

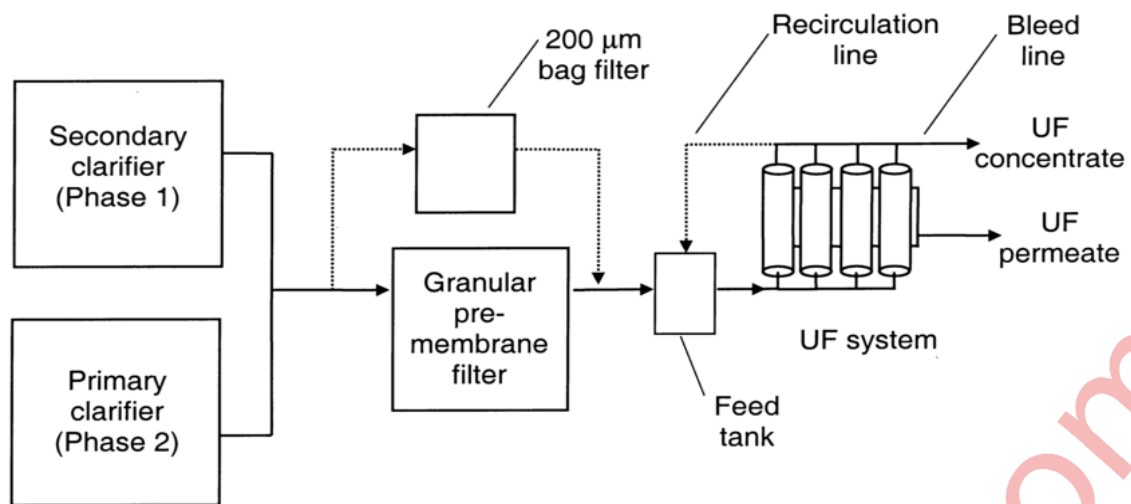
CHEMISTRY SOLUTION

(Rev-2022' Scheme DEC-2022 , SEM-1)

Q.1]A. Write a brief note on Ultrafiltration. [3]

Solution:-

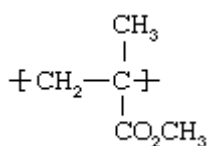
1. Ultrafiltration is performed similarly to reverse osmosis. The main principle of this is the pressure difference created between the solute and solvent along the semi-permeable membrane and the connection between flux and pressure on the solution.
2. The solvent to be filtered is pressured through the ultrafiltration membrane as it also helps to change the taste, odor, and color of the solvent.
3. The ultrafiltration system consists of a feed tank that is connected to a feed pump that directs the feed through the membrane modules.
4. The feed is passed through the membrane and the filtrate collected out is the permeate and one which stands back is the retentate.
5. The retentate is transported back to the feed pump, a separate retentate valve is present that helps further removal of fluids from the Ultrafiltration system.
6. The collection of the desired product depends on the nature of the product. Sometimes, it may be the permeate passed through the membrane or the retentate that stays back.
7. Application of Ultrafiltration are:-]
 - Filtration of effluent from paper pulp mill.
 - Cheese manufacture, Removal of pathogens from milk.



Q.1]B. Write Synthesis, properties and uses of PMMA polymer. [3]

Solution:-

Polymethyl methacrylate (PMMA), a synthetic resin produced from the polymerization of methyl methacrylate. A transparent and rigid plastic, PMMA is often used as a substitute for glass in products such as shatterproof windows, skylights. PMMA, an ester of methacrylic acid ($\text{CH}_2=\text{C}[\text{CH}_3]\text{CO}_2\text{H}$), belongs to the important acrylic family of resins. PMMA, an ester of methacrylic acid ($\text{CH}_2=\text{C}[\text{CH}_3]\text{CO}_2\text{H}$), belongs to the important acrylic family of resins. The structure of the polymer repeating unit is:



Properties of PMMA:-

1. It is hard, fairly rigid material with a high softening temperature of about 139-140 Celsius.
2. It becomes rubber like after reaching 65 Celsius.
3. It has an outstanding shape forming properties due to wide span of temperature from its rigid state to viscous.
4. It has optical transparency.
5. It has high resistance to sunlight and ability of transmission light accurately.

Uses of PMMA:-

1. For making lenses ,optical parts of instruments, aircraft, light fixtures, artificial eyes, wind screen, bonesplints, decorative articles etc.
2. It is found in paint.
3. Acrylic "latex" paints often contain PMMA suspended in water.
4. Used in making window glasses
5. BUNA-S (or STYRENE RUBBER)

Q.1]C. Write Basic postualates of molecular orbital theory.

[3]

Solution:-

Molecular orbitals are formed by combination of atomic orbitals of equal energies(in case of homonuclear molecules) or of comparable energies.(in case of heteronuclear molecules).

The number of molecular orbitals formed is equal to the number of atomic orbitals undergoing combination. The postulates of Molecular Orbital Theory are:

1. The total number of molecular orbitals formed is equal to the total number of atomic orbitals offered by atomic species.
2. The electrons in the molecular orbital are filled in the increasing order of orbital energy (from orbital having lower energy to orbital having higher energy).
3. Orbital with lower energy followed by higher orbital energy is the pattern of electron alignment.

Molecular Orbital Theory describes three types of orbital based on the pattern of electron bonding. These are –

1. Bonding Molecular Orbital
2. Non-bonding Molecular Orbital
3. Anti-bonding Molecular Orbital

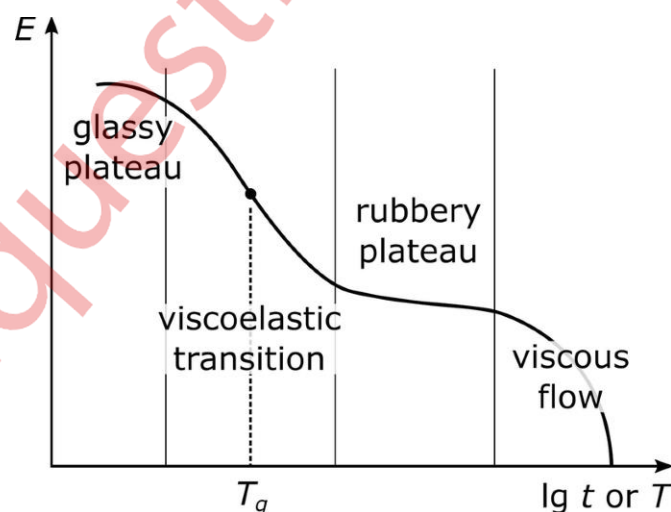
Out of these, antibonding molecular orbitals always have high energy than the parent orbitals.

