

Chemistry-1

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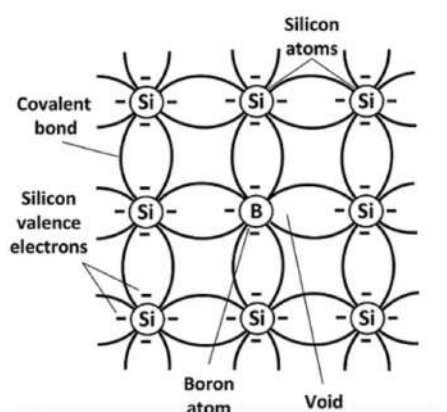
Date of Examination: 16-12-2023

Section A

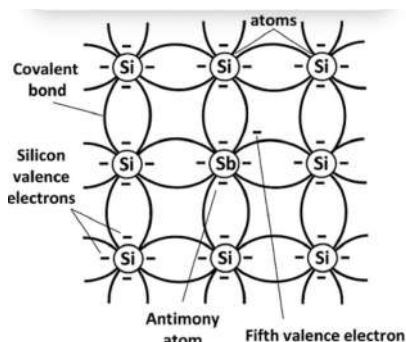
Question 1. Write Briefly:

a) What are N type and P type semiconductors ?

Answer: The P-type semiconductor can be defined as, once the trivalent impurity atoms such as indium, gallium are added to an intrinsic semiconductor, and then it is known as a p-type semiconductor. In this semiconductor, the majority charge carriers are holes whereas minority charge carriers are electrons. The hole's density is higher than the electrons density. The acceptor level mainly lies nearer to the valence band.



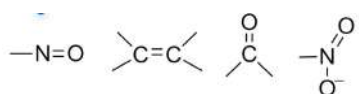
The N-type semiconductor can be defined as, once the pentavalent impurity atoms such as Sb, As is added to an intrinsic semiconductor, and then it is known as an n-type semiconductor. In this semiconductor, the majority charge carriers are electrons whereas minority charge carriers are holes. The electrons density is higher than the density of the holes. The donor level mainly lies nearer to the conduction band.



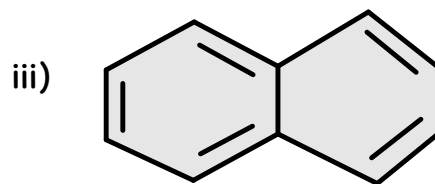
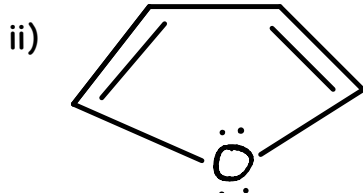
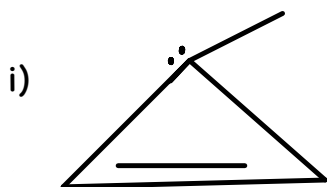
b) What are chromophores? Give examples.

Answer: When an organic compound absorbs the radiation in the visible part of the electromagnetic spectrum, it appears to be colored. The colored properties associated with the organic compounds are due to the presence of few groups of atoms known as chromophores which absorb visible light photons.

In Greek, chroma means color, and phoron means bearer. A chromophore is usually a group of atoms that are having electron-withdrawing nature, possess unsaturation, and when present in conjugation imparts color to the compound by absorption of visible light. Examples of chromophore include groups such as -



c) Out of the following compounds write which are aromatic or anti aromatic?



Answer: If the number of π electrons in the ring(s) satisfies Hückel's Rule $[4n+2]$ it is potentially aromatic. If the number of π electrons in the ring(s) follows $[4n]$ it is potentially anti-aromatic.

i) Anti Aromatic

ii) Aromatic

iii) Aromatic

d) Distinguish between an Ideal gas and Real gas.

