
IV. MORDANT DYES

Example: Alizarin

By the condensation of catechol with phthalic anhydride to get alizarin.
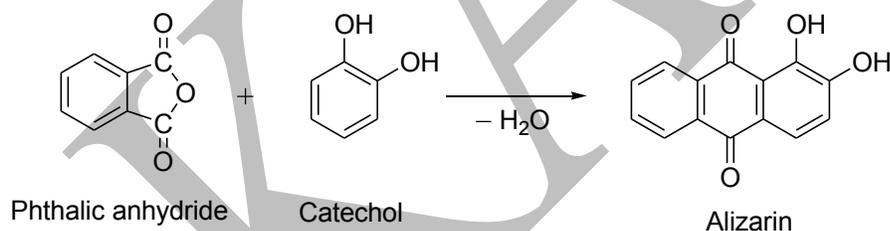
Phthalic anhydride   Catechol   Alizarin

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POLYMERS

Introduction

The **polymers** are defined as macromolecules composed of one or more chemical units (monomers) that are repeated throughout a chain.

A polymer is like a thread joins many coins punched through the center, in the end we get a string of coins, the coins would be the monomers, and the chain with the coins would be the polymer.

The basic part of a polymer are the monomers, the monomers are the chemical units that are repeated throughout the chain of a polymer, eg polyethylene monomer is ethylene, which is repeated x times along throughout the chain.

Polyethylene = ethylene-ethylene-ethylene-ethylene-ethylene-...
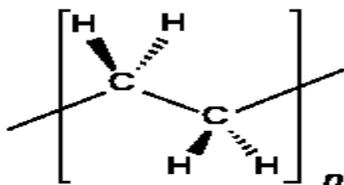
Classification of Polymers

Polymers can be classified as

1) Classification Based on Source

2) Classification Based on Structure of Polymers

3) Classification Based on Mode of Polymerisation

4) Classification Based on Molecular Forces

1) Classification Based on Source
(i) Natural polymers: The polymers which obtain by nature or natural sources like plants and animals are called natural polymers.

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Ex:- Proteins, Cellulose, Starch, Rubber etc.

(ii) Synthetic polymers: The polymers which found by laboratories or industries are called synthetic polymers.

Ex:- Polythene, Fibers, Buna–s etc.

(iii) Semi Synthetic polymers: These types of polymers formed by chemical reaction with neutral polymers.

Ex:- Cellulose acetate (rayon) etc.

2) Classification Based on Structure of Polymers

Based on structure polymers have three types.

(i) Linear polymers: In this type of polymers, monomers are joined with each other and formed long and straight chain.

These polymers have high melting points.

These polymers have high density.

Ex:- Polythene, Polyvinyl chloride, High density polythene (HDPE) etc.

(ii) Branched chain polymers: In this type of polymers, monomers are joined with each other and formed long and straight chain having some branches.

These polymers have low melting points.

These polymers have low density.

Ex:- Low density polythene (LDPE) etc.

(iii) Cross linked or Network polymers: In this type of polymers, monomers are formed from bi-functional and tri-functional monomers and contain strong covalent bonds between various linear polymer chains. These polymers are brittle in nature.

Ex:- Bakelite, Melamine etc.

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3) Based on Mode of Polymerisation

Based on polymerization polymers have two types.

(i) Addition polymers (ii)Condensation polymers

(i) Addition polymers: Theses type of polymers are formed by the repeated addition of monomer molecules.

In this reaction small particles are not eliminated like water, HCl, NH_3 etc.

In this type of polymers monomers are unsaturated hydrocarbons.

Ex: – Vinyl chloride to Poly vinyl chloride.

ii) Condensation polymers: Theses type of polymers are formed by repeated Condensation between two different bi-functional or tri-functional monomeric units.

In this reaction small particles are eliminated like water, HCl, NH_3 etc.

Ex:- Nylone – 66 is formed by condensation of Hexamethelene diamine and adipic acid.

4) Classification Based on Molecular Forces

(i) Elastomers: The polymers that have elastic character like rubber are called elastomers.

In elastomers, the polymer chains are held together by weak inter-molecular forces.

Cause of these weak forces, the polymers can be easily stretched by applying small stress and regain their original shape when the stress is removed.

Ex:- Vulcanised rubber

In this rubber polymers chains are held by sulpher cross bond.

Cause of these cross bond it can be stretched by small stress.

(ii) Thermoplastics: The polymers in which inter-molecules forces are between the elastomer polymers and fiber polymers.

These polymers are softened when it heated and hardened when it cooled.

These polymers do not have any cross bond.

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These polymers can eaily convert into any shape by heating.

Ex:- Polyetene, Polystyrene, PVC etc.

(iii) Thermosetting: Theses polymers are made by low molecular mass semi fluid substance.

These polymers can not convert in other shape by heating.

On heating, they become hard and in-fusible because these polymers have cross bond.

Ex:- Bakelit, Melamine formaldehyde, Resin etc.

(iv) Fibers: These polymers have strong inter-molecules forces between the chains.

These forces are either hydrogen bonds or dipole – dipole interaction.

Cause of these strong forces, the chains are closely packed giving high tensile strength and less elasticity.

Therefore these polymers have high melting points.

Ex:- nylone 66, Dacron, silk etc.

Block copolymers

One kind of copolymer is called a "block copolymer". Recently the terminology "block polymer" has been used. Block copolymers are made up of blocks of different polymerized monomers and is usually made by first polymerizing styrene, and then subsequently polymerizing methyl methacrylate (MMA) from the reactive end of the polystyrene chains. This polymer is a "diblock copolymer" because it contains two different chemical blocks. Triblocks, tetrablocks, multiblocks, etc. can also be made. Diblock copolymers are made using living polymerization techniques, such as atom transfer free radical polymerization (ATRP), reversible addition fragmentation chain transfer (RAFT), ring-opening metathesis polymerization (ROMP), and living cationic or living anionic polymerizations. An emerging technique is chain shuttling polymerization.

The "blockiness" of a copolymer is a measure of the adjacency of comonomers vs their statistical distribution. Many or even most synthetic polymers are in fact copolymers, containing about 1-20% of a minority monomer. In such cases, blockiness is undesirable.

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Polymerization reactions

Polymerization reactions are the set of chemical reactions in which an initiator or hardener monomer active other monomer starting a chain reaction which forms the polymer.

Consider the wick of an explosive, when approaching a heat source such as a match or a lighter, this reacts quickly burning all along the wick, in this example lighter or match would be the initiator monomer and wick burned would be the final polymer that has obtained.

The polymerization reactions are classified as:

- ➢ Radical Polymerization
- ➢ Ionic Polymerization:
- ➢ Anionic polymerization
- ➢ Cationic polymerization

Addition polymerizations

In addition polymerization, monomers react to form a polymer without the formation of by-products. **Addition polymerization**s usually are carried out in the presence of catalysts, which in certain cases exert control over structural details that have important effects on the properties of the polymer.

1. *Addition* **reaction** (sometimes called free radical addition, because an extra electron is added to the monomer to initiate the reaction). There table below shows the structures of some of the most important of these polymers (such as teflon, polyethylene, PVC, polystyrene, natural and synthetic rubber). The monomer usually contains a double bond, e.g.,
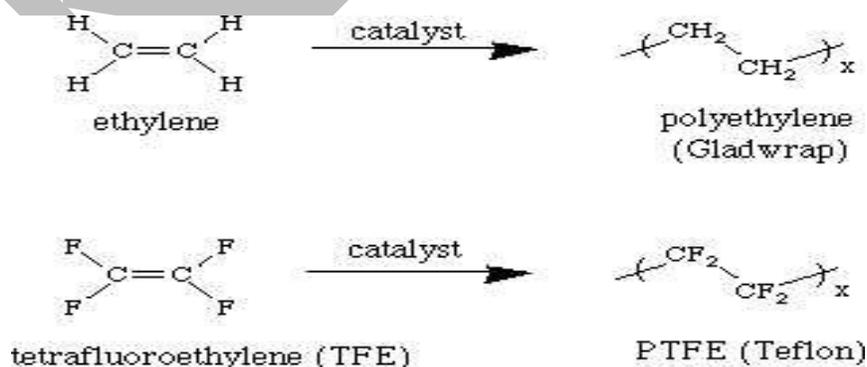
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styrene → polystyrene (Styrofoam)

vinyl chloride → polyvinyl chloride (PVC)

methyl methacrylate (MMA) → PMMA (Plexiglas, Lucite)
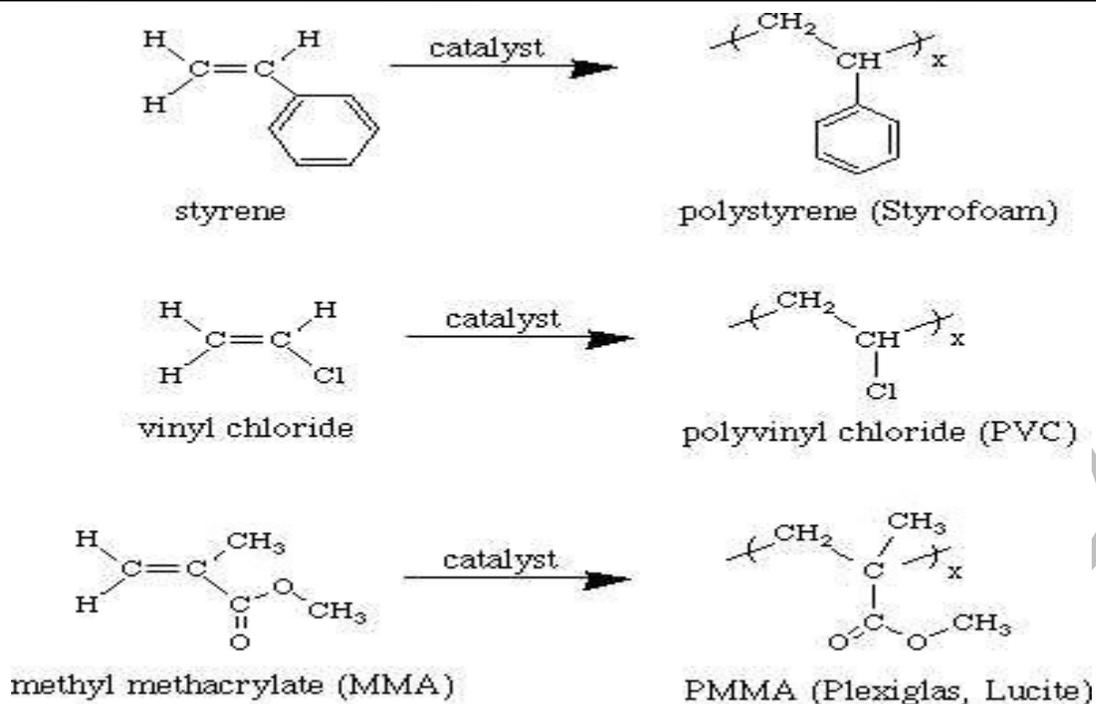
This kind of reaction yields linear polymers without cross-links, i.e. thermoplastic polymers. Cross linking agents for addition polymers are molecules that contain two or more double bonds per molecule, for example divinylbenzene (see drawing below). Cross-linking of linear chain polymers causes them to stiffen and retain their shape, and also makes them insoluble in solvents that dissolve the linear chain polymer. A demonstration was done showing how a styrofoam cup (composed of linear chain - i.e., not cross-linked - polystyrene) dissolves in a polar solvent (acetone). The styrofoam cup is mostly air, which is blown into the polymer as it forms. Materials that contain lots of air pockets are good thermal insulators, which is why your hand doesn't burn when you hold a styrofoam cup full of hot coffee.