However, molecular orbitals always have lower energy than parent orbitals.

Q.1]D. Explain the term ‘ Viscoelasticity’ with reference to the polymers. [3]

Solution:-

- i. Viscoelasticity is a property exhibited by certain materials, including polymers, that combines the characteristics of both viscosity and elasticity. It refers to the ability of a material to display both viscous (liquid-like) and elastic (solid-like) behavior under the influence of external forces, such as stress or strain.
- ii. In the context of polymers, viscoelasticity arises due to their unique molecular structure and behavior.
- iii. Polymers are large, long-chain molecules made up of repeating monomer units. These chains can slide and move past each other, contributing to their ability to flow like a liquid (viscous behavior) when subjected to stress.
- iv. At the same time, polymers also have covalent cross-links and secondary forces (like van der Waals forces and hydrogen bonding) between chains, which give them some degree of elasticity.
- v. When a polymer is subjected to an external force, such as stretching or shearing, the polymer chains start to align and straighten out, contributing to the elastic response.
- vi. As the force is removed, the chains tend to return to their original coiled state, leading to a partially elastic recovery.
- vii. For instance, rubber, which is a viscoelastic material, can bounce back to its original shape after stretching (elasticity), but it also shows some degree of deformation over time (viscosity).



Q.1]E. A hard water sample was found to have following salts: $\text{Ca}(\text{HCO}_3)_2 = 132\text{mg/L}$, $\text{MgSO}_4 = 164\text{mg/L}$, $\text{CaCl}_2 = 127\text{ mg/L}$, $\text{NaCl} = 98\text{mg/L}$. Calculate temporary, permanent and total hardness of the given sample of water. [3]

Solution:-

$\text{Ca}(\text{HCO}_3)_2 = 132\text{mg/lit.}$

$\text{MgSO}_4 = 164\text{mg}$

$\text{CaCl} = 127\text{ mg/L}$

$\text{NaCl} = 98\text{mg/L}$

Calculation of CaCO_3 equivalents

Impurities	Quantity	Multiplying factor	CaCO_3 equivalents in ppm
$\text{Ca}(\text{HCO}_3)_2$	132 mg/lit	$132 \times 100 / 162$	81.48
MgSO_4	164 mg/lit	$164 \times 100 / 120$	136.66
CaCl_2	127 mg/lit	$127 \times 100 / 111$	114.41
NaCl	98 mg/lit	----	----

Here NaCl will not contribute to hardness.

Thus , temporary hardness = $\text{Ca}(\text{HCO}_3)_2 + \text{Mg}(\text{HCO}_3)_2$

$$= 81.48 + 136.66$$

$$= 218.14$$

Thus Permanent hardness = CaCl_2

$$= 114.41$$

Total Hardness = Temporary Hardness + Permanent Hardness

$$= 218.14 + 114.41$$

$$= 332.55$$

Thus,

Temporary Hardness = 218.14 mg/lit.

Permanent Hardness = 114.41 mg/lit.

Total Hardness = 332.55 mg/lit.

Q.1]F. Define the terms involved Gibbs phase rule equation. [3]

Solution:-

The Gibbs phase rule is an important concept used to determine the number of degrees of freedom (F) in a system at equilibrium. It helps in understanding the relationships between the number of components (C), phases (P), and the number of intensive variables (such as temperature, pressure, and concentration) that can be independently varied in a system without disturbing the equilibrium. The Gibbs phase rule equation is given by: $F = C - P + 2$

Where:

F = Number of degrees of freedom (the maximum number of intensive variables that can be independently varied)
C = Number of components (chemically independent constituents, like elements or compounds)
P = Number of phases (distinct physically separate and homogeneous parts of the system)

Let's explain the terms involved:

- **Components (C):** Components are the chemically independent constituents that make up a system. In the context of engineering chemistry, it typically refers to the number of chemical species present in the system. For example, in a water and ethanol mixture, there are two components: water and ethanol.
- **Phases (P):** Phases are distinct physically separate and homogeneous parts of a system that are separated by definite boundaries. Each phase has uniform properties throughout. For example, in a water-ethanol mixture, if both liquids

are present, it forms a two-phase system (liquid-water phase and liquid-ethanol phase).

- Degrees of Freedom (F): Degrees of freedom refer to the number of intensive variables that can be independently varied in a system at equilibrium without disturbing the number of phases. These intensive variables can include temperature (T), pressure (P), and concentrations of components. The degrees of freedom help us understand the flexibility of the system.

Q.1]G. Is Cyclopentadiene molecule aromatic in nature ? why ? [3]

Solution:-

Yes, cyclopentadiene (C₅H₆) is an aromatic molecule. It fulfills all the criteria for aromaticity according to Hückel's rule, which is a set of conditions used to determine if a compound is aromatic:

- Planarity: The molecule must be planar or nearly planar. Cyclopentadiene is a flat, planar molecule, as all the carbon atoms and hydrogen atoms lie in the same plane.
- Cyclic: The molecule must be cyclic, meaning it forms a closed ring of atoms. Cyclopentadiene consists of a five-membered carbon ring, which is cyclic.
- Fully conjugated: The molecule must have a continuous or uninterrupted system of π (pi) electrons, with alternating single and double bonds or resonance forms. In cyclopentadiene, there are three carbon-carbon double bonds, and the π electrons are shared in a delocalized manner over the entire five-membered ring.
- $4n + 2 \pi$ electrons: The number of π electrons in the molecule must satisfy the $4n + 2$ rule, where n is an integer (0, 1, 2, 3, etc.). For aromaticity, the total number of π electrons should be equal to 2, 6, 10, 14, etc.

In cyclopentadiene, there are 6 π electrons (3 carbon-carbon double bonds). Plugging in $n = 1$ into the $4n + 2$ rule gives $4(1) + 2 = 6$, which matches the number of π electrons in cyclopentadiene.

Q.2]A. A standard hard water sample was prepared by dissolving 1.8 g CaCO₃ in 1.5L of distilled water. 50 ml of this water required 46 ml of EDTA. 50 ml of unknown hard water required 36 ml of same EDTA. This unknown hard water was boiled, cooled and filtered. 50 ml of this filtered water required 29 ml of same EDTA, Calculate temporary, permanent and total hardness of unknown hard water sample. [6]

Solution:-

Step 1: Calculate the Normality of EDTA Solution (N): Given that 50 ml of hard water sample requires 46 ml of EDTA, and the hard water sample contains CaCO₃ (calcium carbonate), the reaction is as follows:



From the reaction, it is evident that 1 mole of CaCO₃ reacts with 1 mole of EDTA.

