Engineering Chemistry I Prelim paper solution

Q. 1	**Choose the correct option for following questions. All the questions are compulsory and carry equal marks**
1.	**80 ml of sample contains 1040 ppm of DO. After 5 days the DO is 300 ppm after sample has been diluted to 100 ml. Calculate BOD of sample.**
Ans	Option A: 925 ppm
2.	**Choose the correct option from following wrt Tg**
Ans	Option C: Polyethylene Terephthalate has higher Tg than Polyethylene Adipate
3.	**Calculate number of components for following chemical equilibrium** $Fe(S) + H_2O(g) \rightleftharpoons FeO(S) + H_2(g)$
Ans	Option D: 3
4.	**Which of the following compounds are antiaromatic**
Ans	Option B : II and IV
5.	**Predict magnetic behaviour and calculate bond order of CO^{2-}**
Ans	Option C: paramagnetic and BO=2
6.	**Which of the following technique is not used for desalination of brackish water?**
Ans	Option A: Electrolysis
Q. 2 A	**Calculate carbonate & non-carbonate hardness of given water sample having following impurities in ppm:** **$Mg(HCO_3)_2$= 14.6, $Mg(NO_3)_2$= 29.6, $Ca(HCO_3)_2$= 8.1, $MgCl_2$= 19, $MgSO_4$= 24, SiO_2= 2**

Ans

Q.2.(A)

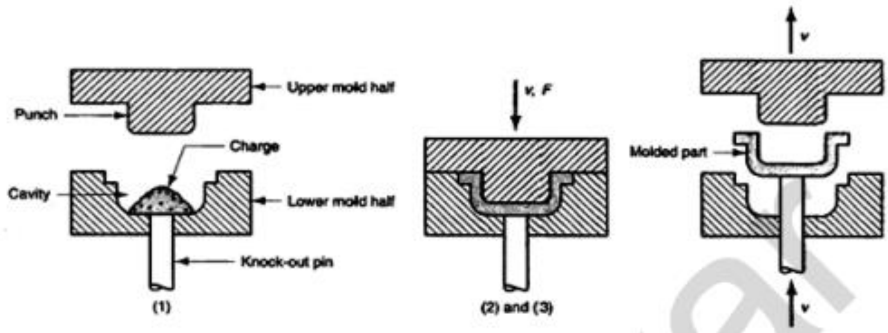
Impurity	Amount (ppm)	M.W.	M.F.	$CaCO_3$ eq. = Amt × M.F.
$Mg(HCO_3)_2$	14.6	146	100/146	10
$Mg(NO_3)_2$	29.6	148	100/148	20
$Ca(HCO_3)_2$	8.1	162	100/162	5
$MgCl_2$	19	95	100/95	20
$MgSO_4$	24	120	100/120	20
SiO_2	2	–		

Carbonate hardness $= [Mg(HCO_3)_2 + Ca(HCO_3)_2]_{CaCO_3}$
$= 10 + 5$
$= 15$ ppm.

Non-Carbonate hardness $= [Mg(NO_3)_2 + MgCl_2 + MgSO_4]$
$= 20 + 20 + 20$
$= 60$ ppm.

Q. 2 B **Write a short note on compression moulding with the help of following points: (i) diagram (ii) detailed process (iii) application**

Ans Compression moulding method is applied to both Thermoplastics and Thermosetting plastics. But mostly it is used for Thermo-setting plastics. In compression moulding : 1. Raw materials of the right composition are placed between the two half pieces of mould. 2. The mould is carefully closed. 3. Then, the mould is subjected to high pressure of the order of 100 – 500 Kg/cm2 , and high temperature of the order of 100 – 180° C. 4. Curing : In case of Thermoplastics curing is done by cooling. In case of Thermo-setting plastics curing is done by heating. 5. After curing mould is opened and plastic article is taken out. Nowadays automatic compression moulding machines are also available.



Compression moulding is used in making buckets, electric boxes, telephones, etc.

