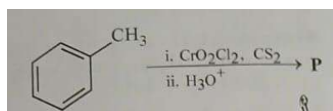


General Instructions

- (i) The test is of 3 hours and 15 minutes duration.
- (ii) This test paper consists of 180 questions. The maximum marks are 720.
- (iii) Physics and Chemistry contains 45 questions each and Biology (Botany and Zoology) contains 90 questions.
- (iv) Each question carries +4 marks for correct answer and –1 mark for wrong answer.

46. Consider the following reaction, and choose the correct option.



- (A) Compound P is obtained by the hydrogenation of benzoyl chloride with Pd on $BaSO_4$.
- (B) On treating compound P with saturated $NaHCO_3$ solution, brisk effervescence is observed.
- (C) Compound P can be prepared by treating benzene with anhydrous $AlCl_3$ and CH_3COCl .
- (D) On treatment with bromine water, compound P gives a white precipitate.

Correct Answer: (A) Compound P is obtained by the hydrogenation of benzoyl chloride with Pd on $BaSO_4$.

Solution:

Step 1: Understanding the Question:

We must identify the organic product P formed from the given reaction and then evaluate four chemical properties/reactions associated with it.

Step 2: Key Formula or Approach:

The reaction of toluene with chromyl chloride (CrO_2Cl_2) followed by acid hydrolysis is known as the **Etard reaction**. It partially oxidizes the methyl group to an aldehyde group, forming benzaldehyde. So, Product **P** is **Benzaldehyde** (C_6H_5CHO).

Step 3: Detailed Explanation:

Let's analyze the options given for Benzaldehyde: 1. **Option A:** Hydrogenation of benzoyl chloride (C_6H_5COCl) using H_2 and a Pd catalyst supported on $BaSO_4$ is the **Rosenmund reduction**. This reaction specifically yields benzaldehyde. This statement is **true**. 2. **Option B:** Brisk effervescence with $NaHCO_3$ is a test for carboxylic acids. Benzaldehyde is an aldehyde and does not react. This statement is **false**. 3. **Option C:** Treating benzene with CH_3COCl and $AlCl_3$ (Friedel-Crafts acylation) produces acetophenone, a ketone, not benzaldehyde. This statement is **false**. 4. **Option D:** White precipitate with bromine water is a characteristic test for phenol or aniline, due to polybromination. Benzaldehyde does not give this test. This statement is **false**.

Step 4: Final Answer:

The correct option is (A).

Quick Tip: The Etard reaction specifically halts oxidation at the aldehyde stage to yield benzaldehyde. Always link it mentally to the Rosenmund reduction, which also selectively prepares benzaldehyde from acid chlorides.

47. The formula of tetraammineaquachloridocobalt(III) chloride is

- (A) $[Co(NH_3)_4(H_2O)Cl]Cl_2$
- (B) $[Co(NH_3)_4Cl_2] \cdot H_2O$
- (C) $[Co(NH_3)_4Cl_3] \cdot H_2O$
- (D) $[Co(NH_3)_4(H_2O)Cl]Cl$

Correct Answer: (A) $[Co(NH_3)_4(H_2O)Cl]Cl_2$

Solution:

Step 1: Understanding the Question:

We are required to construct the chemical formula of a coordination compound from its given IUPAC name.

Step 2: Key Formula or Approach:

Break down the IUPAC name to identify the central metal atom, the ligands inside the coordination sphere, and the counter ions outside. - **tetraammine**: 4 ammonia ligands (NH_3) - **aqua**: 1 water ligand (H_2O) - **chlorido**: 1 chloride ligand inside the sphere (Cl) - **cobalt(III)**: Central metal is Cobalt with an oxidation state of +3 - **chloride**: Chloride counter ions outside the sphere to balance the total charge.

Step 3: Detailed Explanation:

Construct the coordination sphere: $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]$ Now, calculate the net charge of this complex ion: - Cobalt charge = +3 - Ammine charge = 0 (neutral ligand) - Aqua charge = 0 (neutral ligand) - Chlorido charge = -1 Net charge = $+3 + 4(0) + 1(0) + 1(-1) = +2$ The complex ion is $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]^{2+}$. To balance the +2 charge, we need two chloride ions (Cl^-) as counter ions outside the coordination sphere. Therefore, the final formula is $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$.

