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CSIR NET Chemical Science Questions Answers With Solutions





Q2. [*Fe* (*CO*)₅] on reaction with $C_{3}H_{5}I$ gives **Y** with the elimination of two molecules of CO. Consider the following statements

- A. Y obeys the 18-electron rule
- B. The reaction is an example of oxidative addition
- C. Allyl moiety shows η¹ coordination in Y
- D. Y adopts pentagonal bipyramidal geometry

The correct option is

- (a) A, B and C only
- (b) A and B only
- (c) A, B and D only
- (d) B and D only

Q3. The following statements are given with respect to the copper-containing nitrite reductase.

A. It contains both Type-II and Type –III copper proteins.

B. Type-I copper protein is involved in the electron transfer process.

C. Nitrite ion is reduced to NO.

D. Nitrite ion is reduced to NH₃.

- The option with correct statements is:
- (a) A and B only
- (b) B and C only
- (c) A and C only
- (d) A and D only





Q4. The option showing the correct match of metal complexes in Column I with the corresponding Δ_0 (cm⁻¹) values in Column II is

Col	umn –I	Column-II		
А.	$[TiF_{6}]^{3-}$	Р.	21800	
В.	$[MnF_{6}]^{2-}$	Q.	17000	
C.	$[CO(en)_3]^{3+}$	R.	9400	
D.	$[Fe(H_2O)_6]^{2+}$	S.	24000	

(a) $A \rightarrow Q, B \rightarrow P, C \rightarrow S, D \rightarrow R$ (b) $A \rightarrow R, B \rightarrow S, C \rightarrow P, D \rightarrow Q$ (c) $A \rightarrow Q, B \rightarrow P, C \rightarrow R, D \rightarrow S$ (d) $A \rightarrow P, B \rightarrow S, C \rightarrow R, D \rightarrow Q$

Q5. The following reaction is the fastest when OH



Q6. The thermodynamic variable 'X' in the equation, $\binom{\partial S}{\partial P}_T = \frac{1}{\tau} \left[X + \binom{\partial H}{\partial P}_T \right]$ is

- (a)V
- (b)S
- (c)-V
- $(d)C_p$

Q7. For step-wise polymerization, the correct plot of chain length ($\langle N \rangle$) against degree of polymerization ^(p) is







Q8. The reaction of V_2O_5 with an ethanolic HCl produces a species X, which gives an EPR spectrum with an eight-line ⁵¹V hyperfine coupling ⁵¹V : I = 7/2 and a strong infra-red absorption in the region of 950-1035 cm⁻¹. X contains a

- (a) $[V (0)_2 V]^{6+}$ unit
- (b) [V0]²⁺ unit
- (c) $[V(0)(0_2)]^+$ unit
- (d) $[(0)V 0 V(0)]^{4+}$ unit

Q9. For a proton, the gyromagnetic ratio is $26.752 \times 10^7 rad T^{-1}s^{-1}$. The Larmor frequency for a proton (in MHz) in a 21.1 T magnetic field is, approximately,

- (a) 400
- (b) 500
- (c) 600
- (d) 900

Q10. The most effective pharmacophore that confers antibiotic activity to penicillin G is



(d) β -lactam

Q11. The reaction of the given compound with MeI produces







Q12. Of the following atomic transitions, the allowed one is (a) ${}^{1S \rightarrow 5S}$ (b) ${}^{3P \rightarrow 1D}$ (c) ${}^{1S \rightarrow 1D}$ (d) ${}^{3D \rightarrow 3P}$

Q13. 2-Methylbut-2-ene is used in Pinnick oxidation $[R - CHO \rightarrow R - CO_2H \text{ using NaCIO}_2, Na_2HPO_4 \text{ in } t - BuOH/H_2O] \text{ to scavenge}$ (a)HCl (b)H_3PO_4 (c)HClO_2 (d)HOCl

Q14. Among the following, the examples of chemoselective reactions are



(d) LUMO of pentadienyl anion

Q16. The option showing the correct match for the reactants in Column I with the second-order rate constants ($L \mod^{-1} s^{-1}$) in Column II for the outer-sphere reactions in water at 25°C is

	Column –I	Column –II		
А.	$[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$	I.	10 ⁵	
B.	$[Fe(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{3+}$	II.	3	
C.	$[Co(NH_3)_6]^{2+}$ and $[Co(NH_3)_6]^{3+}$	III.	10-6	
D.	$[Co(en)_3]^{2+}$ and $[Co(en)_3]^{3+}$	IV.	10 ⁻⁴	





(a) A-I, B-II, C-III, D-IV
(b) A-IV, B-III, C-II, D-I
(c) A-I, B-II, C-IV, D-III
(d) A-IV, B-II, C-III, D-I

- **Q17.** The number of unpaired electrons in B_2 is
- (a) 0
- (b) 1
- (c) 2

(d) 3

- Q18. Consider the following statements, I. Micelles form above the critical micelle concentration II. Micelles form above the Krafft temperature The correct option is (a) Only I is true (b) Only II is true (c) Both I and II are true
- (d) Both I and II are false

Q19. The correct match for the protons of ethyl acrylate given in Column P with chemical shifts $^{(\delta ppm)}$ given in Column Q is

Ha	Hc
н₀	

Column P		Column Q		
А.	H_a	I.	6.11 (dd, J = 16, 10Hz)	
В.	H _b	II.	6.4 (dd, J = 16, 4Hz)	
C.	H _c	III.	5.8 (dd, J = 10, 4Hz)	

(a) A-I, B-II, C-III
(b) A-III, B-II, C-I
(c) A-III, B-I, C-II
(d) A-II, B-III, C-I

Q20. The correct absolute configuration for the structure shown below is



6





Solutions

S1. Ans.(a)

Sol. Trimethylsilyl and other silyl groups stabilize a positive charge on a β carbon and are lost very easily. They can be thought of as very reactive protons or 'super protons'

The silyl group is replaced by the electrophile at the same atom on the ring-this is known as ipso substitution. The electrophile reacts to produce the most stable cation-in this case β to silicon. Cleavage of the weakened C–Si bond by any nucleophile leads directly to the ipso product. The Latin word ipso means 'the same'—the same site as that occupied by the SiR₃ group.



S2. Ans.(b)

Sol. Iron pentacarbonyl, also known as iron carbonyl, is the compound with formula Fe(CO)₅. Most metal carbonyls have 18 valence electrons, and Fe(CO)₅ fits this pattern with 8 valence electrons on Fe and five pairs of electrons provided by the CO ligands. Fe(CO)₅ adopts a trigonal bipyramidal structure with the Fe atom surrounded by five CO ligands: three in equatorial positions and two axially bound.

For transition metals, oxidative reaction results in the decrease in the dⁿ to a configuration with fewer electrons, often 2e fewer. Oxidative addition is favored for metals that are (i) basic and/or (ii) easily oxidized. Metals with a relatively low oxidation state often satisfy one of these requirements, but even high oxidation state metals undergo oxidative addition.