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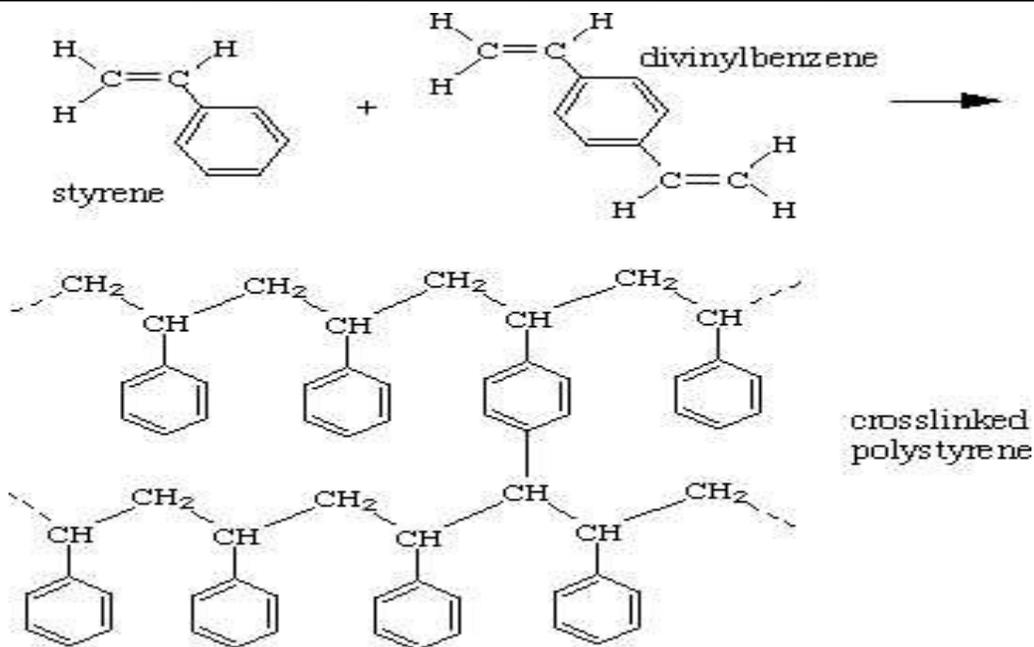
Condensation **polymerization**

Two different monomer units, each containing two functional groups, react by eliminating a small molecule like water. Examples are polyamides, made by reacting a diacid with a diamine, and polyesters, made by reacting a diacid with a diol (a diol is a molecule containing two terminal   OH   groups).
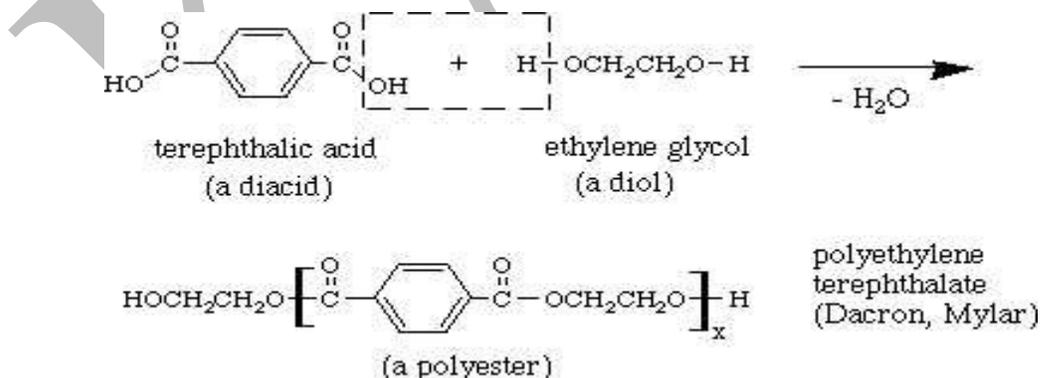
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adipic acid   hexanediamine $- H_2O$

Nylon 66
(a polyamide)
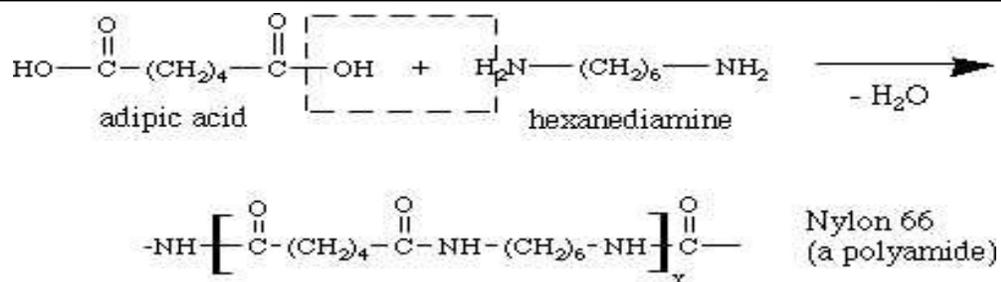
The synthesis of Nylon 66 was demonstrated in class, using a solution of adipoyl chloride (an activated form of adipic acid) in hexane and hexanediamine in water. The hexane solution floats on top of the aqueous solution, and the two reagents meet at the interface between the two solutions, forming the linear polymer. As the polymer is pulled out, the interfacial reaction continues, and a nylon "rope" can be pulled continuously as it forms from the liquid-liquid interface.

3. *Ring-Opening* polymerization. The monomer is a cyclic molecule that opens up and forms a linear chain polymer, e.g., the isomerization of S_8 (crystalline yellow sulfur, a monomer) to linear polymeric sulfur chains:

S_8 S_x

(yellow sulfur,
crystalline monomer)   (rubbery linear polymer)
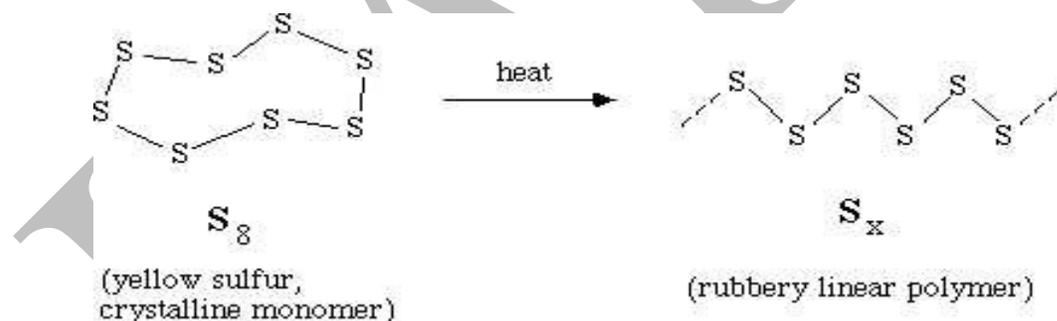
Radical Polymerization.

In order to produce radical polymerization it´s necessary that initiator monomer or hardener, which activates and causes the reaction, contains free radicals, namely unpaired electrons which react with the resin monomer in order to form the polymer.

Radical is defined as chemical material extremely unstable therefore with a high reactive power due it has unpaired electrons.

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The steps that occur in the radical polymerization are:

Initiation of the reaction - free radical is formed by the action of chemical, thermal, electrochemical or photochemical energy.

Formation of radical-R --- RAD> RAD * + * R

Chain initiation RAD * + A ---> RAD-A *

Chain growth

RAD-A * + A ---> RAD-A-A *

RAD-A-A * + A ---> RAD-A-A-A * ...

Chain termination - There are several ways to end the reaction by either:

Combine 2 radicals RAD-AAA-AAA * + * --- RAD> RAD-AAAAAA-RAD

Using inhibitors / regulators – external agents of the polymerization which react with the radical making terminate the reaction.

One of the main disadvantages of radical polymerization is that it can not control the molecular weight and size of the final polymer, because each reaction terminates in an undefined way.

The polymers that are produced by radical polymerization are strongly temperature dependent, if temperature increase will speed up the polymerization reactions causing:

Shorter chains of the polymers and decreasing their mechanical properties (strength and elongation)

Reduction of working time, pot life and curing.

Ionic polymerization.

Ionic polymerization operation is similar to the radical polymerization; the radical in this case is an ion (atom or molecule) in which one of its parts is charged positively or negatively by the absence or presence of electrons.

Features:

Requires less activation energy than the radical polymerization.

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It is not as temperature dependent.

The chain termination occurs only for the use of inhibitors, regulators or other agents that stop the reaction.

Depending on the charge of the ion, ionic polymerization is classified into:

▶**Anionic polymerization** - The ion is an atom or molecule with excess of electrons - negatively charged.

ION-+ A -> ION-A-

ION-A-+ A -> ION-A-A-

ION-A-A-+ A -> ION-A-A-A-
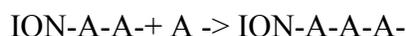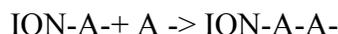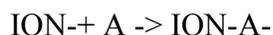
▶**Cationic Polymerization** - The ion is an atom or molecule with lack of electrons - positively charged.

ION + + A -> ION-A +

ION-A + + A -> ION-A-A +

ION-A-A + + A -> ION-A-A-A +
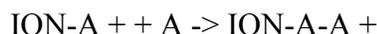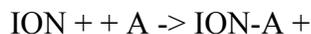
Cationic vinyl polymerization

Cationic vinyl polymerization is a way of making polymers from small molecules, or monomers, which contain carbon-carbon double bonds. Its primary commercial use is for making polyisobutylene.

In cationic vinyl polymerization, the initiator is a cation, which is an ion with a positive electrical charge. It is shown as A+ in the picture. A pair of electrons, negatively charged, from the carbon-carbon double bond will be attracted to this cation, and will leave the carbon-carbon double bond to form a single bond with the initiator, as shown. This leaves one of the former double bond carbons at a loss for electrons, and carrying a positive charge. This new cation will react with a second monomer molecule in the same manner as the initiator reacted with the first monomer molecule. This happens over and over until a high molecular weight is reached, that is, a molecular weight at which the polymer is useful for something.