Q. 2 C **State Gibb's Phase rule. Define phase, component and degree of freedom.**

Ans It is defined as "Provided the equilibrium between any number of phases is not influenced by gravity, or electrical, or magnetic forces, or by surface action and only the temperature, pressure and concentration, then the number of degrees of freedom (F) of the system is related to the number of components (C) and of phases (p) by the phase rule equation." F

<table>
<tr><td></td><td>= C – P + 2 Where, F = the number degrees of freedom or variance of the system, C = the number of component in the system, P = the number of phases in equilibrium

Phase: A phase is defined as “a homogeneous, physically distinct and mechanically separable portion of system, which is separated from other such parts of the system by definite boundary surfaces”

Component: It is defined as “the smallest number of independent variable constituents, taking part in the state of equilibrium, by means of which the composition of each phase can be expressed in the form of chemical equation”

Degree of freedom: Degree of freedom is defined as “the minimum no of independently variable factors, such as temperature, pressure and composition of the phases, which must be arbitrarily specified in order to represent perfectly the condition of a system”</td></tr>
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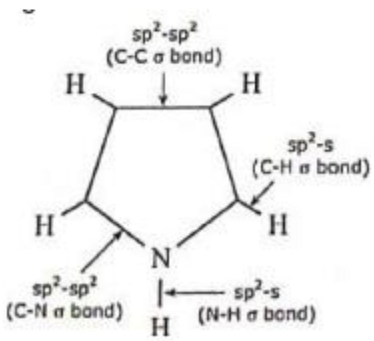
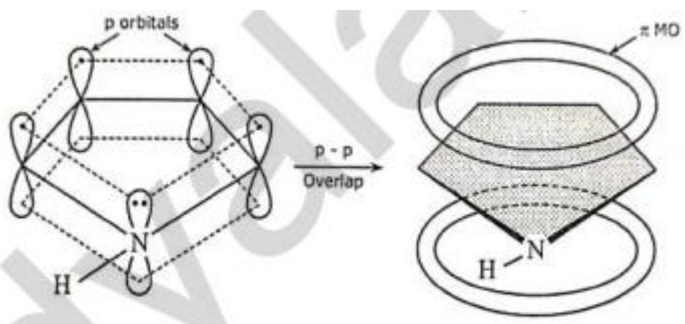
<tr><td>Q. 2 D</td><td>Explain the structure of pyrrole stating hybridization of atoms, nature of bonds and resonating structures.</td></tr>
<tr><td>Ans</td><td>Pyrrole is a heterocyclic compound. Heterocyclic compounds are cyclic compounds in which the ring atoms are of carbon and some other element. The atom of the other element, like N, S, or O, is called the hetero atom.
All the five ring atoms in pyrrole are sp2 hybridised. The sp2 hybrid orbitals overlap with each other and with s-orbitals of the five hydrogen atoms forming carbon - carbon (C - C), carbon - nitrogen (C - N), carbon - hydrogen (C - H) and nitrogen - hydrogen (N - H) σ (sigma) bonds. All these σ bonds lie in one plane.