In classical organometallic chemistry, the formal oxidation state of the metal and the electron count of the complex both increase by two. One-electron changes are also possible and in fact some oxidative addition reactions proceed via series of 1e changes. Although oxidative additions can occur with the insertion of a metal into many different substrates, oxidative additions are most commonly seen with H–H, H–X, and C–X bonds because these substrates are most relevant to commercial applications.

Oxidative addition requires that the metal complex have a vacant coordination site. For this reason, oxidative additions are common for four- and five-coordinate complexes.

Potential ligands that do not have a lone pair or filled π type orbital are still able to interact with transition metal complexes but only by breaking a σ bond. This is the first step in a wide variety of processes and is described as oxidative addition because the formal oxidation state of the transition metal is raised by two, for example, M (0) to M(II), in the process. This is the result of having two extra ligands bearing a formal negative charge.





The number of coordinated ligands also increases by two so the starting complex is usually in low oxidation state (0 or 1; the diagram shows 0) and coordinatively unsaturated, that is, it has an empty site for a ligand whereas the product is usually coordinatively saturated, that is, it cannot accept another ligand unless it loses one first.

The number of atoms involved in bonding to the metal is shown by the hapto number η . The metal can either form a σ bond to a single carbon (hence η^1), or form a π complex with the p orbitals of all three carbons of the allyl system and this would be η^3 . The distinction is very important for electron counting as these two different situations contribute 1 and 3 electrons, respectively, to the complex.



Fe ([Ar] 3d⁶4s²) donates eight electrons, CO donates two electrons, I⁻ donates one electron



Additional Knowledge

In chemistry, a pentagonal bipyramid is a molecular geometry with one atom at the centre with seven ligands at the corners of a pentagonal bipyramid.

S3. Ans.(b)

Sol. Nitrite reductase refers to any of several classes of enzymes that catalyze the reduction of nitrite. There are two classes of NIR's. A multi heme enzyme reduces NO_2^- to a variety of products. Copper containing enzymes carry out a single electron transfer to produce nitric oxide.

Copper Nitrite Reductases are found in many different fungi and bacteria. What is common to all CuNIR is the presence of at least one type 1 copper center in the protein.

Type I copper centres (T1Cu) are characterized by a single copper atom coordinated by two histidine residues and a cysteine residue in a trigonal planar structure, and a variable axial ligand. In class I T1Cu proteins (e.g. amicyanin, plastocyanin and pseudoazurin) the axial ligand is the sulfur of methionine, whereas amino acids other than methionine (e.g. glutamine) give rise to class II T1Cu copper proteins. Azurins contain the third type of T1Cu centres: besides a methionine in one axial position, they contain a second axial ligand (a carbonyl group of a glycine residue). T1Cu-containing proteins are usually called "cupredoxins", and show similar three-dimensional structures, relatively high reduction potentials (> 250 mV), and strong absorption near 600 nm (due to S \rightarrow Cu charge transfer), which usually gives rise to a blue colour. Cupredoxins are therefore often called "blue copper proteins". This may be misleading, since some T1Cu centres also absorb around 460 nm and are therefore green.





Each type 1 Cu is strongly bonded to a thiolate sulfur from a cysteine, two imidazole nitrogens from different Histidine residues, and a sulfur atom of an axial Methionine ligand. This induces a distorted tetrahedral molecular geometry.

The cysteine ligated to the type 1 Cu center is located directly next to a Histidine in the primary structure of the amino acids. This Histidine is bound to the Type 2 Cu center responsible for binding and reducing nitrite. This Cys-His bridge plays an important role in facilitating rapid electron transfer from the type 1 center to the type 2.

Type II copper centres (T2Cu) exhibit a square planar coordination by N or N/O ligands. Since no sulfur ligation is present, the optical spectra of these centres lack distinctive features. T2Cu centres occur in enzymes, where they assist in oxidations or oxygenations.

Proposed mechanism

The type 2 copper center of a copper nitrite reductase is the active site of the enzyme. The Cu is bound by nitrogens of two Histidines from one monomer, and bound by one Histidine from another monomer; the Cys-His bridge to the type 1 Cu. This gives the molecule a distorted tetrahedral geometry. In the resting state, the Cu is also binding a water molecule that is displaced by nitrite.

As nitrite displaces water, Cu is bound by both oxygens in a bidentate fashion. A nearby Aspartic acid residue hydrogen bonds to one of the newly formed oxygen ligands. An incoming electron reduces the Cu from oxidation state (II) to (I). This change facilitates a shift in nitrite binding so that the nitrogen is bound to Cu, and one oxygen has an extended bond length due to hydrogen bonding. A second hydrogen bond forms from Histidine or a nearby water molecule and leads to the cleavage of the N-O bond. The Cu is now five coordinate bonded to nitric oxide and water. Nitric oxide is released as Cu is oxidized to state (II) and returns to the resting configuration.



The biological nitrogen cycle.

Additional Knowledge

Type III copper centres (T3Cu) consist of a pair of copper centres, each coordinated by three histidine residues. These centres are present in some oxidases and oxygen-transporting proteins (e.g. hemocyanin and tyrosinase).

S4. Ans.(a)

Sol. In the model of an octahedral complex used in crystal-field theory, six-point negative charges representing the ligands are placed in an octahedral array around the central metal ion. These charges (which we shall refer to as the 'ligands') interact strongly with the central metal ion, and the stability of the complex stems in large part from this attractive interaction between opposite charges. However, there is a much smaller but very important secondary effect arising from the fact that electrons in different d orbitals interact with the ligands to different extents.





Electrons in dz² and dx²-y² orbitals are concentrated close to the ligands, along the axes, whereas electrons in dxy, dyz, and dzx orbitals are concentrated in regions that lie between the ligands. As a result, the former are repelled more strongly by the negative charge on the ligands than the latter and lie at a higher energy. Group theory shows that the two eg orbitals have the same energy, and that the three t_{2g} orbitals also have the same energy. This simple model leads to an energy-level diagram in which the three degenerate t_{2g} orbitals lie below the two degenerate eg orbitals. The separation of the two sets of orbitals is called the ligand-field splitting parameter, Δ_0 (where the subscript O signifies an octahedral crystal field).

The ligand-field splitting parameter, Δ_0 , varies systematically with the identity of the ligand. The energy of the lowest energy electronic transition (and therefore Δ_0) increases as the ligands are varied along the series. The same order is followed regardless of the identity of the metal ion. Thus, ligands can be arranged in a spectrochemical series, in which the members are arranged in order of increasing energy of transitions that occur when they are present in a complex:

 $\begin{array}{l} I^- < Br^- < S^{2-} < \underline{S}CN^- < Cl^- < N\underline{O}_2^- < N^{3-} < F^- < OH^- < C_2O_4^{\ 2-} < O^{2-} < H_2O \\ < \underline{N}CS^- < CH_3C \equiv N < py < NH_3 < en < bpy < phen < \underline{N}O_2^- < PPh_3 < \underline{C}N^- < CO \end{array}$

Thus, the series indicates that, for the same metal, the optical absorption of the cyano complex will occur at higher energy than that of the corresponding chlorido complex. A ligand that gives rise to a high-energy transition (such as CO) is referred to as a strong-field ligand, whereas one that gives rise to a low-energy transition (such as Br⁻) is referred to as a weak-field ligand.