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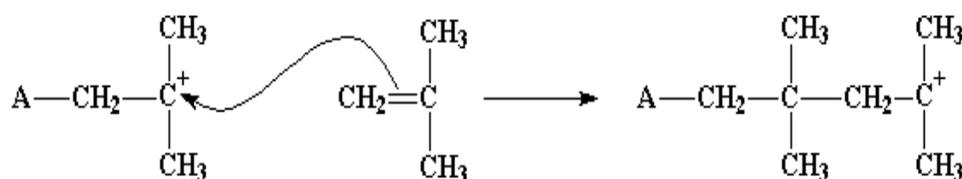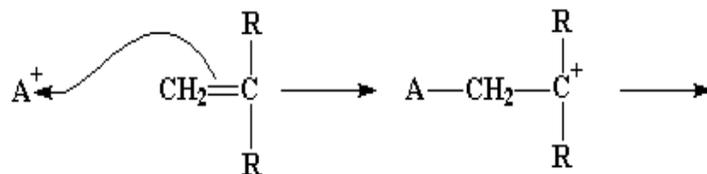
Note: When a line is drawn between two atoms, this
represents a pair of electrons the atoms share.
Sharing one pair of electrons makes a single bond.
Sharing two pairs makes a double bond, shown
by two lines. The curved arrows show the motion
of a pair of electrons.
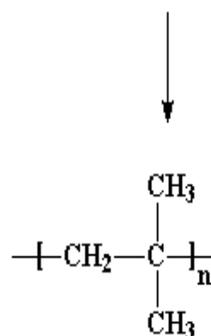
Many times, though, it starts off in little bit more complicated manner than that. Normally, the
initiator used is something like aluminum trichloride, or $AlCl_3$. If you know the octet rule, you'll
know that all atoms on the second row of the periodic table like to have eight electrons in their
outermost shell, or level. The aluminum atom in AlCl3 is sharing electron pairs with only three
other atoms, leaving it with only six electrons, two short of the magical octet. As it sits, it has a
whole orbital (that is, a vacant slot where a pair of electrons should be) empty and ready for
something to come along and fill it. It just so happens, much to the delight of that aluminum
atom, that a very small amount of water is usually present in the system. Now the oxygen atom
in water has two unshared pairs of electrons, and it most graciously donates a pair to the
aluminum atom, forming an $AlCl_3$ and H_2O complex.

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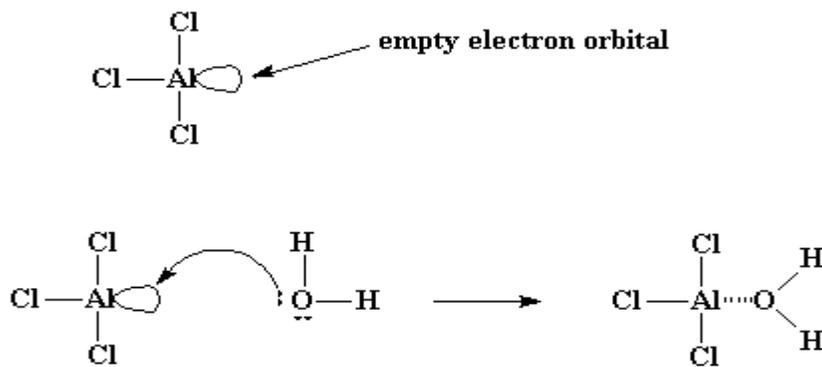
Oxygen, being very electronegative, will tend to pull the electrons it shares with the hydrogens atoms toward itself, leaving the hydrogen atoms with a slight positive charge. This leaves them ripe for attack by a pair of electrons from the double bond of a monomer molecule. The monomer in this way can swipe the hydrogen, making itself a cation, and the $AlCl_3/H_2O$ complex becomes its compliment anion, $AlCl_3OH^-$. This whole process by which the $AlCl_3/H_2O$ complex forms and reacts with the first monomer molecule is called *initiation*.
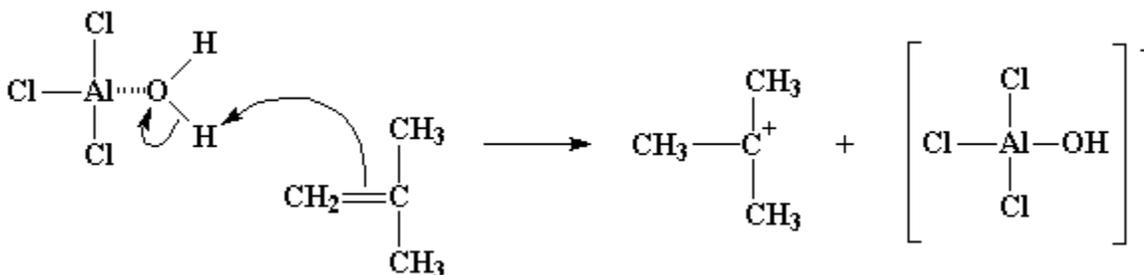
Carbocations are very unstable. They're unstable because the carbon atom in a carbocation only has six electrons in its outermost shell. Six! That's *two* electrons short of the eight that all carbon atoms want to have in their outermost shells. So a carbocation will do just about anything to get two more electrons and reach the magic octet.

So the carbocation looks around, and finds a pair of electrons in the double bond of a nearby monomer molecule. (Remember there are two pairs of electrons in a double bond.) So the carbocation swipes those electrons, and in doing so forms a single bond with the monomer molecule. It also generates another carbocation, as you can see in the picture below. This can

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react with another monomer, and then another, and so on. Eventually we get a long polymer chain.
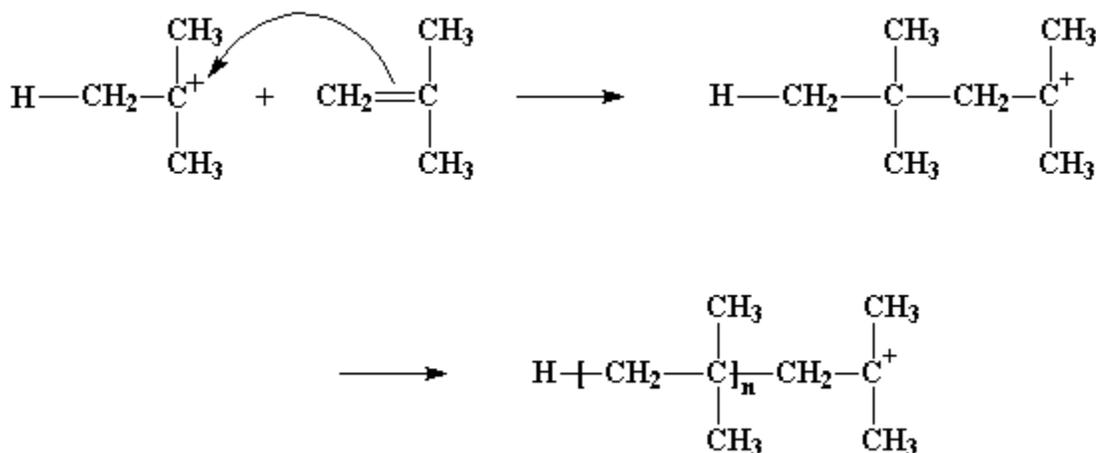
This process, by which monomer after monomer is added to form a polymer, is called *propagation,*

The methyl groups attached to the cationic carbon atom have a little problem: they've got hydrogen trouble. The hydrogens on these methyl groups will, without a whole lot of persuasion, break away and join other molecules. This is just what can happen when they come close to a molecule of monomeric isobutylene. Starved for electrons as they are, being part of a cation, these hydrogens are easily attacked by a pair of electrons from the carbon-carbon bond in the isobutylene molecule. When all the electrons are through rearranging themselves, as shown by the arrows, we're left with a neutral polymer chain with a double bond at its end, and a new cation, formed from the isobutylene molecule. The polymer chain end is now neutral, and can no longer react and grow. But the new cation can start a new chain growing, in the same way as our initiator molecule did. This process is called ***chain transfer***.

It also happens in free radical polymerization, and other kinds of polymerization as well.

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Free radical vinyl polymerization

That particular kind of chain transfer is called *chain transfer to monomer*. But there's another kind of chain transfer. To understand, it helps to remember that for every cation, there is an anion lurking somewhere in the same beaker. Remember that $AlCl_3OH^-$ ion? As we all know, cations and anions have this nasty tendency to react with each another, which can be troublesome when we want our cation to react with something else, like a monomer molecule. Let's take a look at how this happens.

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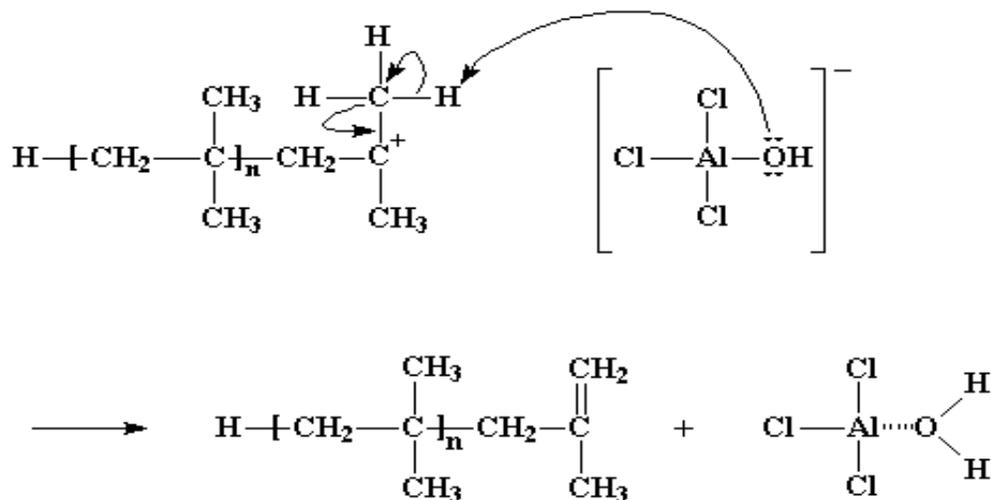
When the cationic initiator reacts, and forms a growing cationic chain, the old anion of the initiating cation becomes the anion of the growing polymeric cation. Remember that anions tend to have pairs of electrons floating around with nothing to do, and, what did mother always say, idle hands do the devil's work? That's just what happens here. The electrons of the anion will, from time to time, attack the hydrogen atoms on the methyl groups adjacent to the cationic carbon. Remember these hydrogen atoms? They're the ones that were so eager to be snatched away by a nearby monomer molecule. Sometimes, not often but sometimes, these hydrogens will very easily react with the unshared electrons of the oxygen atom in the anion in the exact same manner, leaving the same dead polymer chain with a double bond at its end. But on the bright side, the AlCl$_3$/H$_2$O complex is regenerated, and it can start new polymers growing just as it did earlier. Yet another case of the villainous chain transfer.