Each ring atom in pyrrole also has an unhybridised p-orbital and these are perpendicular to the plane of σ bonds. The p-orbitals of carbon atoms contain one electron each. The p-orbital of nitrogen atom contains two electrons, i.e. a lone pair of electrons. The lateral overlap of these p-orbitals produces a molecular orbital containing six electron. Pyrrole shows aromatic properties or aromaticity as the resulting π molecular orbital satisfies the Hückel’s rule, for n = 1 in (4n + 2)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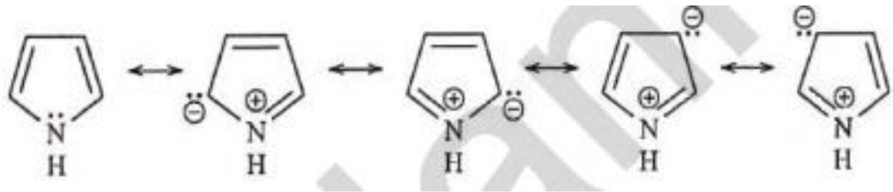
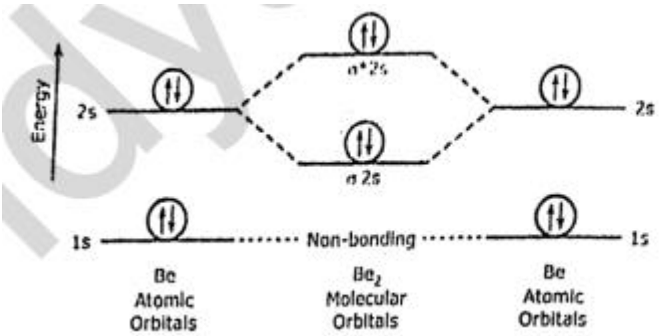
	In pyrrole, the five parallel p-orbitals containing six electrons form a delocalised π–molecular orbitals. According to the resonance theory, pyrrole is considered to be a hybrid of the following five resonance structures. 
Q. 2 E	**Prove that Be2 molecule does not exist with the help of MO diagram.**
Ans	The electronic configuration of Be(4) is 1s 2 2s2 . In a diatomic molecule Be2, there will be a total of eight electrons from two Be atoms, to be filled in the molecular orbitals. The 1s orbital of both the Be atoms, do not take part in the bond formation, i.e., they are non-bonding. The remaining 2s orbitals of the two Be atoms combine to form σ2s (bonding) and * σ2s (anti-bonding) molecular orbitals. The four electrons will be filled in both these molecular orbitals as per Aufbau Principle.  The electronic configuration of the molecule Be2 can be given as, Be2 = σ σ( ) 2 2 * KK 2s 2s KK represents the two non-bonding 1s orbitals of two Be atoms. The bond order (BO) of Be2 molecule = (Nb- Na)/ 2 = (2-2)/ 2 = 0 The zero bond order of Be2 molecule suggests that the Be2 molecule is unstable and does not exist.
Q. 2 F	**Give function and examples of following moulding constituents.** **(i) Plasticizers** **(ii) Fillers** **(iii) Pigments**
Ans	(i) Plasticizers: These materials are added to increase the plasticity and flexibility of plastic. It also reduces the brittleness and softening temperature of plastic. e.g. Camphor, Tricresyl phosphate. The plasticizer molecules occupy the positions in between the polymer molecules and reduce the force of intermolecular attraction. This helps in easy sliding of molecules of polymer which increases the flexibility of polymer molecules

	(ii) Fillers: The main job of filler is : – to reduce the cost of plastic – to reduce the flexibility (to make it stiff) – to decrease the shrinkage during moulding – to increase hardness and tensile strength. Commonly used fillers are saw dust, cotton, paper pulp, c–black, mica, asbestos, clay, quartz, marble powder, metal powders, metallic oxides etc. The fillers can be added upto 50 % (iii) Pigments: Pigments impart colour to the plastic products. They are generally organic dyes or opaque inorganic substances. Some of the pigments are : ultramarine → blue C–black→ black CaCO3, ZnO→ white Chromium trioxide → Green Antimony Sulphide → Crimson red Iron oxide → Red.
Q. 3 A (i)	**30 ml of standard hard water (containing 0.9 g $CaCO_3$ per litre) required 25 ml of EDTA. 50 ml of hard water sample required 28 ml of EDTA. 30 ml of boiled hard water required 14.5 ml of EDTA. Calculate temporary hardness.**
Ans	Q.3 (A) (i) SHW = 0.9 g $CaCO_3$/lit 0.9 mg/ml. 1 ml SHW = 0.9 mg $CaCO_3$. 30 ml SHW = 0.9×30 mg $CaCO_3$ = 25 ml EDTA 25 ml EDTA = 0.9×30 mg $CaCO_3$ ∴ 1 ml EDTA = $\frac{0.9 \times 30}{25}$ mg $CaCO_3$ $\boxed{1\text{ ml EDTA} = \frac{27}{25} \text{ mg } CaCO_3.}$ — (1) 50 ml HW = 28 ml EDTA $= 28 \times \frac{27}{25}$ mg $CaCO_3$ ∴ 1000 ml HW = $28 \times \frac{27}{25} \times \frac{1000}{50}$ $\boxed{\text{Total hardness} = 604.8 \text{ ppm.}}$ ~~50~~ 30 ml BHW = 14.5 ml EDTA $= 14.5 \times \frac{27}{25}$ mg $CaCO_3$ ∴ 1000 ml BHW = $14.5 \times \frac{27}{25} \times \frac{1000}{30}$ $\boxed{\text{Permanent hardness} = 522 \text{ ppm.}}$ Temporary hardness = 604.8 − 522 $\boxed{\text{Temp. Hardness} = 82.8 \text{ ppm.}}$
Q. 3 A (ii)	**Distinguish between bonding and antibonding molecular orbitals.**