Step 4: Final Answer:

The correct formula is $[\text{Co}(\text{NH}_3)_4(\text{H}_2\text{O})\text{Cl}]\text{Cl}_2$.

Quick Tip: Ligands are listed alphabetically in the IUPAC name but do not need to be strictly alphabetical in the formula. Always calculate the net charge of the coordination sphere first to know exactly how many counter ions are required!

48. The lanthanide ion having four unpaired electrons is

(Given : Atomic numbers of Ce = 58, Nd = 60, Tb = 65 and Ho = 67)

(A) Ho^{3+}

- (B) Nd^{3+}
(C) Ce^{3+}
(D) Tb^{3+}

Correct Answer: (A) Ho^{3+}

Solution:

Step 1: Understanding the Question:

We must determine which of the given tripositive lanthanide ions possesses exactly four unpaired electrons in its f-orbital.

Step 2: Key Formula or Approach:

Write the ground state electronic configurations using the Xenon core ($[Xe]$, atomic number 54). Remove 3 electrons (first from the 6s orbital, then from the 4f/5d) to form the +3 ion. Count the unpaired electrons in the 4f subshell, noting that the f-subshell holds up to 14 electrons in 7 orbitals.

Step 3: Detailed Explanation:

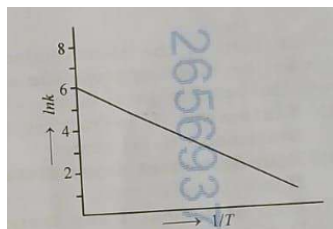
1. **Holmium (Ho, Z = 67):** Ground state: $[Xe]4f^{11}6s^2$ Ion Ho^{3+} : Loses two 6s electrons and one 4f electron $\Rightarrow [Xe]4f^{10}$. An f-subshell has 7 orbitals. 10 electrons will form 3 pairs and leave 4 unpaired electrons ($14 - 10 = 4$). Unpaired electrons = 4.
2. **Neodymium (Nd, Z = 60):** Ground state: $[Xe]4f^46s^2$ Ion Nd^{3+} : $\Rightarrow [Xe]4f^3$. Unpaired electrons = 3.
3. **Cerium (Ce, Z = 58):** Ground state: $[Xe]4f^15d^16s^2$ Ion Ce^{3+} : $\Rightarrow [Xe]4f^1$. Unpaired electrons = 1.
4. **Terbium (Tb, Z = 65):** Ground state: $[Xe]4f^96s^2$ Ion Tb^{3+} : $\Rightarrow [Xe]4f^8$. 8 electrons will form 1 pair and leave 6 unpaired electrons ($14 - 8 = 6$). Unpaired electrons = 6.

Step 4: Final Answer:

The ion with four unpaired electrons is Ho^{3+} .

Quick Tip: For any lanthanide ion Ln^{3+} with electronic configuration $4f^n$, if $n \leq 7$, the number of unpaired electrons is n . If $n > 7$, the number of unpaired electrons is $14 - n$.

49. For an elementary chemical reaction, the Arrhenius plot is given below.



If the energy of activation is 6.64 kJ mol^{-1} and $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$, the temperature at which the rate constant becomes $e^2 \text{ min}^{-1}$, is

- (A) 250 K
- (B) 125 K
- (C) 150 K
- (D) 200 K

Correct Answer: (D) 200 K

Solution:

Step 1: Understanding the Question:

We are given an Arrhenius plot with a visible y-intercept. We must find the specific temperature where the rate constant equals a specific value.

Step 2: Key Formula or Approach:

The Arrhenius equation in logarithmic form is:

$$\ln k = \ln A - \frac{E_a}{RT}$$

From the plot of $\ln k$ vs $1/T$, the y-intercept represents the logarithm of the pre-exponential factor, $\ln A$.