1 mole of CaCO₃ is equal to its molar mass, which is 100.1 g.

So, the normality (N) of EDTA is given by:

$$N = (\text{Weight of CaCO}_3 \text{ in the 50 ml sample} / \text{Volume of EDTA used in ml}) * \text{Molar mass of CaCO}_3$$
$$N = (1.8 \text{ g} / 46 \text{ ml}) * 100.1 \text{ g/mol} \approx 3.91 \text{ N}$$

Step 2: Calculate the Concentration of Calcium (Ca²⁺) ions in the Hard Water Samples:

Using the titration results for the known and unknown hard water samples:

For the known hard water sample: 50 ml of hard water required 46 ml of 3.91 N EDTA.

For the unknown hard water sample: 50 ml of hard water required 36 ml of 3.91 N EDTA (before boiling and filtering). 50 ml of filtered hard water required 29 ml of 3.91 N EDTA (after boiling and filtering).

The difference in EDTA volume before and after boiling and filtering represents the calcium (Ca²⁺) ions that were precipitated as CaCO₃.

$$\text{Calcium ions consumed before boiling} = 36 \text{ ml} - 29 \text{ ml} = 7 \text{ ml}$$

$$\text{Calcium ions precipitated as CaCO}_3 = 46 \text{ ml} - 36 \text{ ml} = 10 \text{ ml}$$

Step 3: Calculate the Hardness of the Hard Water Samples:

Temporary hardness = Calcium ions consumed before boiling * N of EDTA * 50
(conversion to L) Temporary Hardness = 7 ml * 3.91 N * 0.05 L = 1.365 g/L (approx)

Permanent hardness = Calcium ions precipitated as CaCO₃ * N of EDTA * 50
(conversion to L) Permanent Hardness = 10 ml * 3.91 N * 0.05 L = 1.955 g/L (approx)

Total Hardness = Temporary Hardness + Permanent Hardness
Total Hardness = 1.365 g/L + 1.955 g/L ≈ 3.32 g/L

Answer:

The temporary hardness of the unknown hard water sample is approximately 1.365 g/L, the permanent hardness is approximately 1.955 g/L, and the total hardness is approximately 3.32 g/L.

Q.2]B. Describe Bonding in Benzene molecule and explain why it is aromatic? [5]

Solution:-

The concept of bonding in benzene is often described using the valence bond theory and molecular orbital theory:

1. Valence Bond Theory: According to the valence bond theory, the carbon atoms in the benzene ring form sigma (σ) bonds with each other by overlapping their sp² hybridized orbitals. Each carbon atom in the benzene ring has three sigma bonds and one unhybridized p orbital perpendicular to the plane of the ring. The delocalization of pi (π) electrons is crucial to understand the aromaticity of benzene. In a simplified view, each carbon atom contributes one of its three unhybridized p orbitals to form π bonds. These six π electrons are spread out above and below the plane of the carbon atoms, leading to the resonance structure of benzene, which can be represented by two resonance forms

2. Molecular Orbital Theory:

The molecular orbital theory provides a more comprehensive explanation for the aromaticity of benzene. In this theory, the pi (π) molecular orbitals result from the

overlap of the six p orbitals in the benzene ring. When the atomic orbitals combine, they form three molecular orbitals:

π Molecular Orbital 1 (π MO1): This orbital has bonding character and is lower in energy than the atomic p orbitals. It has a nodal plane perpendicular to the plane of the benzene ring.

π Molecular Orbital 2 (π MO2): This orbital has antibonding character and is higher in energy than the atomic p orbitals. It has a nodal plane parallel to the plane of the benzene ring.

π Molecular Orbital 3 (π MO3): This orbital has bonding character and is lower in energy than the atomic p orbitals.

Q.2]C. What is the role played by Plasticizer and Catalyst in making of plastic? [4]

Solution:-

1. Plasticizers:

Plasticizers are chemical additives used in the production of plastics to improve their flexibility, durability, and processability. The primary function of plasticizers is to increase the mobility of polymer chains, making them more flexible and allowing them to move more freely. As a result, the polymer chains can slide past each other more easily, leading to increased flexibility and lower glass transition temperature. The glass transition temperature is the temperature at which a polymer transitions from a hard, brittle state to a softer, more flexible state. The role of plasticizers can be understood as follows:

- i. **Flexibility:** By reducing intermolecular forces, plasticizers increase the chain mobility of the polymer, allowing it to bend and deform without breaking. This makes the plastic material more flexible and easier to process into various shapes.
- ii. **Softness:** Plasticizers can impart a soft or rubbery texture to the plastic, depending on the type and amount used. This property is essential for applications such as flexible PVC used in hoses, cables, and inflatable products.

2. Catalyst:

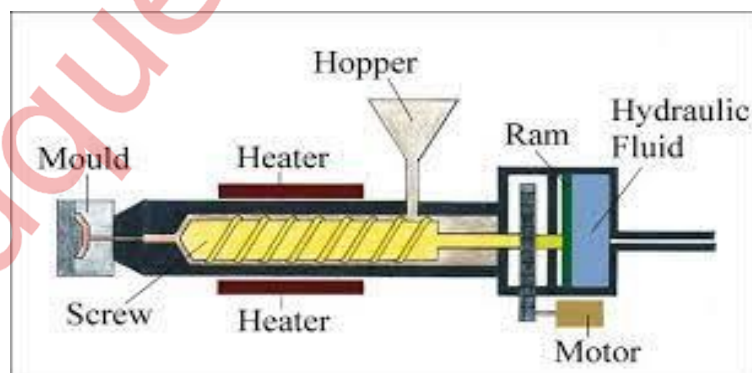
Catalysts are substances that increase the rate of a chemical reaction without being consumed in the process. In the context of plastic manufacturing, catalysts are used during polymerization reactions to initiate and facilitate the formation of polymer chains. Polymerization is the process by which small monomer molecules join together to form long chains, resulting in the formation of a polymer. The role of catalysts can be understood as follows:

- i. **Initiating Polymerization:** Many polymerization reactions require an initial activation step to start the chain reaction. Catalysts act as initiators, providing the necessary energy to break the double bonds or other reactive sites on monomers and start the polymerization process.
- ii. **Increasing Reaction Rate:** Catalysts increase the rate of polymerization reactions, allowing manufacturers to produce plastics more efficiently and in shorter time frames.

Q.3]A. Draw a neat labelled diagram and explain Extrusion Molding of plastic. [6]

Solution:-

Extrusion molding is a widely used process for manufacturing plastic products with a consistent cross-sectional shape. In this process, plastic materials are pushed through a die to produce continuous lengths of products with a fixed profile. It is commonly used for creating items such as pipes, tubes, rods, sheets, and various profiles.