Ans

	Bonding MO	Anti-Bonding MO
1.	Formed by addition of electron waves $\psi_b = \psi_A + \psi_B$	Formed by subtraction of electron waves $\psi_a = \psi_A - \psi_B$
2.	The two overlapping electron waves are on the same side, i.e., the signs of the two wave functions are same.	The two overlapping electron waves are on opposite sides, i.e., the signs of the two wave functions are different.
3.	The electron density between the two nuclei is maximum and results in less internuclear repulsion	The electron density between the two nuclei is nil and results in more internuclear repulsion.
4.	Energy is lower and hence is more stable than the overlapping atomic orbitals.	Energy is higher and hence is less stable than the overlapping atomic orbitals.
5.	Overlap integral is positive and creates bonding situation.	Overlap integral is negative and does not create bonding situation.

Q. 3 A (iii) **Calculate the number average molecular weight, weight average molecular weight and polydispersity index of the following polymer.**
100 molecules of molecular weight 500
200 molecules of molecular weight 800
300 molecules of molecular weight 1000

Ans

Q.3. A (iii)

$$\overline{M_n} = \frac{\sum n_i m_i}{\sum n_i}$$

$$= \frac{(100 \times 500) + (200 \times 800) + (300 \times 1000)}{100 + 200 + 300}$$

$$= \frac{5 \times 10^4 + 16 \times 10^4 + 3 \times 10^5}{600}$$

$$= \frac{510000}{600} = 850$$

$$\boxed{\overline{M_n} = 850}$$

$$\overline{M_w} = \frac{\sum n_i m_i^2}{\sum n_i m_i}$$

$$= \frac{[100 \times (500)^2] + [200 \times (800)^2] + [300 \times (1000)^2]}{100 \times 500 + 200 \times 800 + 300 \times 1000}$$

$$= 888.235 \qquad \boxed{\overline{M_w} = 888.235}$$

$$PDI = \frac{\overline{M_w}}{\overline{M_n}} = \frac{888.235}{850} = 1.0449$$

$$\boxed{PDI = 1.0449}$$

Q. 3 B (i) **Describe deionization process with following points: (i) Principle (ii) diagram (iii) Process (iv) Reactions (v) Advantages (vi) Disadvantages**

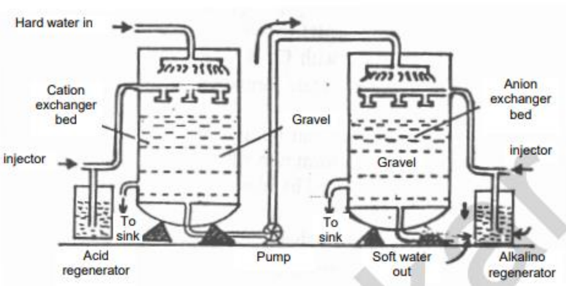
Ans

(i) **Principle:** Ion exchange resins are of two types 1. Cation exchange resins 2. Anion exchange resins

Cation exchange resins are resins which are capable of exchanging H + ions, with other cations. They contain functional groups like – SO3H, –COOH, –H etc.

Anion exchange resins are resins which are capable of exchanging OH– ions, with other anions. They contain functional groups like – NH2 or –NH as an integral part of the resin matrix. When they are treated with dilute NaOH solution, they act as an anion exchange resins and are represented as R – $(OH)_2$

(ii) **Diagram:**



(iii) **Process:**

The hard water is first passes through the cation exchange column when all the cations like Ca^{2+}, Mg^{2+} etc are removed (taken up by resin) & an equivalent amount of H^+ is released from resin to water. Subsequently, this water is passed through the anion exchange column when all the anions like Cl^-, SO_4^{2-} etc are removed (taken up by the resin) and an equivalent amount of OH^- is released from this column to water. The H^+ and OH^- released respectively from cation exchanger and anion exchanger combine to give water.