Answer:

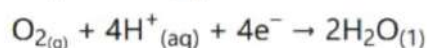
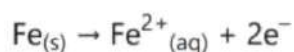
Difference between Ideal gas and Real gas	
IDEAL GAS	REAL GAS
No definite volume	Definite volume
Elastic collision of particles	Non-elastic collisions between particles
No intermolecular attraction force	Intermolecular attraction force
Does not really exist in the environment and is a hypothetical gas	It really exists in the environment
High pressure	The pressure is less when compared to Ideal gas
Independent	Interacts with others
Obeys $PV = nRT$	Obeys $P + \frac{(n^2a)}{V^2}$ $(V - nb) = nRT$

e) What is electrochemical corrosion? Discuss.

Answer: The metal is oxidised by oxygen in the presence of moisture. The redox process which causes the deterioration of metal is called corrosion.

Corrosion of iron is known as Rusting and it is an electrochemical process.

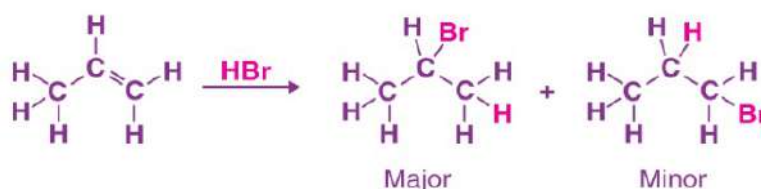
Electrochemical mechanism of corrosion – The formation of rust requires both oxygen and water. Since it is an electrochemical redox process, it requires both an anode and cathode in different places on the iron. The iron surface and a droplet of water on the surface form a tiny galvanic cell. The region enclosed by water is exposed to low amount of oxygen and it act as anode. The remaining area has high amount of oxygen and it act as cathode. So based on oxygen amount, an electrochemical cell is formed.



f) What is Markonikov's rule ? Give an example.

Answer: To simplify the rule, it can also be stated as – “Hydrogen is added to the carbon with the most hydrogens and the halide is added to the carbon with the least hydrogens”.

An example of a reaction that observes Markovnikov's rule is the addition of hydrobromic acid (HBr) to propene, which is shown below.



g) What is Lewis concept of Acids and Bases ?

Answer:

According to Lewis's theory of acid–base reactions, “a species that has vacant orbitals and can accept an electron pair is called Lewis acid.”

An electrophile is a Lewis acid as it is an electron-deficient group and can accept electrons easily. Acid uses its lowest unoccupied molecular orbital (LUMO) to form bonds with bases. For example: All cations are Lewis acids. Cu^{2+} , Zn^{2+} , H^+ , AlF_3 .

According to Lewis's theory of acid–base reactions, “a species that has a lone pair of electrons and can donate an electron pair is called Lewis base.”

A nucleophile is a Lewis base as it is an electron surplus group and can donate electrons easily. The base uses its highest occupied molecular orbital (HOMO) to form bonds with acids. For example: H^- , F^- , NH_3 , H_2O .

h) Why electron affinity of Noble gases are zero?

Answer: • The quantity of energy released when the isolated and neutral atom in the gaseous phase forms negatively charged species (anion) by the gain of one electron is termed as electron affinity.

- Electron affinity gives the idea about the ease with which an atom of any element accepts an electron to form its respective anion.

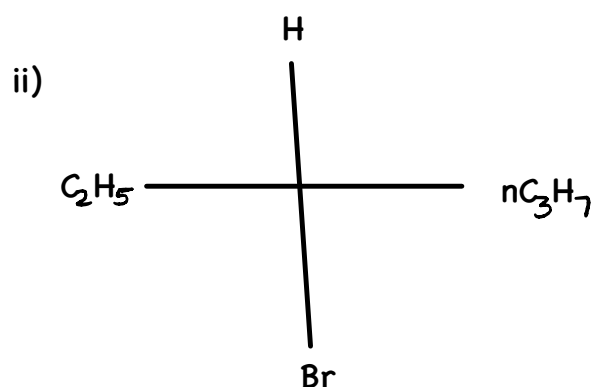
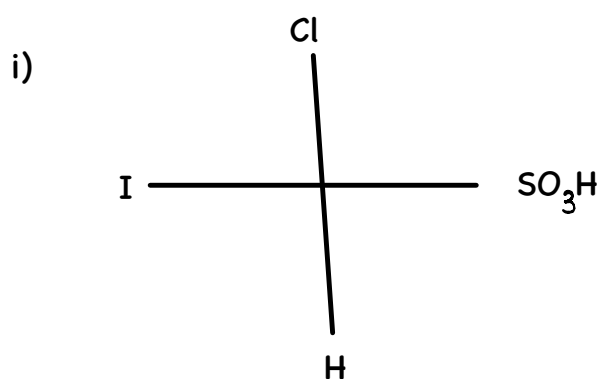
- Elements present in Group 18 or zero Group of the periodic table are termed as noble gases or inert gases.