Explanation of Extrusion Molding:

1. Extruder: The extrusion process starts with a machine called an extruder. The extruder is a specially designed screw-type mechanism that consists of a barrel and a rotating screw. The plastic material, in the form of pellets, granules, or powder, is fed into the hopper of the extruder.
2. Hopper: The hopper is the upper part of the extruder where the plastic raw material is loaded. It feeds the plastic material into the barrel of the extruder.
3. Barrel: The barrel is a heated cylindrical chamber through which the plastic material is transported by the rotating screw. The barrel is equipped with heaters to maintain a controlled temperature suitable for the specific plastic being processed.
4. Screw: The screw is the main component responsible for pushing the plastic material forward and mixing it within the barrel. As the screw rotates, it conveys the plastic material towards the die while subjecting it to heat, which melts the material. The design of the screw is critical in achieving the desired homogeneity and uniformity of the melted plastic.
5. Die: The die is a specially shaped opening or aperture located at the end of the extruder barrel. It determines the final shape and size of the extruded product. The plastic material passes through the die, which imparts the desired cross-sectional profile to the extrudate.
6. Cooling and Calibration: As the plastic material exits the die, it is still in a semi-molten state. To retain the desired shape, the extrudate needs to be cooled and calibrated.

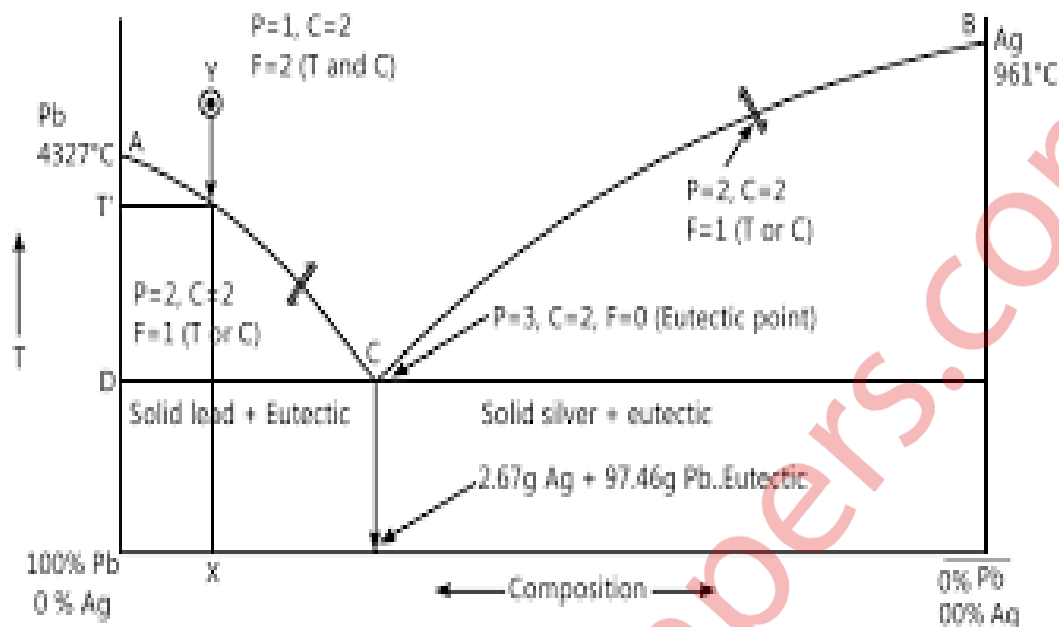
Q.3]B. Draw a neat labelled phase diagram of Pb-Ag system and explain the validity of reduce phase rule equation.

[5]

Solution:-

The Pb-Ag system refers to the binary alloy system composed of lead (Pb) and silver (Ag). This system is of significant interest due to the wide range of applications that involve the use of Pb-Ag alloys. The phase diagram of the Pb-Ag system illustrates the relationship between temperature, composition, and the various phases that form

when these two metals are combined. Phase Diagram of the Pb-Ag System: The phase diagram of the Pb-Ag system typically consists of temperature (vertical axis) and composition of Ag (horizontal axis). Phase Diagram of Pb-Ag system is as follows:-



The general features of the phase diagram are as follows:

1. **Liquidus Line:** This is the upper boundary that separates the liquid phase from the solid phase regions. It represents the temperature at which the alloy starts to melt and transform into a liquid.
2. **Solidus Line:** This is the lower boundary that separates the liquid phase from the solid phase regions. It represents the temperature at which the alloy is completely solidified.
3. **Solid Solution (α -phase and β -phase):** At low temperatures and low silver concentrations, the diagram will show two separate solid solution phases - one with Ag dissolved in Pb (α -phase) and the other with Pb dissolved in Ag (β -phase). These are single-phase regions.
4. **Eutectic Point (E):** The eutectic point is the lowest temperature point in the diagram, and it represents the composition and temperature at which the Pb and Ag form a eutectic mixture.
5. **Eutectic Composition ($\alpha + \beta$):** The region between the eutectic point (E) and the solidus line represents the two-phase region where both the α and β phases coexist.

Validity of the Reduced Phase Rule Equation:

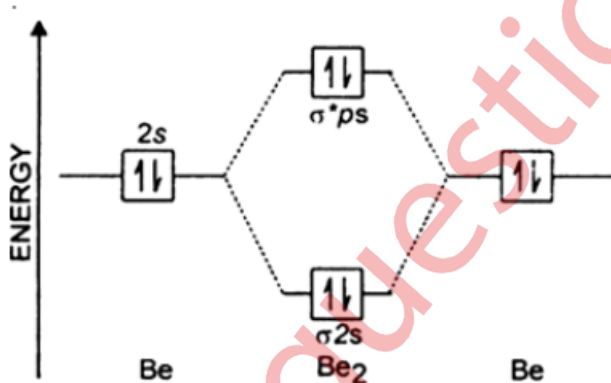
In the case of the Pb-Ag system, let's consider the phases present:

- i. Solid α (α -phase)
- ii. Solid β (β -phase)
- iii. Liquid (L)

The number of phases (P) in the Pb-Ag system is 3, and the number of components (C) is 2 (Pb and Ag). Now, we can use the reduced phase rule equation to calculate the degrees of freedom (F): $F = 2 - 3 + 2 = 1$. The result is 1, indicating that the Pb-Ag system has only one degree of freedom. This means that at a given temperature and pressure, once the composition of either Pb or Ag is fixed, the composition of the other component and the phases present are also fixed.