$H^+ + OH^- \rightarrow H_2O$

Thus, water flowing out of the anion exchange column is free from all the cations and anions and becomes ion–free or deionised or demineralised. When capacities of cation and anion exchangers to exchange H^+ & OH^- ions respectively are lost, they are said to be exhausted. These columns are regenerated by respective acid and alkali solutions as stated before. The cation exchanger is regenerated by diluted H_2SO_4 and then washed with deionised water and washing (Containing Ca^{2+}, Mg^{2+} and Cl^-, SO_4^{2-} ions) is passed to the sink. The anion exchanger is regenerated by diluted NaOH and then washed with de-ionised water & washing (containing Na^+ and Cl^- , SO_4^{2-} ions) is passed to the sink. The regenerated column is used again.

(iv) **Reactions:**

(a) Reactions of softening

R – H2 + Ca(HCO3)2 → R – Ca↓ +2H2 CO3 .....(In Cation exchanger)
R – H2 + CaCl2 → R – Ca↓ + 2HCl .....(In Cation exchanger)
R – (OH)2 + H2CO3 → R – CO3 ↓ + 2H2O .....(In Anion exchanger)
R – (OH)2 + 2HCl → R – Cl2 ↓ + 2H2O .....(In Anion exchanger)

(b) Reactions of Regeneration:

During the ion–exchange process, the resins get exhausted. In order to regenerate cation exchange resins, diluted HCl is passed through it where following reactions take place.

$R - Ca + 2HCl \rightarrow R - H_2 + CaCl_2$

$R - Mg + 2HCl \rightarrow R - H_2 \downarrow + MgCl_2$

While in order to regenerate anion exchange resins, diluted NaOH is passed through it.

$R - CO_3 + 2NaOH \rightarrow R - (OH)_2 \downarrow + Na_2CO_3$

$R - Cl_2 + 2NaOH \rightarrow R - (OH)_2 \downarrow + 2NaCl$

(v) **Advantages:**
1. The process can be used to soften highly acidic or alkaline waters.
2. It produces water of very low hardness (upto 2 ppm)

(vi) **Disadvantages:**
1. The equipment is costly and more expensive chemicals are needed.
2. If water contains turbidity then the output of the process is reduced.

Q. 3 B (ii) **Apply the Gibb's Phase rule to one component system, Water.**

Ans

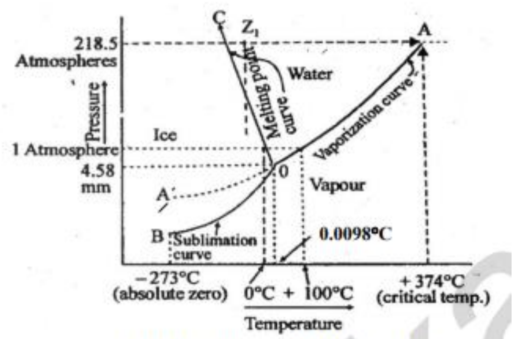
The water system consists of 3 phases, i.e. ice, water and water vapour.

Ice(s) ↔ Water(l) ↔ Water vapour (g)

It is a one component system, hence from phase rule, when C = 1, F = C – P + 2 = 1 – P + 2 = 3 – P

Hence, the maximum no. of degrees of freedom is 2 for any one component system.

Therefore, such a system can be represented completely by a two – dimensioned diagram



The Phase diagram of Water system

A] Area:

(1) It consists of three areas namely BOC (ice), COA (water) and AOB (vapour). (2) A system can be completely defined at any point in an area both temperature and pressure are fixed and it has two degrees of freedom. (bivariant). ∴ Hence, from phase rule equation, when C = 1, P = 1.

F = C – P + 2 F = 1 –1 + 2 F = 2

B] Boundary Lines:

(1) The lines OA, OB and OC separate the areas and connect the point of which the two phases can co – exist in equilibrium.