The oxidation state of the metal also contributes to the size of Δ_0 between the high and low energy levels. As the oxidation state increases for a given metal, the magnitude of Δ_0 increases. The smaller distance between the ligand and the metal ion results in a larger Δ_0 , because the ligand and metal electrons are closer together and therefore repel more.

More is the nuclear charge; more will be the repulsion between the d orbital (having electrons) of the metal and the electrons of the ligand. The higher oxidation state of the metal causes the ligands to approach more closely to it, and therefore the ligands cause more splitting of the metal d orbitals.

In $[TiF_6]^3$, Ti is in +3 oxidation state. This complex comprises of weak field ligands.

In [MnF₆]²⁻, Mn is in +4 oxidation state. This complex comprises of weak field ligands.

In $[Co(en)_3]^{3+}$, Co is in +3 oxidation state. This complex comprises of strong field ligands.

In $[Fe (H_2O)_6]^{2+}$, Fe is in +2 oxidation state.

	lons	Ligands Cl ⁻	H ₂ O		en
d³	Cr ³⁺	13 700	17 400	1.5	21 900
d⁵	Mn ²⁺	7500	8500		10 100
	Fe ³⁺	11 000	14 300		
1 ⁶	Fe ²⁺		10 400		
	Co3+		(20 700)		(23 200)

Ligand-field splitting parameters Δ_0 of ML₆ complexes^{*}





S5. Ans.(c)

Sol. The addition-elimination mechanism involves addition of the nucleophile followed by elimination of the leaving group. The nucleophilic aromatic substitution reaction proceeds via the addition-elimination mechanism. A typical nucleophilic aromatic substitution has:

a. An oxygen, nitrogen, or cyanide nucleophile

- b. A halide for a leaving group
- c. A carbonyl, nitro, or cyanide group ortho or para to the leaving group

Information Booster

It is not necessary to have a carbonyl group-any electron-withdrawing group will do-the only requirement is that the electrons must be able to get out of the ring into this anion-stabilizing group. Here is an example with a para-nitro group.



In a two-step mechanism, one step is slower and rate-determining; the other is unimportant to the rate. In the mechanism for nucleophilic aromatic substitution, it is the first step that is slower because it disturbs the aromaticity. The second step restores the aromaticity and is faster.

The nucleophile is a good one, the negative charge can be pushed through on to the oxygen atom(s) of the nitro group.

Any anion-stabilizing (electron-withdrawing) group ortho or para to a potential leaving group can be used to make nucleophilic aromatic substitution possible.



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S6. Ans.(c)

Sol. The Maxwell relations

An infinitesimal change in a function f(x,y) can be written df=gdx+hdy where g and h are functions of x and y. The mathematical criterion for df being an exact differential (in the sense that its integral is independent of path) is that



Frem (Gunt) The Maxwell relations

From U:	$\left(\frac{\partial T}{\partial V}\right)_{S} = -\left(\frac{\partial p}{\partial S}\right)_{V}$
From H:	$\left(\frac{\partial T}{\partial p}\right)_{S} = \left(\frac{\partial V}{\partial S}\right)_{p}$
From A:	$\left(\frac{\partial p}{\partial T}\right)_{V} = \left(\frac{\partial S}{\partial V}\right)_{T}$
From G:	$\left(\frac{\partial V}{\partial T}\right)_p = -\left(\frac{\partial S}{\partial p}\right)_T$

how H changes as both P and T change, $(\partial H/\partial P)_T$ must be calculated. The partial derivative $(\partial H/\partial P)_T$ is less straightforward to determine in an experiment than $(\partial H/\partial T)_P$. As will be seen, for many processes involving changes in both P and T, $(\partial H/\partial T)_P dT \gg (\partial H/\partial P)_T dP$ and the pressure dependence of H can be neglected relative to its temperature dependence. However, the knowledge that $(\partial H/\partial P)_T$ is not zero is essential for understanding the operation of a refrigerator and the liquefaction of gases. The following discussion is applicable to gases, liquids, and solids.

Given the definition H = U + PV, we begin by writing dH as

$$dH = dU + P \, dV + V \, dP$$

Substituting the differential forms of dU and dH,

$$C_P dT + \left(\frac{\partial H}{\partial P}\right)_T dP = C_V dT + \left(\frac{\partial U}{\partial V}\right)_T dV + P dV + V dP$$
$$= C_V dT + \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] dV + V dP$$

For isothermal processes, dT = 0, where t = 0 is the structure of the

$$\left(\frac{\partial H}{\partial P}\right)_T = \left[\left(\frac{\partial U}{\partial V}\right)_T + P\right] \left(\frac{\partial V}{\partial P}\right)_T + V$$

$$\begin{pmatrix} \frac{\partial H}{\partial P} \end{pmatrix}_T = T \begin{pmatrix} \frac{\partial P}{\partial T} \end{pmatrix}_V \begin{pmatrix} \frac{\partial V}{\partial P} \end{pmatrix}_T + V$$
$$= V - T \begin{pmatrix} \frac{\partial V}{\partial T} \end{pmatrix}_P$$

S7. Ans.(c)

Sol. The degree of polymerization, which is defined as the average number of monomer residues per polymer molecule. This quantity is the ratio of the initial concentration of A, $[A]_0$, to the concentration of end groups, [A], at the time of interest, because there is one -A group per polymer molecule. For example, if there were initially 1000 A groups and there are now only 10, each polymer must be 100 units long on average. Because we can express [A] in terms of p, the average number of monomers per polymer molecule, <n>, is





 $< n > = \frac{[A]_0}{[A]} = \frac{1}{1-p}$

This result is illustrated in figure. Expressing p in terms of the rate constant k $\langle n \rangle = 1 + kt[A]_0$

The average length grows linearly with time. Therefore, the longer a stepwise polymerization proceeds, the higher the average molar mass of the product.



EXAMPLE The average chain length of a polymer as a function of the fraction of reacted monomers, *p*. Note that *p* must be very close to 1 for the chains to be long.

S8. Ans.(b)

Sol. Electron paramagnetic resonance (EPR) spectroscopy (also called electron spin resonance (ESR) spectroscopy), is used to study paramagnetic species with one or more unpaired electrons, e.g. free radicals, diradicals, metal complexes containing paramagnetic metal centres, defects in semiconductors and irradiation effects in solids. While diamagnetic materials are EPR silent, paramagnetic species always exhibit an EPR spectrum. This consists of one or more lines, depending on the interactions between the unpaired electron (which acts as a 'probe') and the molecular framework in which it is located. Analysis of the shape of the EPR spectrum (the number and positions of EPR lines, their intensities and line widths) provides information about the paramagnetic species, e.g. the structure of a free radical, characterization of the coordination sphere around the metal centre in a coordination complex, or the presence of multiple paramagnetic species.