Q.3]C. Draw a suitable Molecular Orbital Diagram and explain why Be₂ does not exist a molecule? [4]

Solution:-



Molecular Orbital Diagram for Be₂:

In the molecular orbital diagram above, we have two atomic orbitals from each beryllium atom, one 2s and one 2p orbital. These atomic orbitals combine to form

molecular orbitals, which are filled with electrons based on their energy levels and the Aufbau principle.

Beryllium has an electron configuration of $1s^2 2s^2$. When two beryllium atoms come together to form Be_2 , they each contribute two electrons. In the molecular orbital diagram, we can see that all the molecular orbitals up to the $\pi 2p^*$ level are filled, accommodating the four electrons contributed by the two beryllium atoms.

The problem with Be_2 arises due to the high ionization energy of beryllium. Beryllium has a relatively low electron affinity and a strong tendency to lose its two valence electrons to achieve a stable electron configuration similar to helium ($1s^2$). By losing its two electrons, each beryllium atom becomes a Be^{+2} ion.

In a molecular context, Be_2 would represent two beryllium cations (Be^{+2}) coming together. However, the presence of two positive charges on each Be^{+2} ion would result in strong electrostatic repulsion between them. The repulsive forces between the positively charged ions would overcome any bonding interactions that might form between the two Be^{+2} ions, preventing the formation of a stable Be_2 molecule.

- Be_2 does not exist as a molecule because it is not energetically favorable for two beryllium ions to come together and form a stable bond due to the repulsion between the positive charges.

Q.4]A. Write a short note on 'Ion exchange method' of demineralization of the hard water . [6]

Solution:-

Hard water contains high concentrations of calcium, magnesium, and other metal ions that can cause scale formation and other undesirable effects in industrial processes and household appliances. The ion exchange method aims to replace these unwanted ions with more desirable ones, typically sodium ions, which do not cause the same issues as calcium and magnesium ions.

2. Principle of Ion Exchange: The process of ion exchange involves passing the hard water through a resin bed containing ion exchange resins. These resins are tiny beads with functional groups that can exchange certain ions from the water for other ions present in the resin. In the case of water softening, cation exchange resins are used, which have negatively charged functional groups that can attract and hold positively charged ions.

3. Cation Exchange Process: In water softening, the cation exchange resins are usually in the sodium form, meaning they contain sodium ions (Na^+). As the hard water flows through the resin bed, the calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions present in the water are attracted to the negatively charged functional groups of the resin and replace the sodium ions. The sodium ions, in turn, are released into the water.

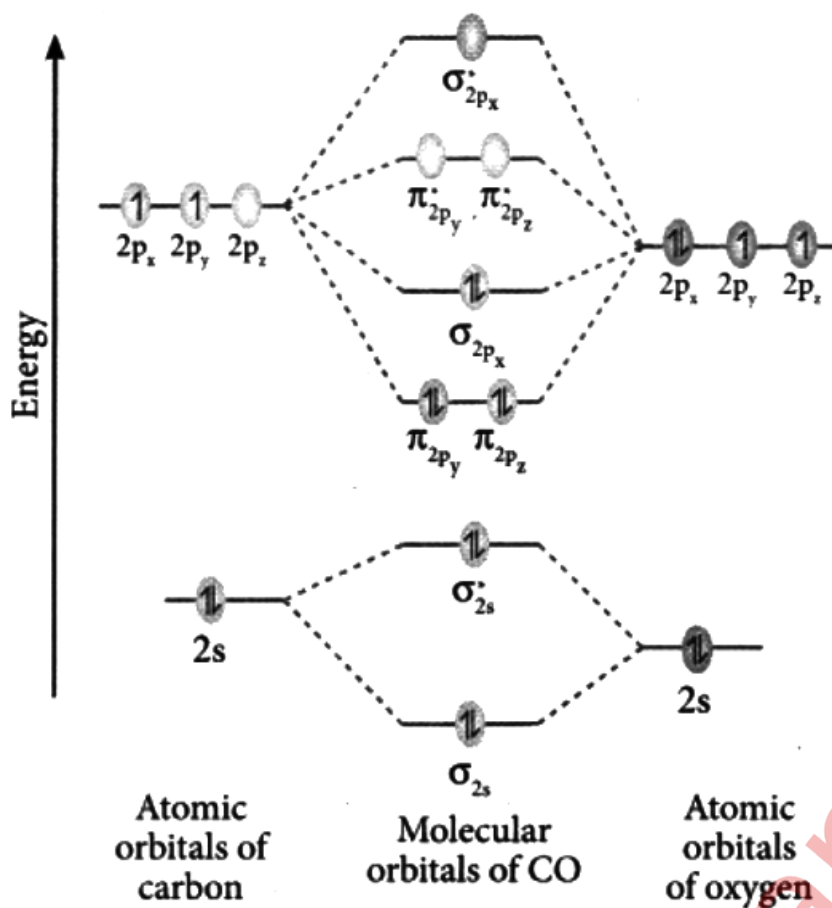
4. Regeneration: Over time, the ion exchange resins become saturated with calcium and magnesium ions, and the ability to exchange ions diminishes. To regenerate the resins and restore their sodium form, a solution of sodium chloride (common salt) is passed through the resin bed. The high concentration of sodium ions in the salt solution displaces the calcium and magnesium ions from the resin, which are then flushed out as waste along with the salt solution.

5. Benefits of Ion Exchange Method: Water softening through the ion exchange method prevents scale formation in pipes, boilers, and household appliances, thus increasing their efficiency and lifespan. It improves the effectiveness of soaps and detergents, as soft water allows them to lather more easily. The ion exchange method is a reliable and cost-effective process for large-scale water treatment in industries and water supply systems.

6. Limitations: The ion exchange process is not effective in removing other types of impurities like dissolved gases, organic compounds, or microorganisms. Additional treatment steps may be required for complete purification. The regeneration process requires a significant amount of water and can lead to the discharge of brine solutions, which may pose environmental concerns if not handled properly.

Q.4]B. Draw a neat labeled molecular diagram of CO (CARBON MONOXIDE) molecule and explain its bond order and magnetic property. [5]

Solution:-



The bond order is a measure of the number of chemical bonds between two atoms in a molecule. It is calculated as the difference between the number of bonding electrons and the number of antibonding electrons divided by two.

For CO: Number of bonding electrons = 6 (two shared pairs in the triple bond) Number of antibonding electrons = 2 (one lone pair in the oxygen atom)

Bond order = $(6 - 2) / 2 = 4 / 2 = 2$. The bond order of CO is 2, indicating that it has a double bond character between the carbon and oxygen atoms.