	(2) To locate any point on the particular line, either temperature or pressure co-ordinate should be known or in other words, if the value of either the temperature or pressure is fixed, the value of the other is automatically fixed and the system is completely defined. Any point on the boundary lines has one degree of freedom or is univariant. F = C – P + 2 F = 1 – 2 + 2 F = 1 **The curve OA (Vapour Pressure Curve)**: (1) The water and vapour are in equilibrium, along curve OA. (2) The system has one degree of freedom and hence it is univariant. (3) The curve OA terminates at A, the critical point 218 atmosphere and 374° temperature. (4) At the lower end, the curve terminates at the point O, where water freezes to form ice and on eliminating solid particles, water may be cooled far below its freezing point, without crystallization of ice. ((2) **Metastable equilibrium curve**: Dotted curve OA' shows the vapour pressure of super – cooled water. It represents meta – stable equilibrium and will at once change into solid ice even with the slightest disturbance. **The curve OB (Sublimation Curve):** Along the curve OB, ice and vapour are in equilibrium with each other. It is known as sublimation curve. The curve OB terminates at the lower end at absolute zero (–273°C) where no vapour can be present and only ice exists **The curve OC (Melting point curve):** Along the curve OC, two phases, namely ice and water, are in equilibrium with each other. This is known as melting point of freezing point curve. This curve describes the effect of pressure on the melting point of the ice. The slope of the curve shows that (1) Increase of pressure decreases the melting point of ice. (2) ice melts with decreases of volume. At any point on this curve, if either the pressure of the temperature is changes one of the phases disappear. **C] Triple Point:** The curves OA, OB and OC meet at a point 'O'. This is called the 'triple point' where all the three phases, viz., ice, water and vapour co-exist. Only at a particular value of temperature and pressure represented by the triple point, all the three phases can co-exist. So, the system has no degrees of freedom (invariant) at this point. The triple point corresponds to a temperature of 0.0098°C and a pressure of 4.58 mm.
Q. 4 A (i)	**An alloy AB of 50 g weight contains 35% of A. The molten AB on cooling gave out B. An eutectic alloy exists at equal percentage of A & B. What is the amount of B that has formed?**

Ans

Q.4 (A)

(i) An alloy of AB = 50 gm.

Alloy (AB) (100%)	A	B
	35%	65%

As A is 35%, B will be 65%

∴ In 50gm ∴ A 17.5 g ∴ B 32.5 gm.

∴ In eutectic 50% 50%

17.5 g 17.5 g.

~~Hence~~ As in eutectic A is constant weight in eutectic mixture & B is precipitating out.

Amount of B precipitated out from alloy is

= 32.5 g − 17.5 g

= 15 gm

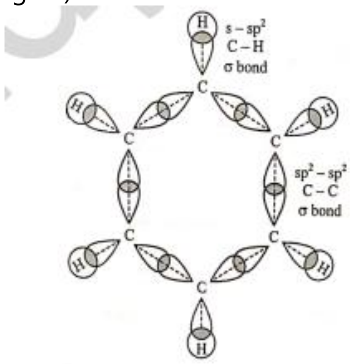
(15 gm of B has been formed)

Q. 4 A (ii) **Explain stability of benzene molecule with the help of MOT**

Ans

According to molecular orbital theory, all the six carbon atoms in benzene are sp2 hybridised. This is confirmed experimentally by the fact that all the bond angles of the carbon atoms in the benzene ring are 120°

The sp2 hybrid orbitals of carbons overlap with each other forming C-C σ (sigma) bonds. The sp2 hybrid orbitals of each carbon also overlap with s-orbitals of the six hydrogen atoms forming six C - H σ (sigma) bonds.



Each carbon atom in benzene possesses an unhybridised p-orbital containing one electron. These p-orbitals are perpendicular to the plane of σ-bonds. The lateral overlap of these p-orbitals give rise to a π (pi) molecular orbital containing six electrons. One half of this π molecular orbital lies above and the other half lies below the plane of the σ–bonds

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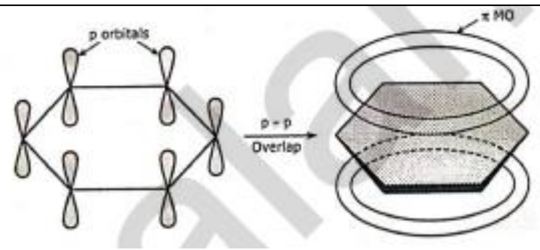
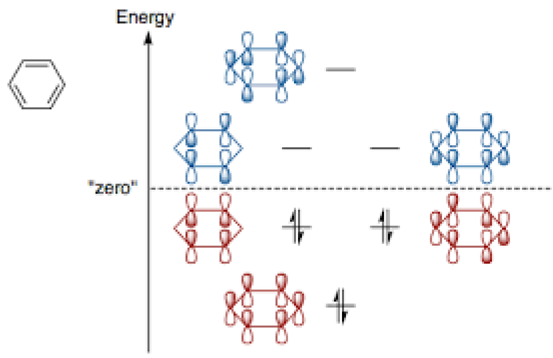