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This process is called *termination*, because no new chains are started. It's the last of the three major steps in any chain growth polymerization, the first two being initiation and propagation, of course. When termination happens, the polymerization is over.

Ziegler–Natta catalysis and polymerization

Historical Development of Ziegler–Natta Initiators

Various mechanisms have been proposed to explain the stereoselectivity of Ziegler- Natta initiators. Most mechanisms contain considerable details that distinguish them from each other but usually cannot be verified. In this section the mechanistic features of Ziegler–Natta polymerizations are considered with emphasis on those features that hold for most initiator systems.

The major interest will be on the titanium–aluminum systems for isoselective polymerization, more specifically, $TiCl_3$ with $Al(C_2H_5)_2Cl$ and $TiCl_4$ with $Al(C_2H_5)_3$—probably the most widely studied systems, and certainly the most important systems for industrial polymerizations. Before proceeding with the mechanistic consideration it is useful to review the evolution of the Ti-Al initiator system for industrial applications. The original initiator used by Ziegler for ethylene polymerization was obtained in situ as a precipitate on mixing the components $TiCl_4$ and $Al(C_2H_5)_3$ in a hydrocarbon solvent. The mixture was used directly for initiating polymerization. Natta, recognizing that the major product of the reaction was b-$TiCl_3$ (brown in color), explored various methods of preforming it outside the polymerization system, for example, by reduction of TiCl4 with hydrogen, aluminum, and various alkylaluminum

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compounds. The stereoselectivity of these early initiator systems was low with isotactic indices of only 20–40% for polypropene. The isotactic index, a measure of the isotactic content of a polymer, is the percentage of the sample insoluble in a hydrocarbon solvent such as boiling n-heptane. This is not as informative a technique as high-resolution NMR since insoluble molecules may contain some syndiotactic and atactic sequences and soluble molecules may contain some isotactic sequences. It does, however, give a simple measure of isotacticity that is usually within about 10% of the value obtained from NMR,

especially for highly isotactic samples.

There was a dramatic increase in stereoselectivity when the α-, δ-,or γ-crystalline form of $TiCl_3$ (all violet in color) was used directly. The early generations of industrial processes used $TiCl_3$ together with $Al(C_2H 5)_3$ and/or $Al(C_2H 5)_2Cl$. Over a two decade period starting in the late 1950s, the isotactic indices for polypropene increased to the low 90 percentile range. The initiator activity was enhanced by various ball milling and heat treatments of the initiator components before and after mixing. Ball milling involves mechanical grinding and not only increases surface area but also facilitiates reactions between the initiator components.

However, the activities were too low to allow the polymer products to be used without purification (by treatment with base or acid) to remove the residual metals, a process referred to as deashing. Also, optimization of the physical properties of the product often required removal of the atactic fraction. The initiator systems were inefficient with less than 1% of the Ti being active in polymerization. The later generations of initiators, starting in the late 1970s, increased initiator efficiency and activity without sacrificing stereoselectivity [Bohm, 2001; Busico and Cipullo, 2001; Cecchin et al., 2001; Chadwick, 2001; Chadwick et al., 2001; Chien et al., 1982; Hu and Chien, 1988]. The effective surface area of the active component of the initiator system was increased by close to 2 orders of magnitude by using $MgCl_2$ as a solid support in which $TiCl_4$ is finely dispersed. Stereoselectivity was kept high and actually increased by the addition of electron-donor additives.

A typical recipe for a present-day superactive or high-mileage initiator system involve ball milling of $MgCl_2$ (or the alkoxide) and TiCl4 followed by the addition of $Al(C_2H 5)_3$ with an electron donor (such as dialkyl phthalate and alkoxysilane) usually added in each step of preparation. Activity is 50–200 kg polymer per gram of initiator system. Typically, the initiator system is no more than 2–4% Ti, which makes the activity about 1500–6000 kg polymer per gram of Ti. The high activity not only minimizes initiator and production costs but also avoids the costly task of initiator removal from the polymer product (except possibly for food- and medical-grade products). Isotactic indices for polypropene have been increased to 98% or higher

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with (mmmm) pentad fractions up to 98% and higher. This not only improves the product's physical properties but also avoids the need to remove the a tactic fraction.

**Chemical Nature of Propagating Species**

Some early polymerizations reported as Ziegler–Natta polymerizations were conventional free-radical, cationic, or anionic polymerizations proceeding with low stereoselectivity.Some Ziegler–Natta initiators contain components that are capable of initiating conventional ionic polymerizations of certain monomers, such as anionic polymerization of methacrylates by alkyllithium and cationic polymerization of vinyl ethers by $TiCl_4$. Most Ziegler–Natta components participate in a complex set of reactions involving alkylation and reduction of the transition-metal component by the group I–III component as shown below for $TiCl_4 + AlR_3$:

$TiCl_4 + AlR_3 \longrightarrow TiCl_3 R + AlR_2 Cl$

$TiCl_4 + AlR2Cl \longrightarrow TiCl_3R + AlRCl_2$

$TiCl3R + AlR_3 \longrightarrow TiCl_2 R_2 + AlRCl_2$

$TiCl_3 R \longrightarrow TiCl_3 + R\bullet$

$TiCl_3 + AlR_3 \longrightarrow TiCl_2 R + AlR_2 Cl$
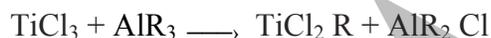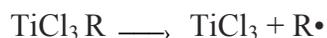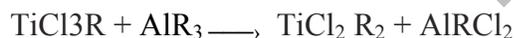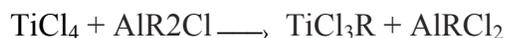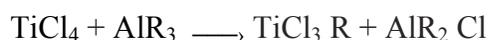
$R\bullet \longrightarrow$ combination + disproportionation
The reverse order is expected for a polymerization involving the conversion of a monomer into the corresponding carbocation. For addition of a carbanion to the monomers, attack occurs at the a-carbon to form the less substituted (and more stable) carbanion. Further, a-substituents sterically hinder the approach of a carbanion and/or counterion with the result that reactivity decreases with increasing substituent size. Evidence for the anionic nature of propagation also comes from studies in which labeled methanol is used to terminate chain growth. The terminated polymer is radioactive when $CH_3 O_3 H$ is used, while termination by $^{14}CH_3 OH$ yields a nonradioactive polymer.

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Mechanism of Isoselective Propagation

R　　Cl
　\　/
　　\/

Cl — Ti—□
　/　\

　　Cl　　Cl

　　XX
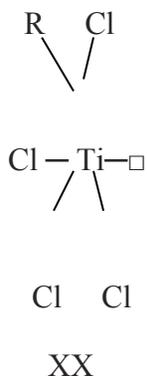
The □ in the structure represents an unoccupied (vacant) site of the octahedral titanium complex. XX represents an active titanium site at the surface of a $TiCl_3$ crystal after modification by reaction with the alkylaluminum component. The titanium atom shares four chloride ligands with its neighboring titanium atoms and has an alkyl ligand (incorporated via exchange of alkyl from the alkylaluminum for chloride) and a vacant orbital.

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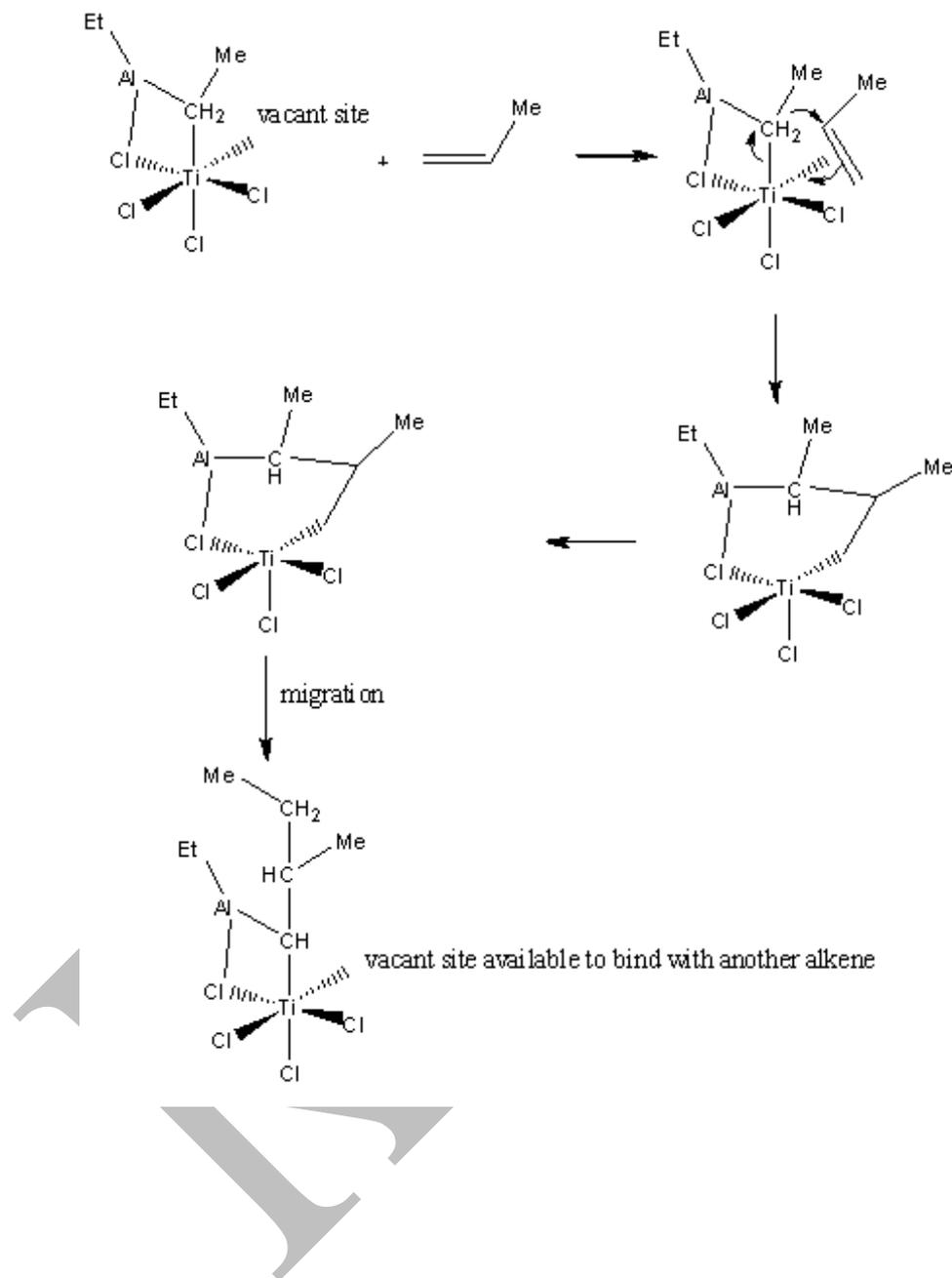
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Natta- Bimetallic Polymerization mechanism
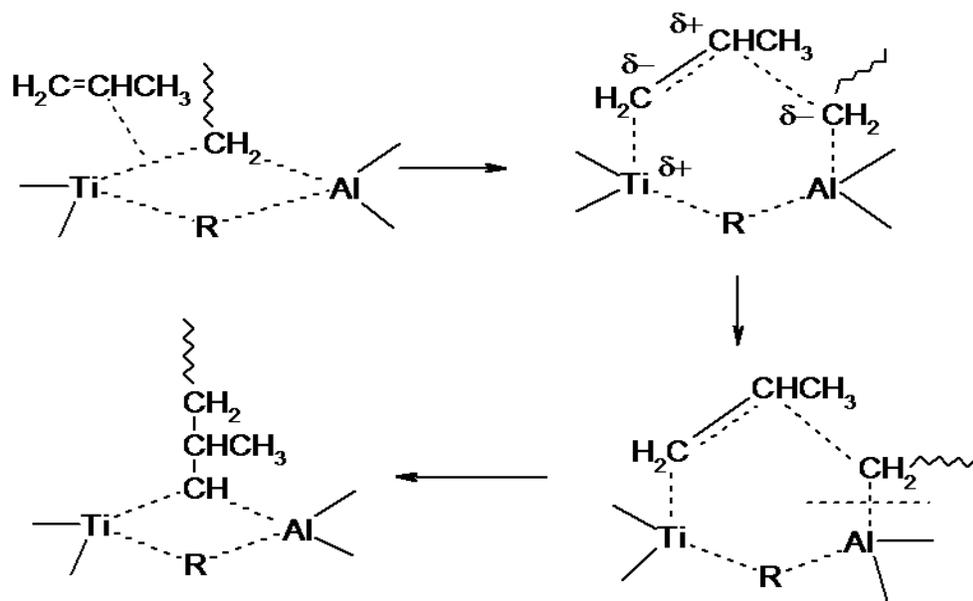
Preparation and applications of thermosetting plastics