- It includes Helium (He), Neon (Ne), Argon (Ar), Krypton (Kr), Xenon (Xe), and Radon (Ra).

- Noble gases have completely filled outermost or valence shells and therefore, their electronic configuration is highly stable.

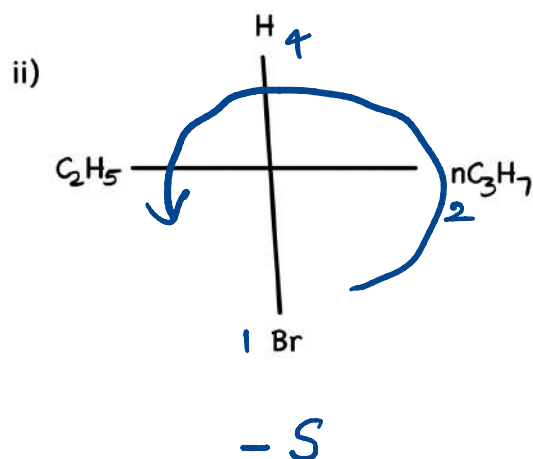
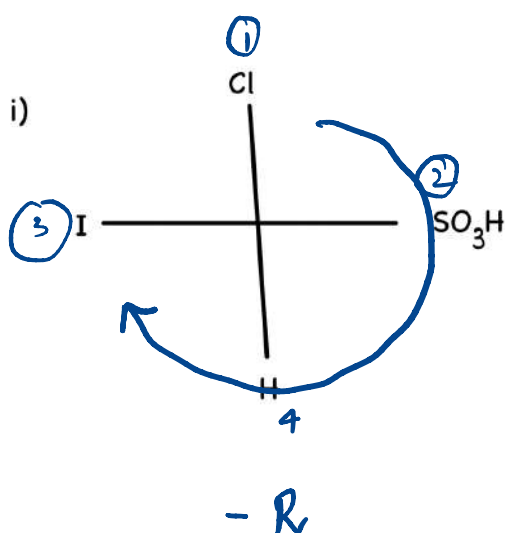
- Due to the stable electronic configuration, the tendency of noble gases to accept the electron is zero.

i) Assign R/S configuration to each of the following compounds.

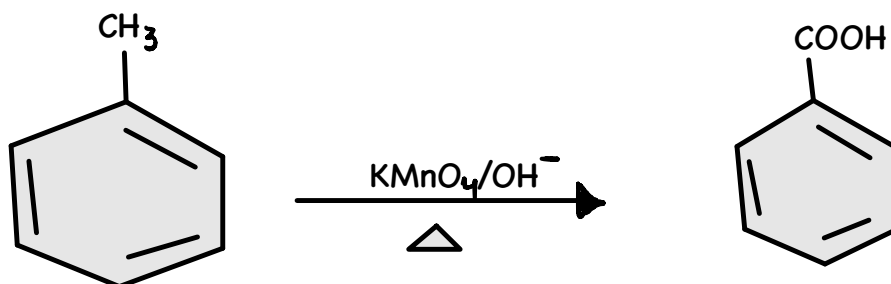


Answer

:



j) Complete the following reaction:



Question 2.

Section B

a) Explain crystal field theory in detail. How it can be utilised in explaining the octahedral complexes of transition elements.