All the carbon atoms are sp2 hybridised. The C - C and C - H σ bonds are formed by sp2 - sp2 and sp2 - s overlap. All the carbon atoms have a p-orbital of them for π bonds.
As the six electrons of the p-orbitals cover all the six carbon atoms, they are said to be delocalised. This delocalisation of p-electrons form stronger π - bonds which makes the molecule of benzene more stable
According to molecular orbital theory, the number of molecular orbitals in a molecule is the same as die number of atomic orbitals which combine to form a molecule. Each molecular orbital can accommodate maximum of two electrons with opposite spins
six p –orbitals, one from each carbon atom of benzene ring, combine to form six π – molecular orbitals. Three of them have energies lower than that of an isolated π–atomic orbital. These are the bonding molecular orbitals. The other three of the π–molecular orbitals have energies higher than that of an isolated π–atomic orbital. These are the anti–bonding molecular orbitals. Orbitals ψ2 and ψ3 have the same energy and are said to be degenerate. The same is the case with orbitals ψ4 and ψ5. The six electrons are all filled in three of the bonding molecular orbitals. The anti-bonding molecular orbitals have no electrons. This clearly explains the stability of benzene molecule



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<tr><td>Q. 4 A (ii)</td><td>Explain Reverse Osmosis with diagram, process and applications.</td></tr>
<tr><td>Ans</td><td>
Principle of Reverse osmosis:
RO is a membrane separation process for removing solvent from a solution. When a semi-permeable membrane separates a dilute solution from a concentrated solution and external pressure (normally 200 to 12000 psi) is applied on the concentrated solution then the solvent crosses from the concentrated to the dilute solution.
Process:
• The feed water is pressurized on one side of a semi-permeable membrane.
• The membrane is highly permeable to water, but impermeable to dissolved solutes, so the pure water crosses the membrane and is known as permeate.
• The water flowing to drain contains concentrated solutes and other insoluble materials, such as bacteria and particles, and is referred to as the reject stream.
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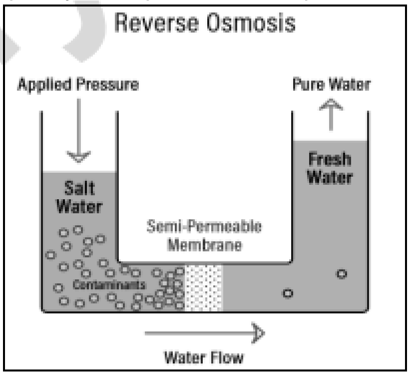
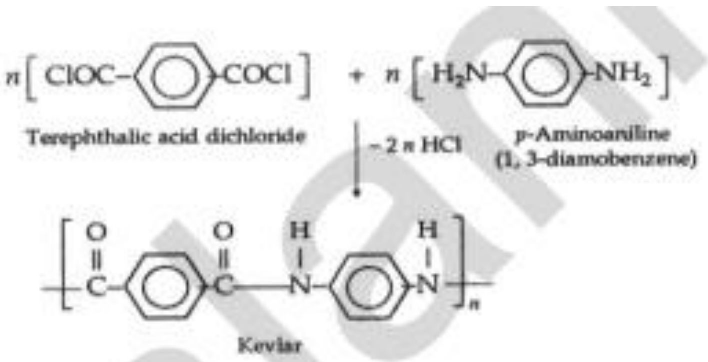
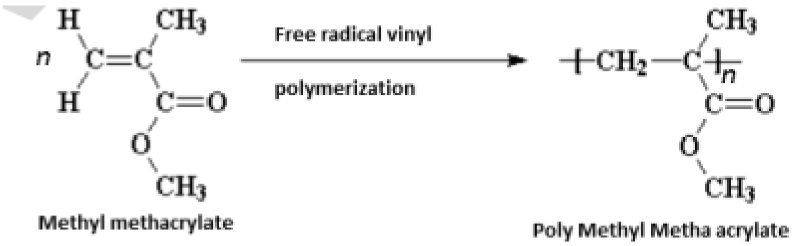
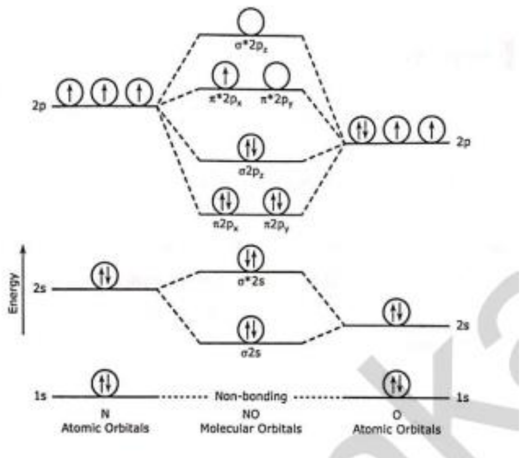
	• The performance of a system depends on factors such as membrane type, flow control, feed water quality , temperature and pressure  **Applications:** • Desalination of sea water as the small pores of semi-permeable membrane are restrictive to salts, minerals, bacteria, disease causing pathogens. • Water purification a domestic level. • Wastewater recovery in the food and beverage processing industries.
Q. 4 B	**Solve any of the following**
(i)	**Give synthesis, properties & uses of Kevlar & PMMA**
Ans	**Kevlar** Kevlar is an aromatic polyamide similar to nylons, but with benzene rings rather than aliphatic chains linked to the amide groups –CONH–. It is prepared by polycondensation between aromatic dischloride and aromatic diamines  **Properties:** Kevlar is exceptionally strong (5 times stronger than steel and 10 times stronger than Al on a weight-for-weight basis). It has high heat stability and flexibility. The unique properties of Kevlar are due to the delocalized bonding which causes the benzene rings to be inflexible. Therefore, Kevlar is far more right than nylons. The high electron-density in the chains of Kevlar also results in relatively stronger van der Waal intermolecular forces between neighbouring polymer molecules. **Uses:** Kevlar is used extensively in the aerospace and aircraft industries, car parts (such as tyre, brakes, clutch linings, etc.,) ropes, cables, protective clothing, bullet-proof vests, motorcycle helmets and other high performance materials. **PMMA**