Phenol-formaldehyde

Phenol-formaldehyde resins, as a group, are formed by a step-growth polymerization reaction that can be either acid- or base-catalysed. Since formaldehyde exists predominantly in solution as a dynamic equilibrium of methylene glycol oligomers, the concentration of the *reactive* form of formaldehyde depends on temperature and pH.

Phenol reacts with formaldehyde at the ortho and para sites (sites 2, 4 and 6) allowing up to 3 units of formaldehyde to attach to the ring. The initial reaction in all cases involves the formation of a hydroxymethyl phenol:

$$HOC_6H_5 + CH_2O \rightarrow HOC_6H_4CH_2OH$$
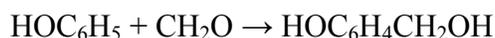
The hydroxymethyl group is capable of reacting with either another free ortho or para site, or with another hydroxymethyl group. The first reaction gives a methylene bridge, and the second forms an ether bridge:

$$HOC_6H_4CH_2OH + HOC_6H_5 \rightarrow (HOC_6H_4)_2CH_2 + H_2O$$

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$$2\ HOC_6H_4CH_2OH \rightarrow (HOC_6H_4CH_2)_2O + H_2O$$
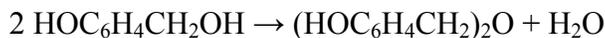
The diphenol $(HOC_6H_4)_2CH_2$ (sometimes called a "dimer") is called bisphenol F, which is an important monomer in the production of epoxy resins. Bisphenol-F can further link generating tri- and tetra-and higher phenol oligomers.

Uses

> ➢ Soft Bakelite are used as binding glue for laminated wooden planks, in varnishes and lacquers.
> ➢ Hard bakelite is used as a thermosetting polymer.
> ➢ It is used for the manufacture of combs, formica-table –tops, electrical switches and gramophone records.

Polyurethanes

Polyurethane (PUR and PU) is a polymer composed of organic units joined by carbamate (urethane) links. While most polyurethanes are thermosetting polymers that do not melt when heated, thermoplastic polyurethanes are also available.
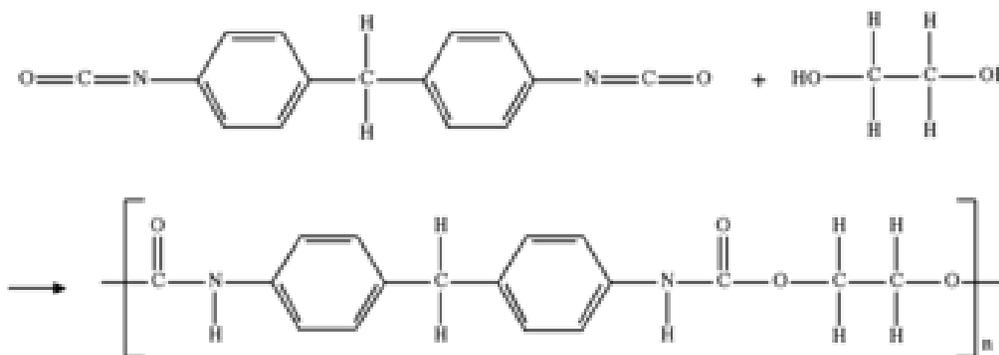
Polyurethane polymers are traditionally and most commonly formed by reacting a di- or poly-isocyanate with a polyol. Both the isocyanates and polyols used to make polyurethanes contain, on average, two or more functional groups per molecule.

Some noteworthy recent efforts have been dedicated to minimizing the use of isocyanates to synthesize polyurethanes, because the isocyanates raise severe toxicity issues. Non-isocyanate based polyurethanes (NIPUs) have recently been developed as a new class of polyurethane polymers to mitigate health and environmental concerns.[1][2][3][4][5]

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Polyurethane products often are simply called "urethanes", but should not be confused with ethyl carbamate, which is also called urethane. Polyurethanes neither contain nor are produced from ethyl carbamate.

Uses

Polyurethanes are used in the manufacture of high-resilience foam seating, rigid foam insulation panels, microcellular foam seals and gaskets, durable elastomeric wheels and tires (such as roller coaster, escalator, shopping cart, elevator, and skateboard wheels), automotive suspension bushings, electrical potting compounds, high performance adhesives, surface coatings and surface sealants, synthetic fibers (e.g., Spandex), carpet underlay, hard-plastic parts (e.g., for electronic instruments), condoms,[6] and hoses.

Preparation and applications of Thermoplastic polymers

PVC

Polyvinyl chloride (PVC), a synthetic resin made from the polymerization of vinyl chloride. Second only to polyethylene among the plastics in production and consumption, PVC is used in an enormous range of domestic and industrial products, from raincoats and shower curtains to window frames and indoor plumbing. A lightweight, rigid plastic in its pure form, it is also manufactured in a flexible "plasticized" form.
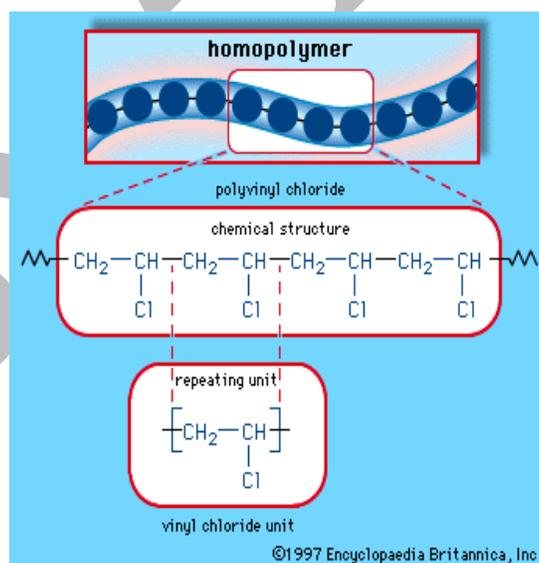
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USES

➢ It is a good electrical insulator and hence is used for coating wires and cables.
➢ It is also used in making gramophone records and pipes.
➢ It is used for making rain coats, hand bags, plastic dols, upholstery, shoe soles and vinyl flooring.

Polyethene

Low density poly(ethene) (LDPE)

The process is operated under very high pressure (1000-3000 atm) at moderate temperatures (420-570 K) as may be predicted from the reaction equation:

$$nC_2H_4 \longrightarrow \left[CH_2 - CH_2 \right]_n \qquad \Delta H^{\ominus} = -92 \text{ kJ mol}^{-1}$$
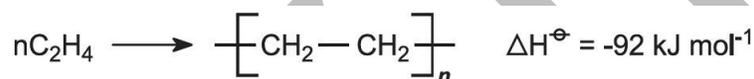
This is a radical polymerization process and an initiator, such as a small amount of oxygen, and/or an organic peroxide is used.

Ethene (purity in excess of 99.9%) is compressed and passed into a reactor together with the initiator. The molten poly(ethene) is removed, extruded and cut into granules. Unreacted ethene is recycled. The average polymer molecule contains 4000-40 000 carbon atoms, with many short branches.

For example,
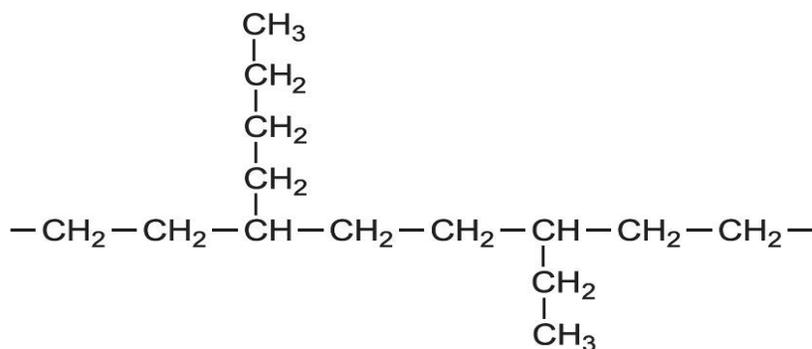
There are about 20 branches per 1000 carbon atoms. The relative molecular mass, and the branching, influence the physical properties of LDPE. The branching affects the degree of

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crystallinity which in turn affects the density of the material. LDPE is generally amorphous and transparent with about 50% crystallinity. The branches prevent the molecules fitting closely together and so it has low density.