Magnetic Property: To determine the magnetic property of CO, we need to consider its electronic configuration and the presence of unpaired electrons. The electronic configuration of carbon (C) is $1s^2 2s^2 2p^2$, and the electronic configuration of oxygen (O) is $1s^2 2s^2 2p^4$. When these atoms combine to form a CO molecule, the electrons are paired in the molecular orbitals as follows:

σ_{2p} (2 electrons) - filled, bonding

σ_{2s} (2 electrons) - filled, bonding

π_{2p} (2 electrons) - filled, bonding

$\pi 2p^*$ (1 electron) - filled, antibonding

Since all the electrons are paired in the molecular orbitals, there are no unpaired electrons. Therefore, CO does not have any unpaired electrons and is diamagnetic. Diamagnetic substances are not attracted to a magnetic field. In conclusion, carbon monoxide (CO) has a molecular diagram consisting of a triple bond between the carbon and oxygen atoms, with a bond order of 2. It is diamagnetic because all the electrons are paired in its molecular orbitals, and thus, it does not exhibit magnetic properties. This information is important in engineering chemistry for understanding the behavior of CO in various chemical reactions and industrial processes.

Q.4]C. Explain bonding in pyrrole molecule.

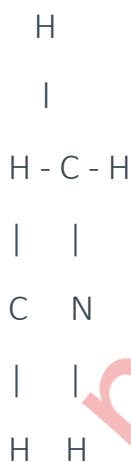
[4]

Solution:-

The bonding in the pyrrole molecule involves a combination of covalent and resonance bonding, which gives it unique aromatic properties. Pyrrole is a heterocyclic aromatic compound, meaning it contains a ring of atoms with at least one atom that is not carbon.

Molecular Structure of Pyrrole: Pyrrole has the molecular formula C_4H_5N and consists of a five-membered ring containing four carbon atoms and one nitrogen atom. The carbon atoms are connected in a cyclic structure, and each carbon is bonded to its adjacent carbon

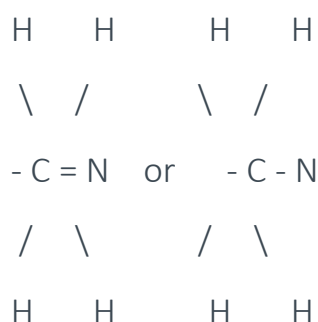
And the nitrogen atom. The molecular diagram of pyrrole can be represented as follows:



Bonding in Pyrrole:

- Covalent Bonding: The bonding between the carbon and hydrogen atoms in pyrrole is typical covalent bonding. Each carbon atom forms a single covalent bond with one hydrogen atom.
- Resonance Bonding: The most significant aspect of bonding in pyrrole is resonance. This delocalization of electrons results in resonance structures.

The resonance structures of pyrrole can be represented as follows:



In the above representation, the double-headed arrow indicates the delocalization of the lone pair of electrons over the carbon atoms in the ring.

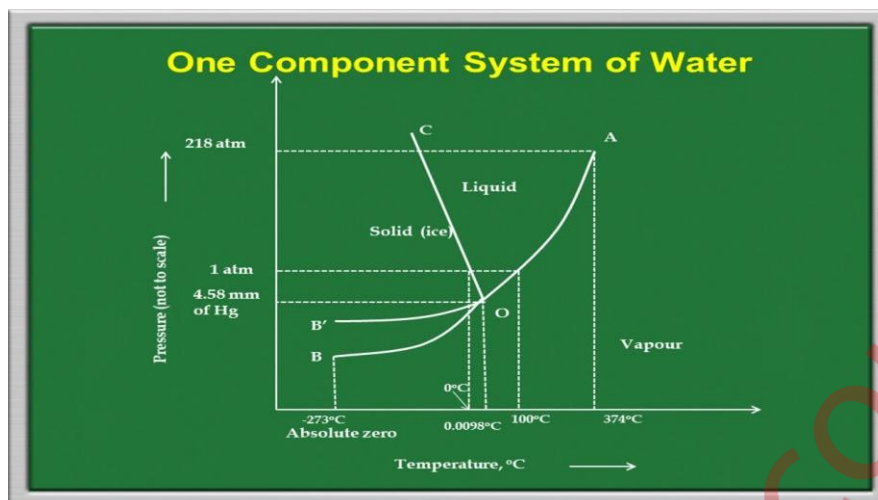
- Aromatic Properties: The resonance in pyrrole makes it aromatic, despite having only six π -electrons (4 from the carbon-carbon bonds and 2 from the lone pair on nitrogen). According to Huckel's rule, a compound with $(4n + 2)$ π -electrons in a cyclic, planar system is considered aromatic, where 'n' is an integer. In the case of pyrrole, $n = 1$, so it fulfills the $(4n + 2)$ condition, making it aromatic.

The aromaticity of pyrrole contributes to its stability, making it less reactive compared to non-aromatic compounds. The bonding in pyrrole involves typical covalent bonding between carbon and hydrogen atoms, and the most important aspect is the resonance bonding due to the delocalization of the lone pair of electrons on the nitrogen atom. This resonance creates aromatic properties in pyrrole, giving it stability and unique chemical behavior.

Q.5]A. Draw a neat phase diagram of one component water system and explain applicability of Gibb's Phase Rule. [6]

Solution:-

Phase Diagram of One-Component Water System:



A phase diagram represents the various phases (solid, liquid, gas) of a substance as a function of temperature and pressure. For a one-component water system, the phase diagram typically consists of three phases: solid (ice), liquid (water), and gas (water vapor).

Explanation of the Phase Diagram:

- **Solid (Ice):** This phase exists at low temperatures and relatively high pressures. It is characterized by a fixed shape and volume, with molecules arranged in a regular crystalline structure.
- **Liquid (Water):** The liquid phase exists at intermediate temperatures and pressures. In this phase, water molecules have enough energy to move freely, allowing water to take the shape of its container but maintaining a relatively constant volume.
- **Gas (Water Vapor):** The gas phase occurs at higher temperatures and relatively low pressures. Water molecules in the gas phase have sufficient energy to break the intermolecular forces and move independently, resulting in a highly compressible and expandable state.

Applicability:

The Gibbs Phase Rule is given by the formula: $F = C - P + 2$ Where:

- **F** is the degrees of freedom (the number of independent variables that can be varied while the system remains at equilibrium).
- **C** is the number of components (chemically independent constituents) in the system (in this case, $C = 1$ for water).
- **P** is the number of phases coexisting in the system.

For the one-component water system, we have:

$C = 1$ (water is the only component).

P can take on values from 1 to 3, depending on the temperature and pressure.

If only one phase is present, $P = 1$; if two phases coexist (e.g., water and ice), $P = 2$; and if all three phases coexist (water, ice, and water vapor), $P = 3$.