Answer: Crystal field theory was proposed which described the metal-ligand bond as an ionic bond arising purely from the electrostatic interactions between the metal ions and ligands.

Crystal field theory considers anions as point charges and neutral molecules as dipoles.

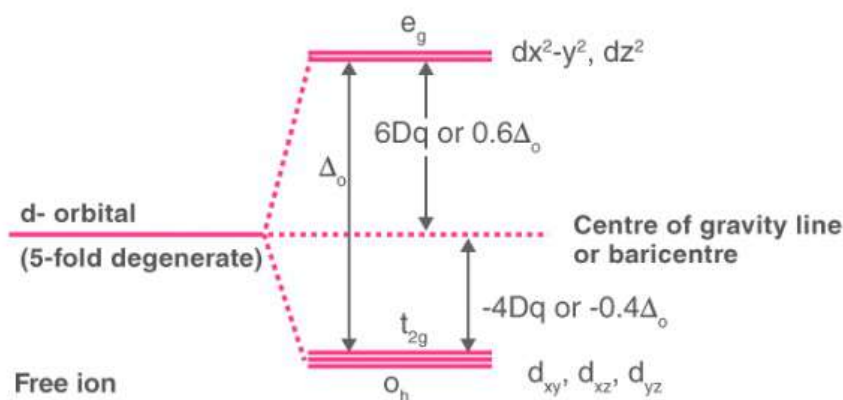
When transition metals are not bonded to any ligand, their d orbitals degenerate that is they have the same energy.

When they start bonding with other ligands, due to different symmetries of the d orbitals and the inductive effect of the ligands on the electrons, the d orbitals split apart and become non-degenerate.

- In the case of an octahedral coordination compound having six ligands surrounding the metal atom/ion, we observe repulsion between the electrons in d orbitals and ligand electrons.
 - This repulsion is experienced more in the case of dx^2-y^2 and dz^2 orbitals as they point towards the axes along the direction of the ligand.
 - Hence, they have higher energy than average energy in the spherical crystal field.
 - On the other hand, dxy , dyz , and dxz orbitals experience lower repulsions as they are directed between the axes.
 - Hence, these three orbitals have less energy than the average energy in the spherical crystal field.

Thus, the repulsions in octahedral coordination compound yield two energy levels:

- t_{2g} - set of three orbitals (dxy , dyz and dxz) with lower energy
- e_g - set of two orbitals (dx^2-y^2 and dz^2) with higher energy



Crystal Field Splitting in Octahedral Complex

This splitting of degenerate level in the presence of ligand is known as crystal field splitting. The difference between the energy of t_{2g} and e_g level is denoted by " Δ_o " (subscript o stands for octahedral). Some ligands tend to produce strong fields thereby causing large crystal field splitting whereas some ligands tend to produce weak fields thereby causing small crystal field splitting.

Question 2. b) differentiate between bonding and anti-bonding molecular orbitals.

Answer:

Bonding molecular orbitals and Anti-bonding molecular orbitals

Bonding Molecular Orbitals	Anti-bonding Molecular Orbitals
(i) They are formed by the additive effect of the atomic orbitals. $\phi_b = \psi_1 + \psi_2$	(i) They are formed by the subtractive effect of the atomic orbitals. $\phi_a = \psi_1 - \psi_2$
(ii) In the region between the nuclei of bonded atoms, the electron density increases.	(ii) The electron density decreases in the region between the nuclei of the atoms and it increases in the region away from the inter-nuclear region. This is responsible for the instability of the bond.
(iii) The electrons present in the bonding orbitals result in an attraction between the two atoms.	(iii) The electrons present in the anti-bonding-molecular orbitals (if any) result in the repulsion between the two atoms.
(iv) Because of attractive forces involved, these molecular orbitals have lower energy than the atomic orbitals from which they are formed. This is the cause of their greater stability.	(iv) Because of the repulsive forces involved, these molecular orbitals have higher energy than the atomic orbitals from which they are formed. This is the cause of their lower stability, i.e., it does not favour bond formation and that is why the name anti-bonding.
(v) They are formed when the lobes of the combining atomic orbitals have the same sign.	(v) They are formed when the lobes of the combining atomic orbitals are of opposite sign.
(vi) These molecular orbitals are represented by σ and π	(vi) These molecular orbitals are represented by σ^* and π^*

Question 3. define the following terms.