High density poly(ethene) (HDPE)

Two types of catalyst are used principally in the manufacture of HDPE:

a Ziegler-Natta organometallic catalyst (titanium compounds with an aluminium alkyl).

an inorganic compound, known as a Phillips-type catalyst. A well-known example is chromium(VI) oxide on silica, which is prepared by roasting a chromium(III) compound at *ca* 1000 K in oxygen and then storing prior to use, under nitrogen.

HDPE is produced by three types of process. All operate at relatively low pressures (10-80 atm) in the presence of a Ziegler-Natta or inorganic catalyst. Typical temperatures range between 350-420 K. In all three processes hydrogen is mixed with the ethene to control the chain length of the polymer.

i)Slurry process

The Ziegler-Natta catalyst, as granules, is mixed with a liquid hydrocarbon (for example, 2-methylpropane (isobutane) or hexane), which simply acts as a diluent. A mixture of hydrogen and ethene is passed under pressure into the slurry and ethene is polymerized to HDPE. The reaction takes place in a large loop reactor with the mixture constantly stirred (Figure 4). On opening a valve, the product is released and the solvent is evaporated to leave the polymer, still containing the catalyst. Water vapour, on flowing with nitrogen through the polymer, reacts with the catalytic sites, destroying their activity. The residue of the catalyst, titanium(IV) and aluminium oxides, remains mixed, in minute amounts, in the polymer.

Fabrics

In general, the term fabric describes the way different parts of something work together to form a single entity. In this context, fabric is used as a metaphor to illustrate the idea that if someone were to document computer components and their relationships on paper, the lines would weave back and forth so densely that the diagram would resemble a woven piece of cloth.

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The term fabric is commonly used to describe data or storage area networks (SANs). Increasingly, however, vendors are using the term to describe the servers, high-speed connections and switches that make up a cloud computing platform.

Acrylic fabrics

Acrylonitrile(CH$_2$=CH-CN)

Acrylic nitrile is one of the important monomer for manufacture of acrylic fibres, however, earlier routes of acrylonitrile manufacture by acetylene, ethylene oxide or acetaldehyde route has being replaced by propylene route due to availability of cheaper propylene from steam cracker plant. This involves ammono-oxidation of propylene. Other uses of acrylonitrile are in the manufacture of nitrile rubber, ABS and SAN plastics, adiponitrile and acrylamide. In addition it is also used in the manufacture of acrylates, intermediates for flocculants, pharmaceuticals, antioxidants, dyes and surface active agents

Acetylene Route
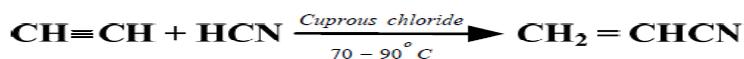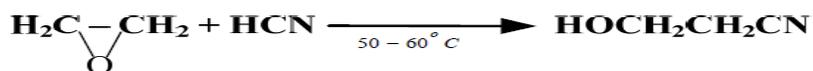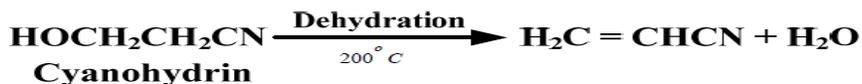
$$CH \equiv CH + HCN \xrightarrow[70-90^\circ C]{Cuprous\ chloride} CH_2 = CHCN$$

Ethylene Oxide Route

$$H_2C \overset{\diagdown}{-} CH_2 + HCN \xrightarrow[50-60^\circ C]{} HOCH_2CH_2CN$$

Epoxide

$$HOCH_2CH_2CN \xrightarrow[200^\circ C]{\textbf{Dehydration}} H_2C = CHCN + H_2O$$

Cyanohydrin

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Acrylonitrile (CH$_2$=CH-CN)

Acetaldehyde Route

$$CH_3CHO + HCN \longrightarrow CH_3CHOHCN$$

$$CH_3CHOHCN \xrightarrow{\text{Dehydration}} CH_2 = CHCN + H_2O$$

Propylene Route

$$CH_2 = CH - CH_3 + NH_3 + 3/2\ O_2 \xrightarrow[400\text{-}500\ ^0C]{\text{Ammoxidation}} CH_2 = CHCN$$
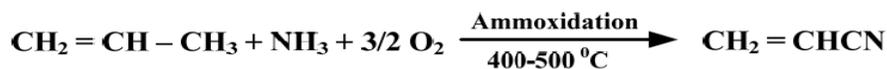
Uses

- ➢ Polyacrylontrile is a hard and high melting material
- ➢ It is used in the manufacture of orlon and Acrrilan fibres used for making clothes, carpets and blankets.
- ➢ It is blended with other polymers to improve their qualities.

Polyamide fabrics

Polyester

Nylon-66 (polyhexamethylene diamine adipamide) is a polyamide made from adipic acid and hexamethylenediamine by polycondensation. The resulting polymer is extruded into a wide range of fiber types. The fibers are drawn, or stretched, in a process that increases their length and reorients the material's molecules parallel to one another to produce a strong, elastic filament. The thermo-plasticity of nylon permits permanent crimping or texturing of the fibers and provides bulk and stretch properties.

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adipic acid + hexamethylene diamine → nylon 6,6
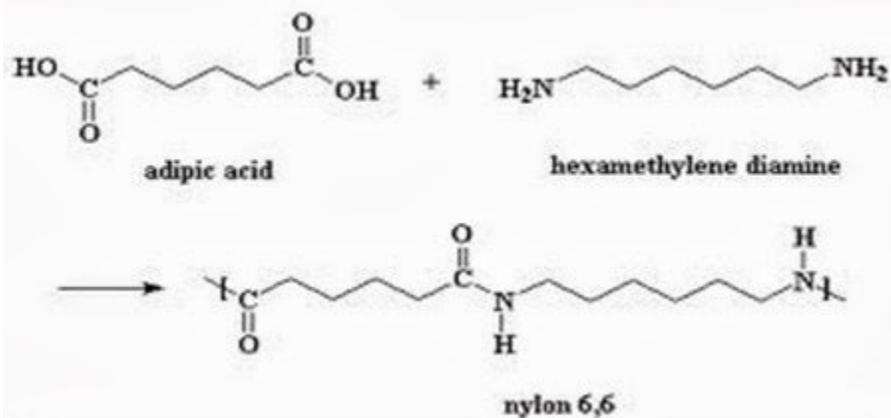
Polyester

Synthesis of polyesters is generally achieved by a polycondensation reaction. See "condensation reactions in polymer chemistry". The general equation for the reaction of a diol with a diacid is :

$$(n+1)\ R(OH)_2 + n\ R'(COOH)_2 \rightarrow HO[ROOCR'COO]_nROH + 2n\ H_2O$$

Rubbers

"Rubber" refers to elastomeric compounds that consist of various monomer units forming polymers that are heat cured (vulcanized). Polymers are long molecular chains that are connected together (cross-linked) to improve their toughness and resilience. The base monomer (or monomers, when blended) is used to classify the type of rubber. For example: Neoprene, SBR or Nitrile.

Natural Rubber

Natural rubber is an addition polymer that is obtained as a milky white fluid known as latex from a tropical rubber tree. Natural rubber is from the monomer isoprene (2-methyl-1,3-butadiene), which is a conjugated diene hydrocarbon as mentioned above. In natural rubber, most of the double fonds formed in the polymer chain have the Z configuration, resulting in natural rubber's elastomer qualities.

Synthetic Rubber

Important conjugated dienes used in synthetic rubbers include isoprene (2-methyl-1,3-butadiene), 1,3-butadiene, and chloroprene (2-chloro-1,3-butadiene). Polymerized 1,3-butadiene

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is mostly referred to simply as polybutadiene. Polymerized chloroprene was developed by DuPont and given the trade name Neoprene.

Natural Rubber-Buna –S Rubber

The synthesis of rubber in nature in somewhat similar the artificial synthesis of rubber except that it takes place within a plant. Instead of the 2-chloro-1,3-butadiene used in the synthesis of neoprene, natural rubber is synthesized from 2-methyl-1,3-butadiene. As an electrophile, the plant synthesizes the pyrophosphate 3-methyl-3-butenyl pyrophosphate is from phosphoric acid and 3-methyl-3-buten-1-ol. This pyrophosphate then catalyzes the reaction that leads to natural rubber.

The 3-methyl-3-butenyl pyrophosphate (OPP) is then used in the polymerization of natural rubber as it pulls electrons off 2-methyl-1,3-butadiene

Neoprene

Neoprene or **polychloroprene** is a family of synthetic rubbers that are produced by polymerization of chloroprene. Neoprene is produced by free-radical polymerization of chloroprene. In commercial production, this polymer is prepared by free radical emulsion polymerization. Polymerization is initiated using potassium persulfate. Bifunctional nucleophiles, metal oxides (e.g. zinc oxide), and thioureas are used to crosslink individual polymer strands.

Uses

It can be used as a base for adhesives, noise isolation in power transformer installations, and as padding in external metal cases to protect the contents while allowing a snug fit. It resists burning better than exclusively hydrocarbon based rubbers, resulting in its appearance in weather

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stripping for fire doors and in combat related attire such as gloves and face masks. Because of its tolerance of extreme conditions, neoprene is used to line landfills. Neoprene's burn point is around 260°C (500°F). Neoprene foam is also used in many applications. Neoprene foam can be produced in either closed-cell or open-cell form. The closed-cell form is waterproof, less compressible and more expensive. The open-cell form can be breathable.

Chloroprene

Polychloroprene is the polymer name for the synthetic rubber known as neoprene (a proprietary trade name of DuPont that has become generic). One of the first successful synthetic elastomers, neoprene was first prepared in 1931 by Arnold Collins, a chemist in Wallace Hume Carothers' research group at DuPont, while he was investigating by-products of divinylacetylene. It is a good general-purpose rubber, but it is limited to special-properties applications because of its high cost.

Polychloroprene is prepared by emulsion polymerization of chloroprene, or 2-chlorobutadiene,
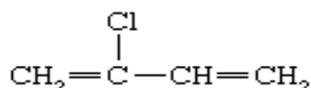
which is obtained by the chlorination of butadiene or isoprene. Of the several structures adopted by the chloroprene repeating unit, the most common is *trans*-1,4 polychloroprene, which can be represented as follows:
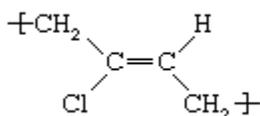
Properties

This polymer tends to crystallize and harden slowly at temperatures below about 10° C (50° F). It also crystallizes on stretching, so that cured components are strong even without fillers. Because the double bond between the carbon atoms is shielded by the pendant atoms and CH_2 groups, the molecular interlinking necessary for producing a cured rubber is usually effected through the chlorine atom. The presence of chlorine in the molecular structure causes this elastomer to resist swelling by hydrocarbon oils, to have greater resistance to oxidation and ozone attack, and to possess a measure of flame resistance.