Step 3: Detailed Explanation:

By observing the graph, the line intersects the y-axis at 6. Therefore:

$$\ln A = 6$$

We are asked to find T when the rate constant $k = e^2 \text{ min}^{-1}$. Taking the natural logarithm:

$$\ln k = \ln(e^2) = 2$$

Substitute the known values into the Arrhenius equation:

$$2 = 6 - \frac{E_a}{RT}$$

Rearranging for the activation energy term:

$$\frac{E_a}{RT} = 6 - 2 = 4$$

Solve for temperature T :

$$T = \frac{E_a}{4R}$$

Given parameters: Activation energy, $E_a = 6.64 \text{ kJ mol}^{-1} = 6640 \text{ J mol}^{-1}$ Gas constant, $R = 8.3 \text{ J K}^{-1} \text{ mol}^{-1}$

$$T = \frac{6640}{4 \times 8.3} = \frac{6640}{33.2}$$
$$T = 200 \text{ K}$$

Step 4: Final Answer:

The temperature is 200 K.

Quick Tip: Never forget to convert activation energy given in kJ into J when using the gas constant $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$. This is a very common source of magnitude errors.

50. The green paramagnetic species formed by heating KMnO_4 at 513 K is

(A) KO_2

- (B) K_2MnO_4
(C) Mn_3O_4
(D) MnO

Correct Answer: (B) K_2MnO_4

Solution:

Step 1: Understanding the Question:

We need to identify the products of the thermal decomposition of potassium permanganate ($KMnO_4$) and pinpoint the species that is green and paramagnetic.

Step 2: Key Formula or Approach:

When heated to around 513 K, solid $KMnO_4$ decomposes according to the following balanced chemical equation:



The products are potassium manganate (K_2MnO_4), manganese dioxide (MnO_2), and oxygen gas (O_2).

Step 3: Detailed Explanation:

Let's analyze the relevant product, potassium manganate (K_2MnO_4): - The oxidation state of Manganese in K_2MnO_4 is +6. - The electronic configuration of Mn ($Z=25$) is $[Ar]3d^54s^2$. - The Mn^{6+} ion will have lost all its 4s electrons and four of its 3d electrons, leaving a configuration of $[Ar]3d^1$. - Since it has 1 unpaired electron in the d-orbital, it is **paramagnetic**. - Manganate salts characteristically exhibit an intense **green color** in aqueous solution and solid state. Thus, K_2MnO_4 perfectly fits the description of a green, paramagnetic species.

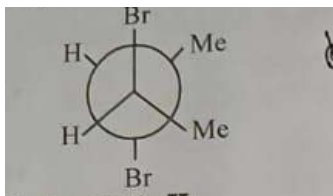
Step 4: Final Answer:

The species formed is K_2MnO_4 .

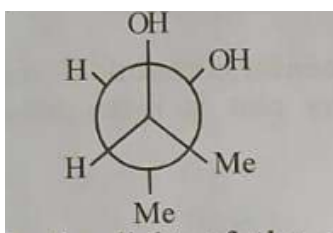
Quick Tip: Permanganate (MnO_4^-) has a d^0 configuration and is diamagnetic and purple. Manganate (MnO_4^{2-}) has a d^1 configuration, making it paramagnetic and green. Memorizing these color-magnetism pairings for transition metal ions saves tremendous time.

51. Given below are two statements:

Statement I: *trans*-But-2-ene upon treatment with Br_2 in CCl_4 gives the following product



Statement II: *cis*-But-2-ene upon treatment with alkaline $KMnO_4$ gives the following product



In the light of the above statements, choose the *most appropriate* answer from the options given below.

- (A) Statement I is incorrect but Statement II is correct
- (B) Both Statement I and Statement II are correct
- (C) Both Statement I and Statement II are incorrect
- (D) Statement I is correct but Statement II is incorrect

Correct Answer: (A) Statement I is incorrect but Statement II is correct

Solution:

Step 1: Understanding the Question:

The question tests the stereochemistry of addition reactions to alkenes and the ability to identify meso and chiral compounds from their 3D projections.

Step 2: Key Formula or Approach:

1. Anti-addition of Br_2 to a *trans*-alkene yields a *meso* product.
2. Syn-addition of cold alkaline $KMnO_4$ to a *cis*-alkene yields a *meso* product.

A *meso* compound must possess a plane of symmetry or center of inversion in at least one conformation.

Step 3: Detailed Explanation:

Statement I: The reaction should produce *meso*-2,3-dibromobutane. If we rotate the back carbon of the given Newman projection by 180° to check for an eclipsed plane of symmetry, the front Br eclipses the back Br, but the front Me eclipses the back H, and the front H eclipses the back Me. This lack of symmetry means the drawn structure is a chiral enantiomer (part of a racemic mixture), not the *meso* compound. Thus, Statement I is incorrect.