- a) Bathochromic Shift
- b) Auxochromes
- c) Fluorescence
- d) Hyperchromic Shift

Answer:

a) Bathochromic Shift: Bathochromic shift is a change of spectral band position in the absorption, reflectance, transmittance, or emission spectrum of a molecule to a longer wavelength (lower frequency). This can occur because of a change in environmental conditions: for example, a change in solvent polarity will result in solvatochromism. A series of structurally related molecules in a substitution series can also show a bathochromic shift.

b) Auxochromes: An auxochrome is a functional group of atoms with one or more lone pairs of electrons when attached to a chromophore, alters both the wavelength and intensity of absorption. If these groups are in direct conjugation with the pi-system of the chromophore, they may increase the wavelength at which the light is absorbed and as a result intensify the absorption. A feature of these auxochromes is the presence of at least one lone pair of electrons which can be viewed as extending the conjugated system by resonance. Examples include the hydroxyl (-OH), amino (-NH₂), aldehyde (-CHO).

c) Fluorescence: Fluorescence is the emission of light by a substance that has absorbed light or other electromagnetic radiation. It is a form of luminescence. In most cases, the emitted light has a longer wavelength, and therefore a lower photon energy, than the absorbed radiation. A perceptible example of fluorescence occurs when the absorbed radiation is in the ultraviolet region of the electromagnetic spectrum (invisible to the human eye), while the emitted light is in the visible region; this gives the fluorescent substance a distinct color that can only be seen when the substance has been exposed to UV light.

d) Hyperchromic Shift: It is the shift where intensity of absorption maximum decrease. When the geometry of a molecule is distorted due to the introduction of group, this type of shift may take place. For example, biphenyl absorbs at lower value, as compared to 2-methyl biphenyl.

Question 4. Explain in detail the Vanderwaal's equation of state for real gases.

Answer:

The Van der Waals equation of state is another name for the Van der Waals equation. The connection between the pressure, volume, temperature, and quantity of actual gases is depicted by the Van der Waals equation. This equation was created in 1873 by Johannes Van der Waals. This new equation is an extension of the ideal gas law, which also discusses how molecules in a gas interact with one another and have finite sizes. The Van der Waals equation is acceptable to both ideal gases and real gases, whereas the ideal gas law only applies to ideal gases. This is the main distinction between the two.

The following is the Van der Waals equation:

$$\left(P + \frac{an^2}{V^2}\right) (V - nb) = nRT$$

Where,

P= pressure

V= volume

a= constant that measures the attractive force between the molecules

b= volume correction factor

nb= volume occupied by the gas molecules

T= Temperature

The Van der Waals equation of state includes two constants, 'a' and 'b', which are known as the Van der Waals constants.

Unit of Van der Waals constant a is atm lit² mol⁻².

Unit of Van der Waals constant b is litre mol⁻¹.

Question 5. a) The e.m.f. of the cell reaction $3\text{Sn}^{+4} + 2\text{Cr} \rightarrow 3\text{Sn}^{+2} + 2\text{Cr}^{+3}$ is 0.89. Calculate the standard free energy change for the reaction.