Applicability Explanation :

One Phase ($P = 1$): If only one phase exists in the system, it can be completely determined by specifying any two of the three variables: temperature, pressure, and composition. This means the system has two degrees of freedom ($F = 2$). For example, if we know the pressure and temperature, we can uniquely determine the phase (e.g., liquid water) at equilibrium.

Q.5]B. A sample of the polymer contains 50 molecules of molecular weight 10000 units each, 30 molecules each with molecular weight of 30000 and 20 molecules each having molecular weight of 60000 units. Calculate number averaged and weight averaged molecular weights of polymer and Poly- dispersity index (PDI). [5]

Solution:-

To calculate the number-averaged and weight-averaged molecular weights of the polymer and the Polydispersity Index (PDI), we need to use the following formulas .

- Number-Averaged Molecular Weight (M_n): $M_n = (\sum(N_i * M_i)) / \sum N_i$
Where: N_i is the number of molecules with molecular weight M_i .
- Weight-Averaged Molecular Weight (M_w): $M_w = \sum(N_i * M_i^2) / \sum(N_i * M_i)$
- Polydispersity Index (PDI): $PDI = M_w / M_n$

Given the following data:

50 molecules of molecular weight 10000 units each

30 molecules of molecular weight 30000 units each

20 molecules of molecular weight 60000 units each

Let's calculate each value step by step:

Step 1: Calculate the number-averaged molecular weight (M_n):

$$M_n = (50 * 10000 + 30 * 30000 + 20 * 60000) / (50 + 30 + 20)$$

$$M_n = (500000 + 900000 + 1200000) / 100$$

$$M_n = 2600000 / 100$$

$$M_n = 26000 \text{ units}$$

Step 2: Calculate the weight-averaged molecular weight (M_w):

$$M_w = (50 * 10000^2 + 30 * 30000^2 + 20 * 60000^2) / (50 * 10000 + 30 * 30000 + 20 * 60000)$$

$$M_w = (50 * 100000000 + 30 * 900000000 + 20 * 3600000000) / (500000 + 900000 + 1200000)$$

$$M_w = (5000000000 + 27000000000 + 72000000000) / 2600000$$

$$M_w = 104000000000 / 2600000$$

$$M_w = 40000 \text{ units}$$

Step 3: Calculate the Polydispersity Index (PDI):

$$PDI = M_w / M_n$$

$$PDI = 40000 / 26000$$

$$PDI = 1.538$$

For the given sample of the polymer:

$$\text{Number-Averaged Molecular Weight (} M_n \text{)} = \underline{26000 \text{ units}}$$

$$\text{Weight-Averaged Molecular Weight (} M_w \text{)} = \underline{40000 \text{ units}}$$

$$\text{Polydispersity Index (PDI)} = \underline{1.538}$$

Q.5]C. Define COD. In determination of COD, 25 ml of sewage water was refluxed with 25 ml of 0.5N of K₂Cr₂O₇ in acidic medium. The unreacted K₂Cr₂O₇ required 19 ml of 0.5N FAS (Ferrous ammonium sulphate). In the blank determination, 25 ml of distilled water was refluxed with 25 ml of 0.5N of K₂Cr₂O₇ in acidic medium which required 24 of 0.5N FAS. Calculate COD. [4]

Solution:-

COD stands for Chemical Oxygen Demand. It is a measure of the amount of oxygen required to chemically oxidize the organic matter present in a water sample. It is widely used to determine the pollution level and organic content in water bodies, especially wastewater.

Calculation of COD:

The COD is determined by the amount of unreacted potassium dichromate (K₂Cr₂O₇) in the water sample. The chemical reaction involved is as follows:



Given data:

Volume of sewage water sample (V₁) = 25 ml

Volume of K₂Cr₂O₇ solution (V₂) = 25 ml

Normality of K₂Cr₂O₇ solution (N₂) = 0.5 N

Volume of FAS solution used in the sewage water determination (V₃) = 19 ml

Volume of FAS solution used in the blank determination (V₄) = 24 ml

Step 1: Calculate the Normality of FAS (N₃):

We can calculate the normality of FAS (N₃) using the blank determination:

$$N_3 = (N_2 * V_2) / V_4$$

$$N_3 = (0.5 * 25) / 24$$

$$N_3 = 0.52083 \text{ N (approximately 0.52 N)}$$

Step 2: Calculate the Normality of Unreacted $K_2Cr_2O_7$ (N_1):

Using the titration results for the sewage water determination:

$$N_1 = (N_2 * V_2) / V_3$$

$$N_1 = (0.5 * 25) / 19$$

$$N_1 = 0.65789 \text{ N (approximately 0.66 N)}$$

Step 3: Calculate the Equivalent Weight of $K_2Cr_2O_7$ (Eq wt):

The equivalent weight of $K_2Cr_2O_7$ is the molecular weight of $K_2Cr_2O_7$ divided by the number of moles of electrons exchanged in the redox reaction. In this case, the equivalent weight (Eq wt) of $K_2Cr_2O_7$ is 51.996 g/mol.

Step 4: Calculate COD:

COD is the amount of oxygen required to oxidize the organic matter in the sewage sample, and it is equal to the amount of $K_2Cr_2O_7$ that remained unreacted during the titration:

$$COD = (N_1 * Eq \text{ wt} * 1000) / V_1$$

$$COD = (0.66 * 51.996 * 1000) / 25$$

$$COD = 17316.36 \text{ mg/L (approximately 17316 mg/L)}$$

Answer:

The Chemical Oxygen Demand (COD) of the sewage water sample is approximately 17316 mg/L.

Q.6]A. Write a brief note on 'Conducting Polymers'. [6]

Solution:-

Conducting polymers, also known as intrinsically conducting polymers (ICPs) or synthetic metals, are a fascinating class of organic materials with unique electrical and optical properties. Unlike traditional insulating polymers, conducting polymers have the ability to conduct electricity, making them an essential area of study in first-year engineering chemistry.

Characteristics of Conducting Polymers:

1. **Electrical Conductivity:** Conducting polymers exhibit electrical conductivity, which can be altered by doping or de-doping the polymer. Doping involves the addition or removal of charge carriers (electrons or holes) to enhance or decrease conductivity, respectively.
2. **Conjugated Structure:** The conductivity in these polymers arises from the presence of a conjugated π -electron system along the polymer backbone. This delocalization of electrons facilitates charge transport, making them electronically active.
3. **Processability:** Conducting polymers are typically soluble in organic solvents and can be processed through methods like solution casting, spin-coating, and ink-jet printing, allowing for easy fabrication of electronic devices.
4. **Redox Behavior:** These polymers can undergo redox reactions, meaning they can accept or donate electrons, resulting in changes in their conductivity. This property is critical for their use in sensors, batteries, and supercapacitors.