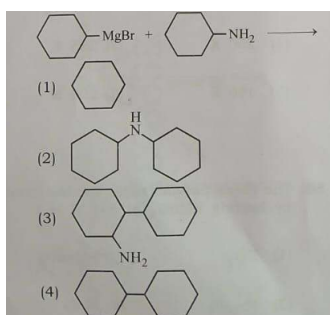
Statement II: The reaction should produce *meso*-butane-2,3-diol. The provided eclipsed projection shows OH eclipsing OH, H eclipsing H, and Me eclipsing Me. This conformation has a clear internal plane of symmetry, confirming it is the *meso* isomer. Thus, Statement II is correct.

Step 4: Final Answer:

Statement I is incorrect but Statement II is correct.

Quick Tip: Remember the CAR and TAM mnemonics: Cis + Anti = Racemic; Trans + Anti = Meso. For syn-additions, the rules reverse: Cis + Syn = Meso; Trans + Syn = Racemic.

52. One of the products formed in the following reaction is



- (A) Cyclohexane
- (B) Dicyclohexylamine
- (C) Bicyclohexyl (coupled product)
- (D) Cyclohexyl-substituted amine

Correct Answer: (A) Cyclohexane

Solution:

Step 1: Understanding the Question:

The question asks for the product of a reaction between a Grignard reagent and a primary amine.

Step 2: Key Formula or Approach:

Grignard reagents ($R-MgX$) are strong bases and strong nucleophiles. When reacted with compounds containing active (acidic) hydrogen atoms (such as alcohols, amines, terminal alkynes, or water), they undergo a rapid acid-base reaction rather than a nucleophilic attack, abstracting the proton to form the corresponding alkane ($R-H$).

Step 3: Detailed Explanation:

Cyclohexanamine ($C_6H_{11}NH_2$) has two slightly acidic hydrogen atoms on the nitrogen. Cyclohexylmagnesium bromide acts as a strong base and abstracts one of these protons.



The abstracted proton converts the cyclohexyl carbanion into cyclohexane (C_6H_{12}).

Step 4: Final Answer:

Cyclohexane is formed as one of the major products.

Quick Tip: Acid-base reactions are kinetically much faster than nucleophilic substitution or addition. Always check for acidic hydrogens (like $-OH$, $-NH$, $-SH$, or terminal alkynes) before proceeding with nucleophilic reactions involving Grignard reagents!

53. Given below are two statements:

Statement-I : Heating $NaCl$ with concentrated H_2SO_4 and MnO_2 results in oxidation of Mn.

Statement-II : Heating NaI with concentrated H_2SO_4 and MnO_2 results in reduction of Mn.

In light of the above statements, choose the *most appropriate* answer from the options given below:

- (A) Statement-I is incorrect but Statement-II is correct.
(B) Both Statement-I and Statement-II are correct.
(C) Both Statement-I and Statement-II are incorrect.
(D) Statement-I is correct but Statement-II is incorrect.

Correct Answer: (A) Statement-I is incorrect but Statement-II is correct.

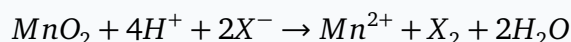
Solution:

Step 1: Understanding the Question:

We need to determine the redox changes occurring to Manganese (*Mn*) when different halide salts are heated with MnO_2 and concentrated sulfuric acid.

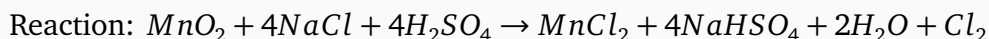
Step 2: Key Formula or Approach:

MnO_2 acts as an oxidizing agent in acidic medium. The general reaction with a halide ion (X^-) is:



Step 3: Detailed Explanation:

Statement I: When $NaCl$ is heated with MnO_2 and conc. H_2SO_4 , chlorine gas is evolved.



The oxidation state of *Mn* changes from +4 (in MnO_2) to +2 (in $MnCl_2$). A decrease in oxidation state is a **reduction**, not an oxidation. Thus, Statement I is incorrect.

Statement II: When NaI is used, I^- is similarly oxidized to I_2 , and MnO_2 is reduced to Mn^{2+} .

The oxidation state of *Mn* goes from +4 to +2, which is a reduction. Thus, Statement II is correct.