Answer: $\Delta G = -nFE^\circ$
 $= -6 \times 0.89 \times 96500 \text{ C mol}^{-1}$
 $= -515310 \text{ J}$
 $= -514.310 \text{ kJ}$

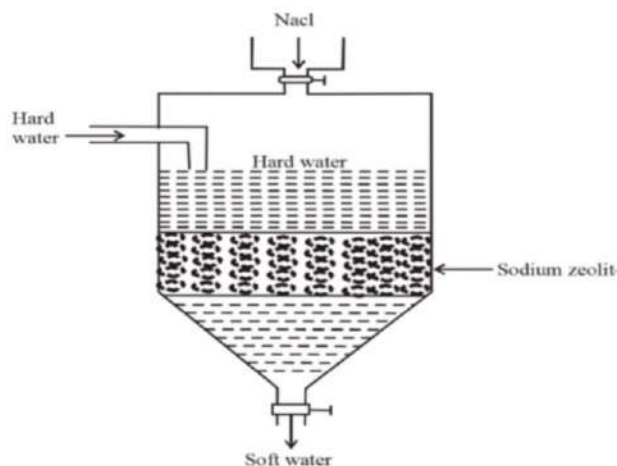
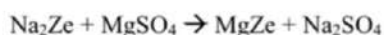
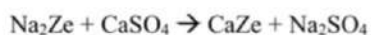
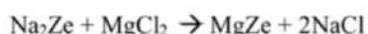
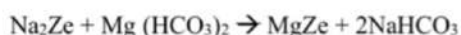
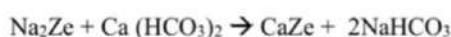
b) Discuss the Zeolite process for softening of water.

Answer: Zeolites are naturally occurring hydrated sodium aluminium silicate, $\text{Na}_2\text{O} \cdot \text{Al}_2\text{O}_3 \cdot x \text{SiO}_2 \cdot y\text{H}_2\text{O}$ where $x = 2$ to 10 and $y = 2$ to 6 . The synthetic form of zeolite is known as permutit. Synthetic zeolite is represented by Na_2Ze . The sodium ions which are loosely held in Na_2Ze are replaced by Ca^{2+} and Mg^{2+} ions present in the water. Natural zeolites are non-porous.

Synthetic zeolites are porous and jelly structure. They are prepared by heating together china clay, feldspar and soda ash. These zeolites are higher exchange capacity per unit weight than natural zeolites.

Process

In this process, the hard water is passed through a bed of sodium zeolite (Na_2Ze). The hardness causing ions (Ca^{2+} , Mg^{2+}) in hard water is replaced by loosely held sodium ions in zeolite bed. The outgoing soft water contains only sodium ions.



Section C

Question 6 Explain why:

a) Electron affinity of fluorine is less than that of chlorine.

Answer: Fluorine is the most electronegative element but still its electron affinity is less than that of chlorine. It is because of the small size of fluorine. All the electrons in the atom repels the incoming electron significantly, this nullify the effect of higher electronegativity of fluorine over chlorine.

b) Ionisation energy decreases down the group and increases along the period.

Answer: As we move down the group, ionization energy decreases because while moving down the group atomic size increases due to this fact the force of attraction between the nucleus and the valence electrons is weaker. So, it becomes easy to remove an electron from an atom. Thus, the ionization decreases down the group.

The atomic number increases moving across a period and subsequently, the nuclear charge also increases. Thus, the valence electrons experience greater pull and the atomic radii decreases. As a result, more energy is required to completely extract a valence electron. Hence, ionisation energy increases across a period.

c) Which has smallest size, Cl or Cl^- and why?

Answer: The size of an ion compared to its corresponding atom is influenced by the addition or removal of electrons. When a Cl atom gains an electron to form a Cl^- ion, the extra electron increases the electron-electron repulsion, causing the electron cloud to expand and the ion to become larger than the atom. Therefore, the size of Cl^- is greater than Cl.

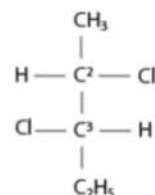
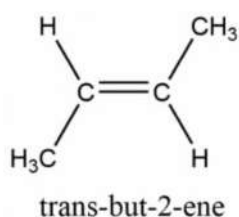
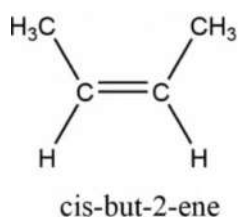
Question. 7 a) what is Diastereomerism? Explain by giving at least two examples.