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Applications

Principal applications are in products such as hoses, belts, springs, flexible mounts, and gaskets where resistance to oil, heat, flame, and abrasion are required.

Vulcanization

Vulcanization, chemical process by which the physical properties of natural or synthetic rubber are improved; finished rubber has higher tensile strength and resistance to swelling and abrasion, and is elastic over a greater range of temperatures. In its simplest form, vulcanization is brought about by heating rubber with sulfur.

In modern practice, temperatures of about 140°–180° C are employed, and in addition to sulfur and accelerators, carbon black or zinc oxide is usually added, not merely as an extender, but to improve further the qualities of the rubber. Anti-oxidants are also commonly included to retard deterioration caused by oxygen and ozone. Certain synthetic rubbers are not vulcanized by sulfur but give satisfactory products upon similar treatment with metal oxides or organic peroxides.

Polymer additives

A large number of plastics have been developed and used as materials for our daily lives or industrial use, such as materials for the bumpers and interior parts of automobiles, electrical and electronic appliances, including televisions and cellular phones, and food containers and packaging.

A number of ingredients are added to both natural and synthetic rubber in order to obtain certain desirable properties. By convention, mix formulations begin with the amount of the designated elastomer—for instance, natural rubber (NR), butadiene rubber (BR), or styrene-butadiene rubber (SBR)—given as 100 parts by weight. The amount of each other ingredient is then expressed in parts by weight added per 100 parts by weight of the elastomer. If two or more elastomers are used, then they are shown in the recipe as fractions of 100 parts—for example, "NR, 60 parts; BR, 40 parts." When the elastomer contains oil already added by the producer, allowance is made for this dilution in the recipe. For example, if SBR 1702 is used, the mix formulation may begin "SBR 1702, 137.5 parts by weight," because that amount of SBR 1702 contains 37.5 parts by weight of oil and 100 parts by weight of SBR elastomer.

Biodegradable polymers

A polymer that can be decomposed by bacteria is called a biodegradable polymer.

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CLASS   **: II B.Sc CHEMISTRY**
COURSE NAME : ORGANIC CHEMISTRY-IV (Organic Spectrascopy)
COURSE CODE : 16CHU403
UNIT: V (Dyes and Polymers)   **BATCH-2016-2019**

The biodegradable polymer are the polymers which are degraded by the micro-organism within a suitable period so that biodegradable polymers & their degraded products do not cause any serious affects on the environment. They degrade by enzymatic hydrolysis & oxidation.The decomposition reactions involves hydrolysis(either enzymatically induced or by non –enzymatic mechanism) to non- toxic small molecules which can be metabolized by or excreted from the body.

The common examples of aliphatic biodegradable polymers are polyglycolic acid(PGA), Polyhydroxy butyrate (PHB), Polyhydroxy butyrates-co-beta hydroxyl valerate(PHBV), Polycaprolactone(pcl), Nylon-2-nylon-6.

These polymers are used mainly for medical goods such as surgical sutures, tissues in growth materials, for controlled drug release,plasma substitutes etc.They are also used in agriculture materials,such as films,seed coatings,fast food wrappers,personal hygiene products etc.

Poly-β-hydroxybutyrate-CO-β- hydroxyvalerate (PHBV) is a biodegradable aliphatic polyester.
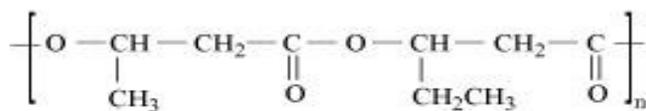
PHBV

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POSSIBLE QUESTIONS

PART-A (One Mark)

(Multiple Choice Questions)

1) Vat dyes are
   a) soluble in water   b) not suitable for dyeing fabrics
   c) insoluble in water   d) unstable

2) 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**

3) Polyvinyl acetate is used for the manufacture of
   a) Polyvinyl chloride   **b) Polyvinyl alcohol**
   c) Poly methyl methacrylate   d) Polyvinyl acetate

4) Natural fibers are consisting of
   a) Linear polymers   b) Nonlinear polymers
   c) Copolymers   d) Chain polymers

5) Malachite green is
   a) an azo dye   **b) triphenylmethane dye**
   c) an anthroquinone dye   d) phthalocyanine dye

6) 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

7) Which one is used in tires and ropes?
   a) Cotton   **b) Nylon**   c) Polyamide   d) Polyester

8) The polyesterification becomes a much more economically feasible reaction when it is
   catalyzed by an ?
   a) Base   **b) Acid**   c) Alkali   d) Neutral
9) Indigo is an example of
   a) a vat dye   b) a azo dye   c) a mordant dye   d) a nitro dye

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10) Which is not a Synthetic polymers?
   a) polyamide   b) Light stabilizers   c) Fibers   d) Glass fibre

11) The alkyl resins are condensation polymers obtained from dibasic acids and
   a) phenol   b) formaldehyde   c) Acetaldehyde   d) Glycol

12) The first step in the reaction of the diol and diacid monomer is to form?
   a) dimer   b) trimer   c) Pentamer   d) Tetramer

13) Methyl orange is an example for
   a) cationic dye   **b) anionic dye**   c) neutral dye   d) acidic dye

14) In a polymer chain the functional group has appreciable mobility due to
   a) the conformational rearrangements
   b) different stereochemical forms
   c)Tautomeric arrangements
   d) Optical activity

15) The catalyst used for the Ziegler–Natta polymerizations?
   a)TiCl$_3$ with Al(C$_2$H$_5$)$_2$Cl   b) BCl$_3$ with Al(C$_2$H$_5$)$_2$Cl
   c) TiCl$_3$ with Fe(C$_2$H$_5$)$_2$Cl   d) TiF$_3$ with Al(C$_2$H$_5$)$_2$F

16) Styrene(butadiene rubber) was commercially introduced during the year
   a) 1943   **b) 1930**   c) 1936   d) 1947

17) Polymers are high molecular weight in the range of ?
   a) 10^4 to 10^7 **b) 10^3 to 10^7**   c) 10^2 to 10^7 d) 10^5 to 10^7

18) Melting Point of Low Density Polyethylene (LDPE) is?
   a) ~115° C   b) ~116 ^{o}C   c) ~117°C   d) ~118 ^{o}C

19) Which is used in clothes, belts and accessories?
   a) Cotton   **b) Nylon**   c) Polyamide   d) Polyester

20) A dimer reacts with a monomer to give
   a) Trimer   b) Dimer   c) Pentamer   d) Tetramer

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PART-B (Two marks)

1) What is SBR? How is it synthesized?

2) Write the preparation and uses of PVC.

3) What is meant by Ziegler-Natta polymerization?

4) Write a note on the classification of dyes.

5) Write the preparation and uses of phenol-formaldehyde.

6) Write the preparation and uses of polyamide fibres.

7) How will you prepare polyethene?

8) How will you prepare phenolphthalein?

9) Write the preparation and uses of rosaniline.

10) Define vulcanization.

PART-C (Six Marks)

(Either or type Questions)

1) Name the various classes of dyes according to (i) Chemical constitution
      (ii) method of application
2) Discuss the mechanism of Cationic addition polymerization.
3) Write the structure, synthesis and applications of Alizarin.
4) Give the preparation and uses of i) Polyethene   ii) Polyester
        iii) Phenol- formaldehyde   iv) Neoprene
5) Give the preparation and uses of   i) Phenolphthalein   ii) Malachite green
        iii) Rosaniline.
6) Write a short note on Condensation polymerization.
7) Write the synthesis and applications of (i) Polythene (ii)Buna-S rubber   (iii) Polyurethanes
8) Write a note on free radical addition polymerization.
9) Write the synthesis and applications of (i) Methyl orange   (ii) Malachite green
        (iii) Phenolphthalein
10) write the preparation and uses of (i) Phenol–formaldehyde   (ii) PVC   (iii) Polyester

UNIT-V

Multiple Choice Questions(Each Carry One Mark)

Questions	Option 1	Option 2	Option 3	Option 4	Answer
The example for triphenylmethane dye is	malachite green	alizarin	picric acid	congo red	malachite green
Vat dyes are	soluble in water	not suitable for dyeing fabrics	insoluble in water	unstable	insoluble in water
Indigo is an example of	a vat dye	a azo dye	a mordant dye	a nitro dye	a vat dye
Malachite green is	an azo dye	a triphenylmethane dye	an anthroquinone dye	a phthalocyanine dye	a triphenylmethane dye
The example for azo dye is	methyl orange	indigo	malachite green	alizarin	methyl orange
The example for phthalein dye is	malachite green	indigo	alizarin	phenolphthalein	alizarin
The example for nitro dye is	picric acid	alizarin	malachite green	eosin	picric acid
Methyl orange is an example for	cationic dye	anionic dye	neutral dye	acidic dye	anionic dye
The example for cationic dye is	alizarin	indigo	chrysoidine	methyl orange	chrysoidine
Indigo dye is prepared from	aniline and dimethylaniline	sulphailic acid and dimethylaniline	aniline and chloroacetic acid	dimethylaniline and benzaldehyde	aniline and chloroacetic acid
The amino group is an example for	chromophore	bathochromic shift	hypochromic shift	auxochrome	auxochrome
Which one is example for auxochrome?	NO_2	N=N	OH	C=O	OH
Which group is responsible for chromophore?	amino group	covalently saturated group	hydroxyl group	covalently unsaturated group	covalently unsaturated group
A covalently unsaturated group responsible for absorption in the UV or visible region is known as a	chromophore	bathochromic shift	hypochromic shift	auxochrome	chromophore
A covalently saturated group which, when attached to a chromophore changes both the wavelength and the intensity of the absorption maximum is known as	chromophore	bathochromic shift	hypochromic shift	auxochrome	auxochrome
The shift of an absorption maximum to a longer wavelength due to the	presence of an auxochrome	presence of an chromophore	presence of an unsaturated group	presence of an double bond	presence of an auxochrome
Red shift is also called as	hypsochromic shift	bathochromic shift	hypochromic shift	chemical shift	bathochromic shift
Hypsochromic shift is also known as	red shift	black shift	blue shift	orange shift	blue shift
The other name for bathochromic shift is	resonance effect	inductive effect	mesomeric effect	solvent effect	solvent effect
The shift of an absorption maximum to a shorter wavelength is called	hypsochromic shift	bathochromic shift	hypochromic shift	auxochrome	hypsochromic shift
The shift of an absorption maximum to a longer wavelength is called	hypsochromic shift	bathochromic shift	hypochromic shift	auxochrome	bathochromic shift
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	hypochromic shift	bathochromic shift	hypsochromic shift	auxochrome	hypsochromic shift
In a polymer chain the functional group has appreciable mobility due to	the conformational rearrangements	different stereochemical forms	Tautomeric arrangements	Optical activity	The conformational rearrangements
The first step in the reaction of the diol and diacid monomer is to form ?	dimer	trimer	Pentamer	Tetramer	Dimer
The rate of a step polymerization is conveniently expressed in terms of the	Concentrations of the reacting functional groups.	concentration of the monomeric	Concentration of monomer and the solvent	Concentration of the functional groups and monomers	Concentration of the functional groups and monomers
A dimer reacts with a monomer to give	Trimer	Dimer	Pentamer	Tetramer	Trimer
The catalyst used for the Ziegler–Natta polymerizations?	$TiCl_3$ with $Al(C_2H 5)_2Cl$	BCl_3 with $Al(C_2H 5)_2Cl$	$TiCl_3$ with $Fe(C_2H 5)_2Cl$	TiF_3 with $Al(C_2H 5)_2F$	$TiCl_3$ with $Al(C_2H 5)_2Cl$
Teflon is a polymer of the monomer or Teflon is obtained by the polymerisation of ?	Monofloroethene	Difloroethene	Trifloroethene	Tetrafloroethene	Tetrafloroethene
Which of the following is an example of condensation polymer?	PVC	Polyamide	Terylene	Polyester	Terylene