Step 4: Final Answer:

Statement-I is incorrect but Statement-II is correct.

Quick Tip: MnO_2 is a classic oxidizing agent. In acidic redox reactions, it practically always reduces to the pale pink/colorless Mn^{2+} state.

54. Among the following options, the correct trend in the electron gain enthalpy is

(A) $I > Br > Cl > F$

(B) $F > Cl > Br > I$

(C) $Br > Cl > F > I$

(D) $Cl > F > Br > I$

Correct Answer: (D) $Cl > F > Br > I$

Solution:

Step 1: Understanding the Question:

We need to identify the correct decreasing order of the magnitude of electron gain enthalpy for the halogens.

Step 2: Key Formula or Approach:

Electron gain enthalpy generally becomes less negative (decreases in magnitude) as we move down a group due to increasing atomic size. However, the second period elements often have lower electron gain enthalpies than third period elements due to severe electron-electron repulsion in their small 2p orbitals.

Step 3: Detailed Explanation:

For halogens, the expected trend based on size is $F > Cl > Br > I$.

However, Fluorine has an exceptionally small atomic size, leading to strong interelectronic repulsions in the compact 2p subshell. This makes adding an extra electron less favorable than in Chlorine (which has larger 3p orbitals).

Thus, Chlorine has the highest negative electron gain enthalpy in the periodic table.

The correct order of magnitude is: $Cl > F > Br > I$.

Step 4: Final Answer:

The correct trend is $Cl > F > Br > I$.

Quick Tip: This is a highly frequent exception in inorganic chemistry. Remember: Chlorine has the highest electron gain enthalpy, but Fluorine is the most electronegative element!

55. Given below are two statements:

Statement-I : $[Fe(ox)_3]^{3-}$ is chiral.

Statement-II : $trans-[Cr(H_2O)_2(ox)_2]^-$ is chiral.

(Given : $oxH_2 = HOOC-COOH$)

In light of the above statements, choose the *most appropriate* answer from the options given below:

- (A) Statement-I is incorrect but Statement-II is correct.
- (B) Both Statement-I and Statement-II are correct.
- (C) Both Statement-I and Statement-II are incorrect.
- (D) Statement-I is correct but Statement-II is incorrect.

Correct Answer: (D) Statement-I is correct but Statement-II is incorrect.

Solution:

Step 1: Understanding the Question:

We need to determine the chirality (optical activity) of two specific coordination complexes.

Step 2: Key Formula or Approach:

A complex is chiral if it lacks an improper axis of rotation (which practically means lacking a plane of symmetry and center of inversion).

- Octahedral complexes of type $[M(AA)_3]$ (where AA is a symmetrical bidentate ligand) are always chiral and exist as Δ and Λ enantiomers.
- Octahedral complexes of type $trans-[M(AA)_2a_2]$ have a plane of symmetry passing through the equatorial ligands and are thus achiral.

Step 3: Detailed Explanation:

Statement I: $[Fe(ox)_3]^{3-}$ is an octahedral complex with three bidentate oxalate ligands ($[M(AA)_3]$ type). It assumes a propeller-like shape that cannot be superimposed on its mirror

image. Therefore, it is chiral. Statement I is correct.

Statement II: In $\text{trans-[Cr(H}_2\text{O)}_2(\text{ox})_2]^-$, the two monodentate H_2O ligands are placed 180° apart (axial positions), and the two oxalate ligands are in the equatorial plane. The equatorial plane itself acts as a plane of symmetry, dissecting the top H_2O and reflecting it into the bottom H_2O . Since it has a plane of symmetry, it is achiral. Statement II is incorrect.

Step 4: Final Answer:

Statement-I is correct but Statement-II is incorrect.

Quick Tip: For $[\text{M}(\text{AA})_2\text{a}_2]$ complexes, the *cis*-isomer is always chiral (optically active), while the *trans*-isomer is always achiral (optically inactive) due to the presence of a plane of symmetry.

56. The correct statement about peptides and proteins is

- (A) In α -helices, the polypeptide chain is twisted into a left-handed screw (helix) through intramolecular hydrogen bonds.
- (B) Tertiary structure of proteins has two or more polypeptide subunits.
- (C) Only the proteins having a quaternary structure are biologically active.
- (D) In β -pleated sheet structures, peptide chains are held together by intermolecular hydrogen bonds.