Answer: The optical isomers which do not mirror images of each other are called diastereoisomers and this phenomenon is called diastereoisomerism.

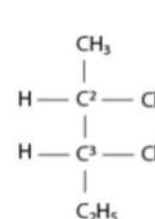
Their characteristics are given below:

- 1 These isomers can not superimposable to each other.
- 2 Diastereoisomerism is found only, in those compounds in which at least two chiral carbon centers are present.
- 3 The physical properties of diastereoisomers of a compound are different. So, these can be separated by fractional distillation,

For Example:



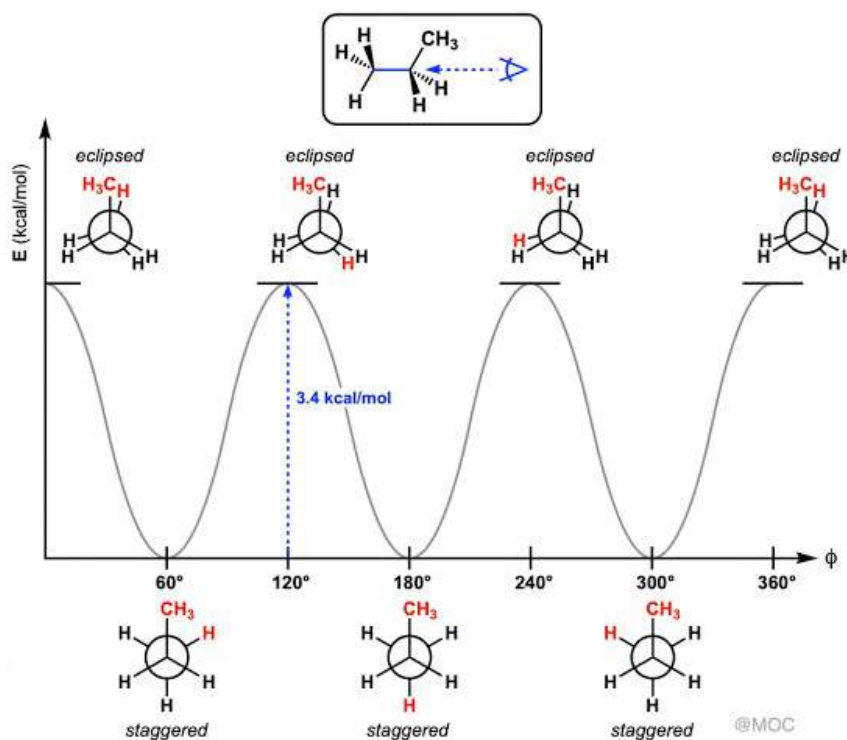
Same configuration



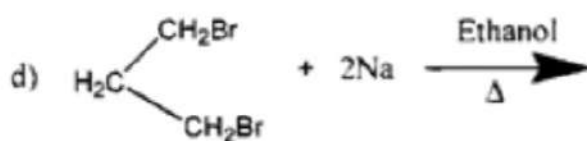
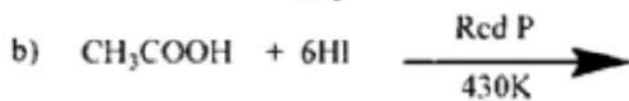
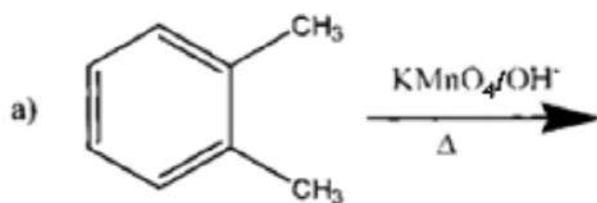
b) Discuss the conformational analysis of propane.