Applications of Conducting Polymers:

1. Conducting polymers have found numerous practical applications due to their unique properties. Some notable applications include:
2. **Organic Electronics:** Conducting polymers are used in organic light-emitting diodes (OLEDs), organic photovoltaic cells (OPVs), and organic field-effect transistors (OFETs) due to their processability and semiconducting behavior.
3. **Sensors:** They are employed as gas sensors, chemical sensors, and biosensors because of their sensitivity to changes in the surrounding environment.
4. **Energy Storage:** Conducting polymers are utilized in batteries and supercapacitors, where their redox behavior enables efficient energy storage and high power delivery.
5. **Corrosion Protection:** Conducting polymers have been investigated for their potential as protective coatings to inhibit corrosion of metals.

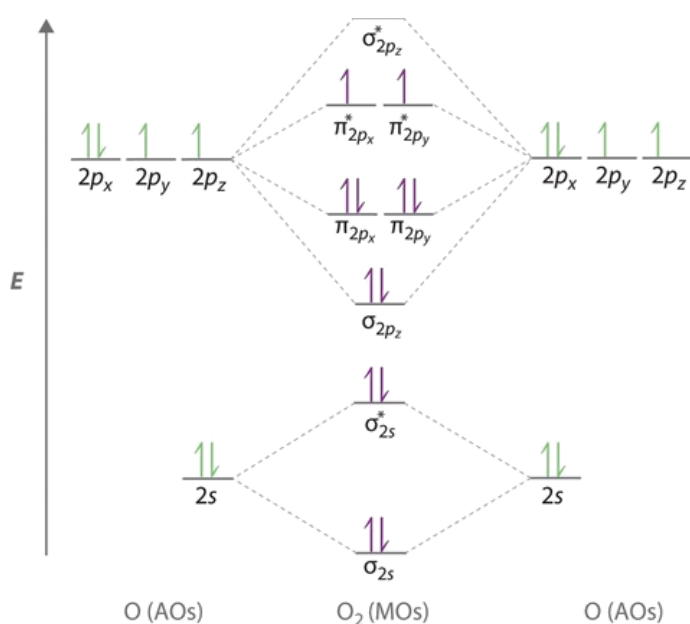
Q.6]B. Draw a molecular orbital diagram of O₂ (oxygen) molecule and explain its bond order and magnetic property.

[5]

Solution:-

The oxygen molecule (O₂) consists of two oxygen atoms, each contributing six valence electrons. When two atoms come close together to form a molecule, their atomic orbitals combine to form molecular orbitals. In the molecular orbital diagram of O₂, the molecular orbitals are formed by combining the atomic orbitals of the oxygen atoms.

The molecular orbital diagram of O₂ is as follows:



In this diagram:

- σ (sigma) orbitals are formed by head-on overlap of atomic orbitals.
- π (pi) orbitals are formed by sideways overlap of atomic orbitals.
- σ^* (sigma star) orbitals are antibonding, while σ (sigma) orbitals are bonding.
- π^* (pi star) orbitals are antibonding, while π (pi) orbitals are bonding.

Bond Order and Magnetic Property: Bond order (BO) is a measure of the strength of the bond between two atoms in a molecule. It is calculated by subtracting the number of antibonding electrons from the number of bonding electrons and dividing the result by 2.

Number of bonding electrons = 10 (5 pairs in σ and π bonding orbitals).

Number of antibonding electrons = 6 (3 pairs in σ^* and π^* antibonding orbitals).

- Bond Order (BO) = (Number of bonding electrons - Number of antibonding electrons) / 2
 Bond Order (BO) = (10 - 6) / 2
 Bond Order (BO) = 4 / 2
 Bond Order (BO) = 2
 The bond order of the oxygen molecule is 2. A bond order of 2 indicates a double bond between the two oxygen atoms.

- **Magnetic Property:** The magnetic property of a molecule depends on the presence of unpaired electrons. In the case of O₂, all the electrons are paired in the molecular orbitals, so there are no unpaired electrons. Therefore, O₂ is diamagnetic, meaning it is not attracted to a magnetic field. Diamagnetic substances have all their electrons paired, resulting in the cancellation of magnetic moments.

Q.6]C. Write merits and demerits of Phase rule. [4]

Solution:-

The Phase Rule, formulated by the American chemist J. Willard Gibbs, is a fundamental concept in thermodynamics used to predict the number of degrees of freedom of a system at equilibrium. It is especially relevant in first-year engineering chemistry to understand the behavior of multi-component systems. Here are the merits and demerits of the Phase Rule:

Merits:

1. **Predicts Equilibrium Conditions:** The Phase Rule helps predict the equilibrium conditions of a multi-component system by determining the number of coexisting phases and the variables that can be independently controlled without changing the system's state.
2. **Simple and Generalized:** The Phase Rule is relatively simple to understand and apply. It provides a general framework applicable to a wide range of systems, making it a fundamental tool in the study of thermodynamics.
3. **Relevant to Many Fields:** The Phase Rule finds applications in various fields, such as chemistry, physics, engineering, material science, and geology. It is used in the analysis of phase diagrams, phase equilibria, and phase transitions.
5. **Phases Identification:** It helps identify the number of phases present in a system and determines their stability regions in terms of temperature and pressure.

Demerits:

1. **Limited Applicability to Real Systems:** The Phase Rule assumes ideal behavior, neglecting factors like intermolecular interactions, molecular size, and non-idealities in real systems. As a result, its predictions may not be entirely accurate for complex real-world systems.

2. Not Suitable for Non-Equilibrium Systems: The Phase Rule is applicable only to systems in equilibrium. It does not provide insights into the kinetics or dynamic behavior of non-equilibrium processes.
 3. Restricted to Simple Systems: While the Phase Rule is valuable for systems with a small number of components and phases, it becomes more complex and challenging to apply for systems with many components or phases.
 4. Inadequate for Systems with Transitions: Systems undergoing phase transitions such as critical phenomena or continuous phase transitions may not be adequately described by the Phase Rule.
 5. Assumes Fixed Components: The Phase Rule assumes that the number of components is fixed, which may not hold in certain cases, such as reactions that alter the number of components.
 6. Despite its limitations, the Phase Rule remains an essential concept in thermodynamics and serves as a valuable starting point for understanding phase equilibria in many engineering and scientific applications. However, when dealing with more complex systems, additional tools and models may be needed to complement the Phase Rule's predictions.
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