We can obtain information about nuclei with nuclear spin quantum number I not equal to 0 which are close to the paramagnetic centre. The spins of such nuclei interact magnetically with the unpaired electron and give rise to a hyperfine interaction.

EPR spectrum of one line is split and the number of lines in the hyperfine pattern is given by 2nI+1, where n is the number of equivalent nuclei with spin quantum number I.

VO²⁺ (3d¹) that is oxidovanadium (IV) complexes: The oxidovanadium (IV) complexes i.e.

oxidovanadium (IV) complexes experience a strong Jahn Teller distortion (The Jahn–Teller theorem essentially states that any non-linear molecule with a spatially degenerate electronic ground state will undergo a geometrical distortion that removes that degeneracy, because the distortion lowers the overall energy of the species) and the orbitally singlet ground state is widely separated from the immediate excited electronic state (i.e. energy separation, $\Delta E >> k_BT$) and consequently, the spin-lattice relaxation process is disfavoured (i.e. spin- lattice relaxation time T_1 is relatively longer). It makes their ESR studies easier and it can be studied even at room temperature. Because of the same ground, the EPR studies of the Cu (II) complexes can be made even at room temperature.

In the monomeric oxidovanadium (IV) complexes, the unpaired electron interacts with the nuclear spin I= 7/2 of vanadium. It splits the ESR signal into equally spaced 8 hyperfine peaks ($2 \times 7/2 + 1 = 8$)





S9. Ans.(d)

Sol. The nuclear magnetic resonance phenomenon occurs when nuclei aligned with an applied field are induced to absorb energy and change their spin orientation with respect to the applied field.

The energy absorption is a quantized process, and the energy absorbed must equal the energy difference between the two states involved.

$$E_{\text{absorbed}} = (E_{-\frac{1}{2}\text{state}} - E_{+\frac{1}{2}\text{state}}) = hv$$

In practice, this energy difference is a function of the strength of the applied magnetic field B_0



field Bo.

The stronger the applied magnetic field, the greater the energy difference between the possible spin states:

 $\Delta E = f(B_0)$

The magnitude of the energy-level separation also depends on the particular nucleus involved. Each nucleus (hydrogen, chlorine, and so on) has a different ratio of magnetic moment to angular momentum since each has different charge and mass. This ratio, called the magnetogyric ratio g, is a constant for each nucleus and determines the energy dependence on the magnetic field:

$$\Delta E = f(\gamma B_0) = hv$$

Since the angular momentum of the nucleus is quantized in units of $h/2\pi$, the final equation takes the form

$$\Delta E = \gamma \left(\frac{h}{2\pi}\right) B_0 = h v$$

Solving for the frequency of the absorbed energy,

$$v = \left(\frac{\gamma}{2\pi}\right) B_0$$





Units:

The SI unit for frequency is the hertz (Hz). One hertz is the same as one cycle per second. The tesla (symbol: T) is the unit of magnetic field.

SI unit of magnetogyric ratio is the radian per second per tesla (rad \cdot s⁻¹ \cdot T⁻¹)

$$v = \left(\frac{\gamma}{2\pi}\right)^{\beta_0}$$

$$v = \frac{21.1T \times 26.752 \times 10^{7} \text{ yead } T^{-1} \text{ s}^{-1}}{2 \times 3.14}$$
$$v = 89.88 \times 10^{7} \text{ Hz} = 898.8 \times 10^{6}$$

= 900MH7

S10. Ans.(d)

Sol. Benzylpenicillin, also known as penicillin G (PenG) or BENPEN, is an antibiotic used to treat a number of bacterial infections. Due to benzylpenicillin's limited bioavailability for oral medications, it is generally taken as an injection in the form of a sodium, potassium, benzathine, or procaine salt. Benzylpenicillin is given by injection into a vein or muscle. Two long-acting forms benzathine benzylpenicillin and procaine benzylpenicillin are available for use by injection into a muscle only.

Benzylpenicillin has relatively low toxicity, except for in the nervous system, in which it is one of the most active drugs among β -lactam agents.

 β -Lactam antibiotics (*beta*-lactam antibiotics) are antibiotics that contain a β -lactam ring in their chemical structure. This includes penicillin derivatives (penams), cephalosporins and cephamycins (cephems), monobactams, carbapenems and carbacephems. Most β -lactam antibiotics work by inhibiting cell wall biosynthesis in the bacterial organism and are the most widely used group of antibiotics.

β-Lactam antibiotics are indicated for the prevention and treatment of bacterial infections caused susceptible organisms.

β-Lactam antibiotics are indicated for the prevention and treatment of bacterial infections caused by susceptible organisms.







S11. Ans.(b)

Sol. Iodomethane, also called methyl iodide, and commonly abbreviated "MeI", is the chemical compound with the formula CH₃I. It is sterically open for attack by nucleophiles, and iodide is a good leaving group. It is used for alkylating carbon, oxygen, sulfur, nitrogen, and phosphorus nucleophiles.

The given fused system comprises of a pyridine ring and a pyrrole ring. In the given fused system, the lone pair on the nitrogen atom (six membered ring) can be donated in the σ^* of MeI.

In the five membered ring, the lone pair on the nitrogen atom are involved in conjugation and thus are not available for donation.

Pyridine is nucleophilic at the nitrogen atom because the lone pair of electrons on nitrogen cannot be delocalized around the ring. They are in a sp² orbital orthogonal to the p orbitals in the ring and there is no interaction between orthogonal orbitals.

lone pair in sp² orbital at right angles to p orbitals in ring: no interaction between orthogonal orbitals

In pyrrole, the nitrogen lone pair is delocalized round the ring. All the delocalization pushes electrons from the nitrogen atom into the ring and we expect the ring to be electron-rich at the expense of the nitrogen atom. The HOMO should go up in energy and the ring become more nucleophilic.



S12. Ans.(d) Sol.

Electronic transitions between energy levels obey the following selection rules:

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Spin selection rule: \Delta S = 0
```

Transitions may occur from singlet to singlet, or from triplet to triplet states, and so on, but a change in spin multiplicity is *forbidden*.

Laporte selection rule: There must be a change in parity:

allowed transitions: $g \leftrightarrow u$ forbidden transitions: $g \leftrightarrow g \qquad u \leftrightarrow u$

This leads to the selection rule:

 $\Delta l = \pm 1$

and, thus, *allowed* transitions are $s \to p$, $p \to d$, $d \to f$; forbidden transitions are $s \to s$, $p \to p$, $d \to d$, $f \to f$, $s \to d$, $p \to f$ etc.





The Laporte rule is a rule that explains the intensities of absorption spectra for chemical species. It is a selection rule that rigorously applies to atoms, and to molecules that are centrosymmetric, i.e. with an inversion centre. It states that electronic transitions that conserve parity are forbidden. Thus, transitions between two states that are each symmetric with respect to an inversion centre will not be observed. Transitions between states that are each symmetric with respect to inversion are forbidden as well. In the language of symmetry, g (gerade = even (German)) $\rightarrow g$ and u (ungerade = odd) $\rightarrow u$ transitions are forbidden. Allowed transitions must involve a change in parity, either $g \rightarrow u$ or $u \rightarrow g$. For atoms s and d orbitals are gerade, and p and f orbitals are ungerade. The Laporte rule implies that s to s, p to p, d to d, etc. transitions occur in the visible region of the spectrum. The Laporte rule is most commonly discussed in the context of the electronic spectroscopy of transition metal complexes. During electronic transition if spin of the electron is not change the relative orientation of an electron spin.



S13. Ans.(d)

Sol. The Pinnick oxidation is an organic reaction by which aldehydes can be oxidized into their corresponding carboxylic acids using sodium chlorite (NaClO₂) under mild acidic conditions. It was originally developed by Lindgren and Nilsson. There exist many different reactions to oxidize aldehydes, but only a few are amenable to a broad range of functional groups. The Pinnick oxidation has proven to be both tolerant of sensitive functionalities and capable of reacting with sterically hindered groups.

$$R1 \xrightarrow{R} CHO \xrightarrow{NaClO_2, t-BuOH} R1 \xrightarrow{R} COOH$$

The proposed reaction mechanism involves chlorous acid as the active oxidant, which is formed under acidic conditions from chlorite.

$$CIO_2^- + H_2PO_4^- \rightleftharpoons HCIO_2 + HPO_4^{2-}$$

First, the chlorous acid adds to the aldehyde. Then resulting structure undergoes a pericyclic fragmentation in which the aldehyde hydrogen is transferred to an oxygen on the chlorine, with the chlorine group released as hypochlorous acid (HOCl).



The HOCl byproduct, itself a reactive oxidizing agent, can be a problem in several ways. It can destroy the NaClO₂ reactant:

$$HOCI + 2CIO_2^- \rightarrow 2CIO_2 + CI^- + OH^-$$





making it unavailable for the desired reaction. It can also cause other undesired side reactions with the organic materials. For example, HOCl can react with double bonds in the organic reactant or product via a halohydrin formation reaction.

To prevent interference from HOCl, a scavenger is usually added to the reaction to consume the HOCl as it is formed. For example, one can take advantage of the propensity of HOCl to undergo this addition reaction by adding a sacrificial alkene-containing chemical to the reaction mixture. This alternate substrate reacts with the HOCl, preventing the HOCl from undergoing reactions that interfere with the Pinnick reaction itself. 2-Methyl-2-butene is often used in this context:



Resorcinol and sulfamic acid are also common scavenger reagents.

S14. Ans.(a)

Sol. Most organic molecules contain more than one functional group, and most functional groups can react in more than one way, so organic chemists often have to predict which functional group will react, where it will react, and how it will react. These questions are what we call selectivity.

Selectivity comes in three sorts: chemoselectivity, regioselectivity, and stereoselectivity. Chemoselectivity is which group reacts; regioselectivity is where it reacts. Stereoselectivity is how the group reacts with regard to the stereochemistry of the product.

a. Lithium borohydride in alcoholic solution will reduce esters-in fact, it has useful selectivity for esters over acids or amides that LiAlH₄ does not have.



b. Fétizon oxidation is the oxidation of primary and secondary alcohols utilizing the compound silver(I) carbonate absorbed onto the surface of celite also known as Fétizon's reagent. The reaction is inhibited significantly by polar groups within the reaction system as well as steric hindrance of the α -hydrogen of the alcohol.

A proposed mechanism for the oxidation of an alcohol by Fétizon's reagent involves single electron oxidation of both the alcoholic oxygen and the hydrogen alpha to the alcohol by two atoms of silver(I) within the celite surface. The carbonate ion then proceeds to deprotonate the resulting carbonyl generating bicarbonate which is further protonated by the additionally generated hydrogen cation to cause elimination of water and generation of carbon dioxide.







Application of Fétizon reagent

Highly hindered alcohols are not attacked, allowing selective oxidation in appropriate cases. Primary alcohols are oxidized more slowly than secondary, which are themselves much less reactive than benzylic or allylic alcohols; in acetone or methanol solution, selective oxidation of benzylic or allylic hydroxyl groups is easily affected.

Adams' catalyst, also known as platinum dioxide, is usually represented as platinum(IV) oxide hydrate, PtO₂•H₂O. It is a catalyst for hydrogenation and hydrogenolysis in organic synthesis.



Two hydrogen atoms are transferred to the alkene, and they are often both added to the same face of the alkene.

Iodolactonization (or, more generally, halolactonization) is an organic reaction that forms a ring (the lactone) by the addition of an oxygen and iodine across a carbon-carbon double bond. It is an intramolecular variant of the halohydrin synthesis reaction.

$$\begin{array}{c} 0 \\ 0 \\ -H \end{array} \xrightarrow[l_2, NaHCO_3]{} \\ 0 \\ CH_2Cl_2 \end{array} \begin{array}{c} 0 \\ Ph \end{array} \xrightarrow[l_2, NaHCO_3]{} \\ 0 \\ 0 \\ 0 \\ Ph \end{array}$$

The reaction mechanism involves the formation of a positively charged halonium ion in a molecule that also contains a carboxylic acid (or other functional group that is a precursor to it). The oxygen of the carboxyl acts as a nucleophile, attacking to open the halonium ring and instead form a lactone ring. The reaction is usually performed under mildly basic conditions to increase the nucleophilicity of the carboxyl group.



S15. Ans.(a)

Sol. Molecular orbitals of compound containing π (*pi*) bonds

We know that, the number of molecular orbitals is always equal to the number of atomic orbitals that combine to form them. The same principle applies to π molecular orbitals. A π electron system derived from the interaction of number *m* of *p* orbitals contain *m* molecular orbitals, that differ in energy. Half of the molecular orbitals are bonding molecular orbitals and remaining half are antibonding molecular orbitals.

 π molecular orbitals of ethylene from the two *p* atomic orbitals of the two carbons can be constructed as follows:





Each *p* orbital consists of two lobes, with opposite phases of the wave function of the two lobes. The plus and minus signs used in drawing these orbitals indicate the phase of the wave function.

In the bonding orbital of ethylene, there is overlap of similar signs (+ with + and – with –) in the bonding region between the nuclei. This reinforcement of the wave function is called *constructive* overlap. In the antibonding orbital there is cancelling of opposite signs (+ and –) in the bonding region. This cancelling of the wave function is called *destructive* overlap.



Following generalisations can be made to construct the molecular orbitals of the conjugated polyenes: 1. A π electron system derived from the interaction of a number of *m* of *p* orbitals contain *m* molecular orbitals (MOs) that differ in energy. Thus, the number of π MOs are always equal to the number of atomic *p* orbitals.

2. Half of the molecular orbitals (*i.e.*, m/2) have lower energy than the isolated p orbitals. These are called bonding molecular orbitals (BMOs). The other half have energy higher than the isolated p orbitals. These are called antibonding molecular orbitals (ABMOs).

3. The bonding MO of lowest energy ψ_1 has no node. Each molecular orbital of increasingly

higher energy has one additional node.

Frontier molecular orbitals

The occupied molecular orbital of highest energy is known as *highest occupied molecular orbital* (HOMO). The other is the unoccupied molecular orbital of lowest energy known as *lowest unoccupied molecular orbital* (LUMO). HOMO and LUMO of any given compound have opposite symmetries. HOMO and LUMO are referred to as *frontier molecular orbitals*.



 π molecular orbitals with electron occupancy of the 2, 4-pentadienyl system

In the given figure, one node (ψ_2) is present. Thus, molecular orbital corresponds to the HOMO of pentadienyl cation

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S16. Ans.(a)

Sol. In this type of reaction, both complexes participating in the reaction undergo substitution reactions more slowly than the rate of electron transfer. The oxidant and the reductant come as close to each other as possible, and the coordination spheres stay intact. The transfer of an electron takes place from the reductant to the oxidant. Thus, an outer sphere mechanism involves electron transfer from the reductant to the oxidant when the intact coordination spheres are in contact at their outer edges, i.e., the distance between two metals is minimal.

An outer sphere electron transfer may occur in the following elementary steps:

In the first step, the oxidant and reductant come closer and form a precursor complex:

 $\begin{array}{cccc} Ox &+ & Red & \longrightarrow & Ox \parallel Red \\ & & & Precursor Complex \end{array}$

In the second step, there is activation of the precursor complex, which includes reorganization of the solvent molecules and changes in M–L bond lengths, occurring before electron transfer. Then, the electron transfer takes place:

 $Ox \parallel Red \implies Ox \parallel Red^+$

In the final step, the ion pair is dissociated into products:

 $-Ox \parallel Red^+ \implies Ox^- + Red^+$

Bond

Salient Features of the Outer Sphere Mechanism

1.Both the oxidant and reductant should be kin<mark>etically in</mark>ert. If one complex is labile (prone to exchange ligands), the inert complex must not have a donor atom that could bridge with the labile complex.

If both the oxidant and reductant are labile and there is a possibility of electron transfer from π^* of reductant to the π^* of oxidant, then the reaction proceeds through outer sphere mechanism.

$[Fe(H_2O)_6]^{3+}$	+ $[Fe(H_2O)_6]^{2+}$ -	$\longrightarrow [\operatorname{Fe}(\operatorname{H}_2\operatorname{O})_6]^{2+} + [\operatorname{Fe}(\operatorname{H}_2\operatorname{O})_6]^{3+}$		
HS	HS			
$(t_{2g}^3 e_g^2)$	$(t_{2g}^4 e_g^2)$		_	
Labile	Labile			
$\mathrm{Fe}^{3+}_{1}-\mathrm{OH}_{2}$	$\mathrm{Fe}^{3+}-\mathrm{OH}_2$			
d length = 78 pm	Bond length = 92 pm			

In this reaction, the reactants and products are the same except the position of radioactive label. The energy of activation for this reaction is 32kJ mol⁻¹ which indicates that the rate of electron transfer is slow (second order rate constant $K_{11} = 4L \text{ mol}^{-1}\text{s}^{-1}$).

According to Frank-Condon principle, electron transfer takes place when the energy levels of the participating orbitals are same and the electron transfer takes place much more rapidly than the change in position of nuclei. Thus, during electron transfer M-L bond lengths remain unchanged.

In this reaction an electron is transferred from t_{2g} of Fe (II) to t_{2g} of Fe (III). The Fe²⁺-OH₂ and Fe³⁺-OH₂ bond lengths are 92 pm and 78 pm respectively, i.e., Fe³⁺-OH₂ bond length is 14 pm smaller than that of Fe²⁺-OH₂. This indicate that the energy levels of the orbitals are not equal. Since the Fe-O bond length does not change during the electron transfer, this transfer of electron without any input of energy will produce [Fe (H₂O)₆]³⁺ with Fe-O bond similar to Fe-O bond in [Fe (H₂O)₆]²⁺ and the [Fe(H₂O)₆]²⁺ with Fe-O bond similar to [Fe(H₂O)₆]³⁺. These two products are in vibrationally excited sate. Both the products will release energy in the form of heat by vibrating to reach the equilibrium bond length. It seems that energy is created but it is the violation of the first law of thermodynamics. Consequently, an enough vibrational activation energy has been provided to each complex ion to bring them to the same energy levels and then transfer of electron to take place.





Consequently, the electron transfer is most probable when an activation energy has been given to each complex ion. The activation energy causes the shortening of the bonds in $[Fe (H_2O)_6]^{2+}$ and lengthening of the bonds in $[Fe (H_2O)_6]^{3+}$ until the participating orbitals are of the same energy. In case of self-exchange reaction, the Fe-O bond lengths have reached the same intermediate value. For cross reactions, the M-L bond lengths do not become same values but the orbital energy may be.

2.When both the reactants are inert with respect to ligand exchange e.g., $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ a close approach of the metal ions is impossible and the electron transfer takes place by a tunneling or outer sphere mechanism. The rate of electron transfer depends upon the ability of electrons to tunnel through the ligands.

$[Fe(CN)_{6}]^{4-}$	+ $[Fe(CN)_6]^{3-}$ —	$\rightarrow [\text{Fe}(\text{CN})_6]^{3-} + [\text{Fe}(\text{CN})_6]^{4-}$
Low spin	Low spin	
$(t_{2g}^{6}e_{g}^{0})$	$(t_{2g}^5 e_g^0)$	
Inert	Inert	
$Fe^{2+} - CN^{-}$	$\mathrm{Fe}^{3+}-\mathrm{CN}^{-}$	
Bond length = 195 pm	Bond length = 192 pm	

The rate of electron transfer is fast for the following reasons:

(i) Both the complexes $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ are inert, and electron transfer is faster than cyanide exchange for either reactant.

(ii) Electron transfer is spin-allowed.

(iii) The electron transfer occurs from t_{2g} of $[Fe(CN)_6]^{4-}$ to t_{2g} of $[Fe(CN)_6]^{3-}$ complex. The t_{2g} orbitals point between the ligands and are not engaged in Fe-CN σ -bonding. Therefore, electron transfer becomes easy.

(iv) Since t_{2g} orbitals point between the ligands, the M-L distance does not change appreciably.

(v) The ligand CN^{-} is unsaturated and a π -acceptor, which facilitates the electron tunneling. Also, since the CN^{-} ligand is a π -acceptor, it therefore stabilizes complexes in lower oxidation states by the formation of back π -bonding.

3.