Question					
The polyethene polymer formed by the addition polymerisation process using the Ziegler- Natta catalyst is a?	High density and high melting point	Low density and high melting point	High density and low melting point	Low density and low melting point	High density and high melting point
What method would you use to synthesize a triblock copolymer?	Free radical polymerization	Anionic polymerization	Using a Ziegler Natta catalyst	Condensation polymerization	Free radical polymerization
Suspension free radical polymerization of styrene would be preferred over bulk polymerization to overcome the problem of ?	Branching	Cross-linking	Stereo-isomerism	Polymeric impurities	Branching
Polymers are ?	Large molecule	Small molecule	Small chain molecule	Large chain molecule	Large chain molecule
Polymers are high molecular weight in the range of ?	10^4 to 10^7	10^3 to 10^7	10^2 to 10^7	10^5 to 10^7	10^3 to 10^7
Melting Point of Low Density Polyethylene (LDPE) is?	~115° C	~116 ^{o}C	~117°C	~118 ^{o}C	~115° C
Which is more flexible than HDPE due to lower crystallinity?	Polyethylene	Low Density Polyethylene	Polyamide	Low density polyamide	Low Density Polyethylene
Which one is a natural polymer?	Polyamide	Polyester	Cellulose	PVC	Cellulose
Synthetic fiber is?	Rayon	Boron filaments	Glass fibre	Polyvinylalcohol	polyvinylalcohol
Polymethyl methacrylate is a colourless and transparent ?	Plastic	Rubber	Cotton	Nylon	Plastic
Polymethyl methacrylate can be prepared by using acetone cyanohydrin and	Nitric acid	Acetic acid	Sulphuric acid	Hydrochloric acid	Sulphuric acid
Silicones was commercially introduced in ?	1943	1930	1936	1947	1943
Polyvinyl chloride was commercially introduced in ?	1943	1930	1936	1947	1936
Polyvinyl acetate monomer is prepared by the reaction of acetic anhydride with ?	Benzaldehyde	Acetaldehyde	Acetic acid	Sodium acetate	Acetaldehyde
Polyvinyl acetate is used for the manufacture of ?	Polyvinyl chloride	Polyvinyl alcohol	Poly methyl methacrylate	Polyvinyl acetate	Polyvinyl alcohol
Styrene(butadiene rubber) was commercially introduced during the year	1943	1930	1936	1947	1930
Polyvinyl acetate is insoluble in which solvent?	Alcohols	Aromatic solvents	Esters	Water	Water
Nylon threads are made of	Polyester polymer	Polyamide polymer	Polyvinyl chloride	Acrylic polymer	Polyamide polymer
Acrylic resins are	Brown colour	Colourless	Gold colour	White colour	Colourless
Which one of the following can be polymerised to polythene	Ethylene	Ethyl amide	Ethyl ketone	Ethyl acetate	Ethylene
Hydrolysis of cellulose gives	D-glucose	L- glucose	D-fructose	L-fructose	D-glucose
Cellulose acetate, polyacrylonitrile, and polyurethane are spun by this technique?	Melt spinning	Dry spinning	Wet spinning	Spinning	Dry spinning
Natural fibers are consisting of ?	Linear polymers	Nonlinear polymers	Copolymers	Chain polymers	Linear polymers
Polyacrylonitrile is soluble in which solvent?	Dimethylformamide (DMF)	Methanol	Water	Acetone	Dimethylformamide (DMF)
It is used as a plastic as well as a fibre	Polyamides	Polyester	Acrylic fibre	Polyethylene	Polyamides
Which one is used in tires and ropes?	Cotton	Nylon	Polyamide	Polyester	Nylon
Which is used in clothes, belts and accessories?	Cotton	Nylon	Polyamide	Polyester	Nylon
which is not a Synthetic polymers?	polyamide	Light stabilizers	Fibers	Glass fibre	polyamide
The alkyl resins are condensation polymers obtained from dibasic acids and	phenol	formaldehyde	Acetaldehyde	Glycol	Phenol
The first step in the reaction of the diol and diacid monomer is to form ?	dimer	trimer	Pentamer	Tetramer	Dimer
The rate of a step polymerization is conveniently expressed in terms of the	Concentrations of the reacting functional groups.	concentration of the monomeric	Concentration of monomer and the solvent	Concentration of the functional groups and monomers	Concentration of the functional groups and r
A dimer reacts with a monomer to give	Trimer	Dimer	Pentamer	Tetramer	Trimer
In thermal catalyzed polymerizations the most widely used mode of generating radicals to initiate polymerization ?	Homolytic dissociation of initiators	Heterolytic dissociation of initiators	Decomposition of the initiator	Association of the initiator	Homolytic dissociation of initiators
The Polyesterification of a diol and a diacid will illustrate the general kinetics of a typical ?	Step polymerization	Ionic polymerization	Radical polymerization	Self catalysted polymerization	Step polymerization
The carboxyl concentration is comprised of two first-order dependencies, one for the carboxyl as the reactant and another one as?	Product	Reactant	Reagent	Catalyst	Catalyst

The polyesterification becomes a much more economically feasible reaction when it is catalyzed by an ?	Base	Acid	Alkali	Neutral	Acid

[16CHU403]   Reg. No----------------------

KARPAGAM ACADEMY OF HIGHER EDUCATION

(Deemed to be University Established Under Section 3 of UGC Act 1956)

(For the candidates admitted from 2016 onwards)

SEMESTER- IV

B.Sc. Degree Examination

II B.Sc. Chemistry

Internal Exam-I

ORGANIC CHEMISTRY-IV

(Organic Spectroscopy)

Date: Maximum: 50 marks

Time: 2 hrs

Part A

Answer all the questions (20 x 1 = 20 marks)

1. Which among the following is the laws of Photochemistry?
   a. Hooks law   b. Beer-Lambertz law   c. Charls law d. Avagdros law

2. The emission of radiation is quantized and each quantum of radiation is called
   a. Photon   b. neutron   c. electron   d. proton

3. The unit of frequency is
   a. Hertz   b. centimetre   c. newton   d. pascal

4. _____ mainly involves in the promotion of electrons from ground state to excited state.
   a. UV Spectroscopy   b. IR Spectroscopy   c. NMR Spectroscopy   d. Mass Spectroscopy

5. Structural information deducible from UV spectra is mainly about
   a. Inductive effect   b. Conjugation   c. Steric hindrance   d. Mesomeric effect

6. Isolated Covalently bonded group shows the characteristic absorption in UV region is called
   a. Chromophore   b. Auxochrome   c. Hypsochromic shift   d. bathochromic shif

7. The Auxochrome present in Aniline is
   a. NH_3 b. NH_2 c. benzene   d. $C=C$

8. Chromophore - Auxochrome combination is termed as
   a. Chromogen   b. ionization   c. chemisorption   d. absorption

9. The absorption maximum is shifted towards longer wavelength is called
   a. Bathochromic shift   b. hypsochromic shift   c. Hyperchromic shift   d. hypochromic shift

10. Hypsochromic shift is also called as
    a. Yellow Shift   b. Red Shift   c. green shift   d. Blue shift

11. The carbonyl group of aldehydes undergoes_____
    a. $n-\pi^*$ b. $\pi-\pi^*$ c. $\sigma-\sigma^*$ d. $n-\sigma^*$

12. 1,3 butadiene undergoes_____ type of transission
    a. $n-\pi^*$ b. $\pi-\pi^*$ c. $\sigma-\sigma^*$ d. $n-\sigma^*$

13. The intensity of absorption maximum increases in_____
    a. Bathochromic shift   b. hypsochromic shift   c. Hyperchromic shift   d. hypochromic shift

14. The region between 2000 to 4000Å is called
    a. Near UV region   b. far UV region   c. Visible region   d. IR region

15. The λ_{max} basic value for 1,3 butadiene
    a. 215 nm   b. 217 nm   c. 253 nm   d. 202 nm

16. Conjugated double bond present in the same ring termed as
    a. execyclic b. heteroannular   c. Homoannular   d. endocyclic

17. The IR range is from
    a. 200-4000 cm⁻¹   b. 200-800 cm⁻¹   c. 400-8000 cm⁻¹   d. 400-4000 cm⁻¹

18. The IR stretching frequency of aldehyde is
    a. 1714 cm⁻¹   b. 1780 cm⁻¹   c. 1880 cm⁻¹   d. 1814 cm⁻¹

19. The distance between two atoms increases or decreases but atoms remain the same bond axis is called
    a. Stretching vibrations   b. bending vibrations   c. wagging vibrations   d. rocking vibrations

20. The IR stretching frequency of acetone is
    a. 1620 cm⁻¹   b. 1820 cm⁻¹   c. 1720 cm⁻¹   d. 1420 cm⁻¹

Part B

Answer all the questions (3 x 2 = 6 marks)

21. Write a short note on electromagnetic spectrum.

22. What are absorption laws?

23. Name the various types of bending vibrations.

Part C

Answer all the questions (3 x 8 = 24 marks)

24. a. Explain the Woodward-Fischer rules for calculating absorption maximum in α, β unsaturated carbonyl compounds with three examples

OR

b. Discuss the various types of electronic transitions and explain the effect of the polarity of the solvent on each type of transition.

25. a. Describe the Woodward-Fischer rules for calculating absorption maximum in dienes with examples.

OR

b. Define the following terms:

(i)   Bathochromic shift   (ii) hypsochromic shift   (iii) A chromophore

(iv) Auxochrome

26. a. Explain the electronic factors which influence the absorption frequency.

OR

b. Write note on finger print region.