Answer: Experiments show that there is a 14 kJ/mol (3.4 kcal/mol) barrier to rotation in propane. The most stable (low energy) conformation is the one in which all of the bonds are as far away from each other as possible (staggered when viewed end-on in a Newman projection). The least stable (high energy) conformation is the one in which, for any two adjacent carbon atoms, the six bonds (five C-H and one C-C) are as close as possible (eclipsed in a Newman projection). All other conformations lie between these two limits.

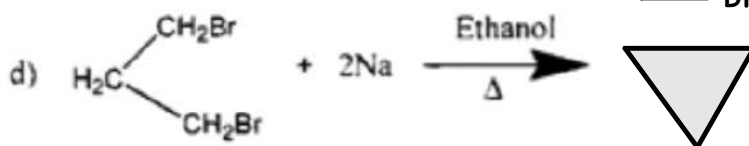
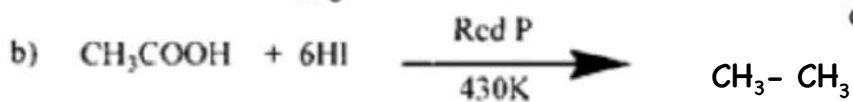
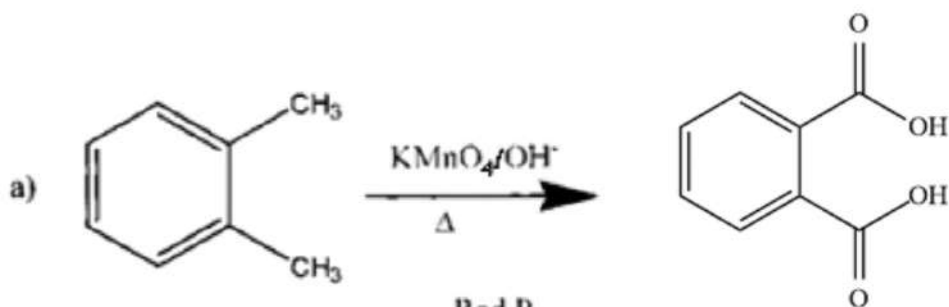
Energy Diagram for Rotation Of The C-C Bond In Propane



Question. 8 Complete the following reactions.



Answer:



Question. 9. Explain the following:

a) HSAB Principle: Hard Acid Soft Base Theory (HSAB):

- This theory works on the principle that soft acid reacts with the soft base while hard acid reacts with the hard base.
- HSAB is widely used for explaining the stability of compounds/molecules and the reaction mechanisms as well as pathways.
- In this theory, "Hard" stands for small species that have high charge states while "Soft" stands for big species with low charge states.

Examples of Hard and Soft acid/base:

- The hard acids can be Li^+ and Na^+ while the hard bases can be F^- and Cl^- .
- The soft acids are Cu and Ag while the soft bases are CN^- and I^- .

b) Enantiomerism: Enantiomers are a pair of molecules that exist in two forms that are mirror images of one another but cannot be superimposed one upon the other. A pair of enantiomers is distinguished by the direction in which when dissolved in solution they rotate polarized light, either dextro (d or +) or levo (l or -) rotatory; hence the term optical isomers. When two enantiomers are present in equal proportions they are collectively referred to as a racemic mixture, a mixture that does not rotate polarized light because the optical activity of each enantiomer is cancelled by the other.

c) Electronegativity: Electronegativity, symbolized as χ , is the tendency for an atom of a given chemical element to attract shared electrons (or electron density) when forming a chemical bond.[1] An atom's electronegativity is affected by both its atomic number and the distance at which its valence electrons reside from the charged nucleus. The higher the associated electronegativity, the more an atom or a substituent group attracts electrons.

d) Free Energy: In thermodynamics, the free energy is one of the state functions of a thermodynamic system (the others being internal energy, enthalpy, entropy, etc.). The change in the free energy is the maximum amount of work that the system can perform in a process at constant temperature, and its sign indicates whether the process is thermodynamically favorable or forbidden. Since free energy usually contains potential energy, it is not absolute but depends on the choice of a zero point. Therefore, only relative free energy values, or changes in free energy, are physically meaningful.