 $\begin{bmatrix} \operatorname{Co}(\operatorname{NH}_3)_6 \end{bmatrix}^{3+} + \begin{bmatrix} \operatorname{Co}(\operatorname{NH}_3)_6 \end{bmatrix}^{2+} \longrightarrow \begin{bmatrix} \operatorname{Co}(\operatorname{NH}_3)_6 \end{bmatrix}^{2+} + \begin{bmatrix} \operatorname{Co}(\operatorname{NH}_3)_6 \end{bmatrix}^{3+} \\ \text{Low spin} & \text{High spin} \\ (t_{2g}^5 e_g^0) & (t_{2g}^5 e_g^2) \\ \text{Inert} & \text{Labile} \\ \operatorname{Co} - \operatorname{NH}_3 & \operatorname{Co} - \operatorname{NH}_3 \\ \text{Bond length} = 193.6 \text{ pm} \quad \text{Bond length} = 211.4 \text{ pm} \end{bmatrix}$

The rate of electron transfer for this reaction is slow (second order rate constant = 10^{-6} L mol⁻¹ s⁻¹)

because of the following reasons :

[Co $(NH_3)_6$]³⁺ is low spin $(t_{2g}^6e_g^0)$ and [Co $(NH_3)_6$]²⁺ is high spin $(t_{2g}^5e_g^2)$. Low spin [Co $(NH_3)_6$]³⁺ has an electronic configuration t_{2g}^6 with all the metal d-electrons pointing in between the ligands. On the other hand, the high spin [Co $(NH_3)_6$]²⁺ has an electronic configuration $t_{2g}^5e_g^2$ with two e_g electrons pointing directly at the ligands. The electrons present in e_g orbitals cause more repulsion with the ligands than that of t_{2g} electrons. Therefore, Co²⁺-NH₃ bond distance is larger than that of Co³⁺-NH₃. The Co³⁺-NH₃, bond distance is 193.6 pm and the Co²⁺-NH₃ bond distance is 211.4 pm. In this case M-L bond lengths are different enough and more activation energy is needed to make them the same in the transition state. Since Co(II) and Co(III) complexes are high spin and low spin respectively, no simple addition or removal of an electron can convert these configurations into one another. Therefore, it is necessary to excite the oxidation states before the reaction can occur as shown below:





$$\begin{array}{c} \operatorname{Co}^{2+}(t_{2g}^{5}e_{g}^{2}) \underbrace{t_{2g}^{6}e_{g}^{1}}_{Co^{3+}(t_{2g}^{6}e_{g}^{0})} \underbrace{t_{2g}^{6}e_{g}^{1}}_{t_{2g}^{5}e_{g}^{1}} \underbrace{\underbrace{t_{2g}^{2} \operatorname{to}^{1} t_{2g}^{2}}_{\operatorname{Transitions}} t_{2g}^{5}e_{g}^{1}}_{f_{2g}^{6}e_{g}^{1}} \underbrace{t_{2g}^{6}e_{g}^{0}}_{t_{2g}^{5}e_{g}^{2}} \operatorname{Co}^{3+} \underbrace{t_{2g}^{6}e_{g}^{0}}_{t_{2g}^{5}e_{g}^{2}} \operatorname{Co}^{2+} \operatorname{Co}^{3+} \underbrace{t_{2g}^{6}e_{g}^{0}}_{t_{2g}^{5}e_{g}^{2}} \operatorname{Co}^{2+} \operatorname{Co}^{3+} \operatorname{Co$$

The electronic ground and excited states can also be written as follows :

If the ligands are arranged in increasing order of crystal field splitting:

 $\mathrm{OX} < \mathrm{H_2O} < \mathrm{EDTA} < \mathrm{NH_3} < \mathrm{en} < \mathrm{phen} < \mathrm{CN^-}$

transfer of electron from Co (II) to Co (III) is faster either at the weak end or the strong end but slow in the middle.

According to Frank-Condon principle, the electronic transition occurs much more rapidly than rearrangement of atoms so that bond distances do not change during very short time of electronic transition.

The electron transfer is very fast when both the complexes are low spin including that the electron transfer takes place from $t_{2g}(\pi^*)$ of reductant to the $t_{2g}(\pi^*)$ of oxidant. The first reason is that energy levels of these two t_{2g} orbitals are same. The t_{2g} orbitals are not shielded from the ligands and the electron transfer from and to is easier and no input energy is required. The second reason is that there is no appreciable change in M-L bond length due to π^* - π^* electron transfer.

The rates of electron transfer are much faster between the complexes which have π -acceptor ligands (like CN-, phen, bpy etc) than for complexes of the same metal having purely σ -donor ligands (like H₂O, NH₃, en etc). The π -acceptor ligands have vacant π^* orbitals that can accept electron being transferred, then pass them on to the receiving metal ion (i.e., oxidant) whereas the σ -donor ligands do not have such tendency. Thus, outer sphere electron transfer is direct electron transfer from one metal to another in case of complexes having π -donor ligands. On the other hand, electron transfer is indirect (i.e., from one metal to ligands to another metal) if the complexes have π -acceptor ligands.

S17. Ans.(c)

Sol. Molecular orbitals are classified as σ , π , or δ according to their rotational symmetry about the internuclear axis, and (in centrosymmetric species) as g or u according to their symmetry with respect to inversion.

σ orbitals are formed by allowing overlap between atomic orbitals that have cylindrical symmetry around the internuclear axis, which is conventionally labelled z. The notation σ signifies that the orbital has cylindrical symmetry; atomic orbitals that can form σ orbitals include the 2s and 2p_z orbitals on the two atoms. From these four orbitals (the 2s and the 2p_z orbitals on atom A and the corresponding orbitals on atom B) with cylindrical symmetry we can construct four σ molecular orbitals, two of which arise predominantly from interaction of the 2s orbitals, and two from interaction of the 2p_z orbitals. These molecular orbitals are labelled $1σ_g$, $1σ_u$, $2σ_g$, and $2σ_u$, respectively. Interaction between a 2s on one atom and a 2p_z orbital on the other atom is possible if their relative energies are similar.





The remaining two 2p orbitals on each atom, which have a nodal plane containing the z-axis, overlap to give π orbitals. Bonding and antibonding π orbitals can be formed from the mutual overlap of the two 2p_x orbitals, and also from the mutual overlap of the two 2p_y orbitals. This pattern of overlap gives rise to the two pairs of doubly degenerate energy levels (two energy levels of the same energy) and labelled $1\pi_u$ and $1\pi_g$.

For homonuclear diatomic, it is sometimes convenient to signify the symmetry of the molecular orbitals with respect to their behaviour under inversion through the centre of the molecule. The operation of inversion consists of starting at an arbitrary point in the molecule, travelling in a straight line to the centre of the molecule, and then continuing an equal distance out on the other side of the centre. The orbital is designated g (for gerade, even) if it is identical under inversion, and u (for ungerade, odd) if it changes sign. Thus, a bonding σ orbital is g and an antibonding σ orbital is u and an antibonding π orbital is g.



 $\label{eq:started} \begin{array}{l} \mathcal{D}\mathcal{D}\mathcal{D}\mathcal{D}\sigma A \ \sigma \ \text{orbital can be formed in} \\ \text{several ways, including s,s overlap, s,p} \\ \text{overlap, and p,p overlap, with the p orbitals} \\ \text{directed along the internuclear axis.} \end{array}$



to an one (a) Bonding and (b) antibonding σ interactions with the arrow indicating the inversion.

Nodal plane

neutaht Two p orbitals can overlap to form a π orbital. The orbital has a nodal plane passing through the internuclear axis, shown here from the side.



ພ່ມ)ຄຳການ(a) Bonding and (b) antibonding π interactions with the arrow indicating the inversions.



BotDDBIn The molecular orbital energy level diagram for Period 2 homonuclear diatomic molecules from Li, to N₂.





The electronic configuration of boron is $1s^2 2s^2 2p^1$. Thus, B, comprises of ten electrons.

The number of unpaired electrons in B₂ is two.



S18. Ans.(c)

Sol. Surfactant molecules or ions can cluster together as micelles, which are colloid-sized clusters of molecules, for their hydrophobic tails tend to congregate, and their hydrophilic heads provide protection.

Micelles form only above the critical micelle concentration (CMC) and above the Krafft temperature.