	The monomer used in methyl methacrylate (an ester of methyl acrylic acid is produced from acetone). Polymethyl methacrylate is obtained by polymerization of methyl methacrylate in presence of acetyl peroxide or hydrogen peroxide. It is an acrylic polymer  **Properties:** 1. It is colourless, transparent, hard and fairly rigid material. 2. It is amorphous because of the presence of bulky side groups in the molecules. 3. It has high softening point of about 130°C to 140°C and becomes rubber like a temperature above 65°C. 4. It has high optical transparency. **Uses:** 1. Its sheets are used for signs, glazing skylights and decorative purposes. 2. It is used for making artificial eyes, emulsion, paints, TV screens etc
(ii)	**(a) Give electronic configuration of Cr & V.** **(b) Draw MO diagram of NO molecule and state BO, magnetic behaviour & electronic configuration of the molecule.**
Ans	(a) Electronic configuration of Cr & V are as follows: Cr[Z=24]= $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^1$, $3d^5$ V[Z=23]= $1s^2$, $2s^2$, $2p^6$, $3s^2$, $3p^6$, $4s^2$, $3d^3$ (b) Molecular Orbital diagram of NO molecule The electronic configuration of nitrogen and oxygen atoms can be given as, N(7) = $1s^2\ 2s^2\ 2p^3$ O(8) = $1s^2\ 2s^2\ 2p^4$  The electronic configuration of NO molecule can be represented as NO = KK $\sigma_{2s}^2\ \sigma^*{}_{2s}^2\ (\pi_{2PX}^2\ \pi_{2Py}^2)\ \sigma_{2PZ}^2\ \ \pi_{2px}^1$ OR π_{2py}^1

	Bond Order (BO) = (Nb-Na)/2= (8- 3)/ 2 = 2.5 The NO molecule has bond order of 2.5. Since the bond order is less than in N2 molecule (BO = 3), NO molecule is weaker than N2 molecule As molecule has 1 unpaired electron, it is paramagnetic in nature.