In colloidal and surface chemistry, the critical micelle concentration (CMC) is defined as the concentration of surfactants above which micelles form and all additional surfactants added to the system will form micelles. The CMC is an important characteristic of a surfactant. Before reaching the CMC, the surface tension changes strongly with the concentration of the surfactant. After reaching the CMC, the surface tension remains relatively constant or changes with a lower slope. The value of the CMC for a given dispersant in a given medium depends on temperature, pressure, and (sometimes strongly) on the presence and concentration of other surface active substances and electrolytes.

In colloidal chemistry, the Krafft temperature (or Krafft point) is defined as the minimum temperature at which the formation of micelles occurs in a solution of dissolved surfactant. It has been found that solubility at the Krafft point is nearly equal to critical micelle concentration (CMC). Below the Krafft temperature, the maximum solubility of the surfactant will be lower than the critical micelle concentration, meaning micelles will not form. The Krafft temperature is a point of phase change below which the surfactant remains in crystalline form, even in an aqueous solution.

The CMC is detected by noting a pronounced change in physical properties of the solution, particularly the molar conductivity. There is no abrupt change in properties at the CMC; rather, there is a transition region corresponding to a range of concentrations around the CMC where physical properties vary smoothly but nonlinearly with the concentration. The hydrocarbon interior of a micelle is like a droplet of oil.



unary of a spherical micelle. The hydrophilic groups are represented by spheres and the hydrophobic hydrocarbon chains are represented by the stalks; these stalks are mobile.







Concentration of surfactant

nhitition The typical variation of some physical properties of an aqueous solution of sodium dodecylsulfate close to the critical micelle concentration (CMC).

S19. Ans.(b)

Sol. Nuclear magnetic resonance (NMR) spectroscopy is a resonance technique involving absorption of radiofrequency energy. The magnetic environment of a nucleus affects its resonance frequency and allows structural information to be deduced.

Structural assignment is often helped by the observation of the spin–spin coupling, which gives rise to multiplets in the spectrum due to interactions between nuclear spins. Spin–spin coupling arises when the orientation of the spin of a nearby nucleus affects the energy of another nucleus and causes small changes in the location of the latter's resonance. A multiplet of 2I+1 lines is obtained when a spin-1/2 nucleus (or a set of symmetry-related spin-1/2 nuclei) is coupled to a nucleus of spin I. The coupling of the nuclear spins of different elements is called heteronuclear coupling. Homonuclear coupling between nuclei of the same element is detectable when the nuclei are in chemically inequivalent locations.

J-couplings are mediated through chemical bonds connecting two spins. It is an indirect interaction between two nuclear spins that arises from hyperfine interactions between the nuclei and local electrons. In NMR spectroscopy, *J*-coupling contains information about relative bond distances and angles. Most importantly, *J*-coupling provides information on the connectivity of chemical bonds. The J coupling (always reported in Hz) is field-independent (i.e. J is constant at different external magnetic field strength), and is mutual (i.e. $J_{AX} = J_{XA}$).

Neighbouring nuclei might interact through space or through the electrons in the bonds. Coupling is in fact a 'through bond effect' because of the way coupling constants vary with the shape of the molecule. The most important case occurs when the protons are at either end of a double bond. If the two hydrogens are cis, the coupling constant J is typically about 10 Hz but, if they are trans, J is much larger, usually 15–18 Hz.

 H_a will couple with H_b and H_c to give a doublet and a doublet respectively. H_c will couple with H_a and H_b to give a doublet and a doublet respectively. H_b will couple with H_a and H_c to give a doublet and a doublet respectively.





Typical coupling constants



S20. Ans.(a)

Sol. The R/S system is an important nomenclature system for denoting enantiomers. This approach labels each chiral center R or S according to a system by which its substituents are each assigned a *priority*, according to the Cahn–Ingold–Prelog priority rules (CIP), based on atomic number. When the center is oriented so that the lowest-priority substituent of the four is pointed away from the viewer, the viewer will then see two possibilities: if the priority of the remaining three substituents decreases in clockwise direction, it is labeled R (for Latin: *rectus* – right); if it decreases in counterclockwise direction, it is S (for Latin: *sinister* – left).

The Cahn–Ingold–Prelog (CIP) sequence rules are a standard process to completely and unequivocally name a stereoisomer of a molecule. The purpose of the CIP system is to assign an *R* or *S* descriptor to each stereocenter.

- 1. Compare the atomic number (*Z*) of the atoms directly attached to the stereocenter; the group having the atom of higher atomic number Z receives higher priority (i.e. number 1).
- 2. If there is a tie, the atoms at distance 2 from the stereocenter have to be considered: a list is made for each group of further atoms bonded to the one directly attached to the stereocenter. Each list is arranged in order of decreasing atomic number Z. Then the lists are compared atom by atom; at the earliest difference, the group containing the atom of higher atomic number Z receives higher priority.







Application in Bicyclic Systems

- In bicyclic compounds, stereochemical descriptors (R or S) are assigned to chiral centers considering the three-dimensional arrangement.
- When evaluating priorities, the rigid structure of bicyclic compounds ensures that substituents are fixed in specific spatial orientations, aiding in the determination of configurations.

Carbon number 1: The highest priority is assigned to the carbon which has an OH group attached to it. Second priority goes to the carbon which is further attached to three carbons. Third priority should be given to the carbon which is attached to one carbon atom and two hydrogen atoms. Lastly, methyl group gets the fourth priority. Thus, the configuration is S.

Carbon number 2: First priority is assigned to the OH group. Second priority goes to the carbon which is further attached to three carbons. Third priority should be given to the carbon which is attached to one carbon atom and two hydrogen atoms. Lastly, hydrogen atom gets the fourth priority. Thus, the configuration is S.

Carbon number 4: The highest priority goes to the carbon which is further attached to three carbons. Second priority is assigned to the carbon which is attached to one carbon (which has an OH group attached to it) and two hydrogen atoms. Third priority goes to the carbon which is attached to one carbon atom and two hydrogen atoms. Hydrogen atom gets the fourth priority. As the hydrogen atom is coming towards the observer, the configuration changes from R to S.

Carbon 2









Information Booster

 In Fischer projections it is commonly the case that the #4 ranked substituent (often H) is pointing to the front of the page (on a "wedge"). To obtain the true absolute configuration in these cases apply the "opposite rules" to get the true value





Now Assign R or S To The Chiral Center





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