Correct Answer: (D) In β -pleated sheet structures, peptide chains are held together by intermolecular hydrogen bonds.

Solution:

Step 1: Understanding the Question:

Evaluate four statements regarding the structural levels and properties of proteins.

Step 3: Detailed Explanation:

Let's analyze each option:

- (A) α -helices are structurally most stable as **right-handed** helices, not left-handed. (Incorrect)

- (B) The tertiary structure refers to the overall 3D folding of a **single** polypeptide chain. Having two or more polypeptide subunits defines a quaternary structure. (Incorrect)
- (C) Many functional proteins exist purely with tertiary structure (e.g., myoglobin, many enzymes). Quaternary structure is not a strict requirement for biological activity. (Incorrect)
- (D) In β -pleated sheets, adjacent polypeptide chains (or widely separated segments of one chain) are held together via **intermolecular** (or inter-strand) hydrogen bonding between the $C=O$ and $N-H$ groups of the peptide backbone. (Correct)

Step 4: Final Answer:

The correct statement is (D).

Quick Tip: α -helices = Intramolecular H-bonds (within the same helical turn). β -sheets = Intermolecular H-bonds (between neighboring strands).

57. Given below are two statements:

Statement-I : Oxidation of *p*-nitrotoluene with acidic $KMnO_4$ gives an acid that is stronger than benzoic acid.

Statement-II : Reduction of *p*-nitrotoluene with Sn/HCl followed by neutralization gives an amine that is more basic than aniline.

In light of the above statements, choose the *most appropriate* answer from the options given below.

- (A) Statement-I is incorrect but Statement-II is correct.
- (B) Both Statement-I and Statement-II are correct.
- (C) Both Statement-I and Statement-II are incorrect.
- (D) Statement-I is correct but Statement-II is incorrect.

Correct Answer: (B) Both Statement-I and Statement-II are correct.

Solution:

Step 1: Understanding the Question:

We need to analyze the products of oxidation and reduction of *p*-nitrotoluene and compare their acidic and basic strengths with benzoic acid and aniline, respectively.

Step 3: Detailed Explanation:

Statement I: Oxidation of *p*-nitrotoluene with acidic $KMnO_4$ oxidizes the methyl group to a carboxylic acid group, forming *p*-nitrobenzoic acid. The nitro group ($-NO_2$) is highly electron-withdrawing through both inductive ($-I$) and mesomeric ($-M$) effects. This stabilizes the conjugate base (carboxylate anion), making *p*-nitrobenzoic acid a stronger acid than benzoic acid. Statement I is correct.

Statement II: Reduction of *p*-nitrotoluene with Sn/HCl reduces the nitro group to an amine group, yielding *p*-methylaniline (also known as *p*-toluidine). The methyl group ($-CH_3$) is electron-donating via inductive ($+I$) and hyperconjugation effects. This increases the electron density on the nitrogen atom, enhancing its ability to donate a lone pair, thereby making it a stronger base than aniline. Statement II is correct.

Step 4: Final Answer:

Both Statement-I and Statement-II are correct.

Quick Tip: Electron-withdrawing groups (EWG) increase acidity and decrease basicity. Electron-donating groups (EDG) decrease acidity and increase basicity.

58. Identify the reactions which give aniline as the major product.



Choose the correct answer from the options given below.

- (A) C and D only
- (B) A and B only
- (C) B and D only
- (D) A and C only

Correct Answer: (C) B and D only

Solution:

Step 1: Understanding the Question:

Evaluate four organic transformation pathways to identify which ones produce aniline ($C_6H_5NH_2$) as the major product.

Step 3: Detailed Explanation:

Let's predict the product for each reaction:

A. Benzonitrile ($Ph-CN$) treated with a strong reducing agent like $LiAlH_4$ reduces the nitrile completely to a primary amine, forming benzylamine ($Ph-CH_2NH_2$), not aniline.

B. Benzamide ($Ph-CONH_2$) reacts with Br_2 in the presence of KOH . This is the **Hoffmann bromamide degradation** reaction, which removes the carbonyl carbon as carbonate and yields a primary amine with one less carbon: Aniline ($Ph-NH_2$).

C. Nitrobenzene ($Ph-NO_2$) with $NaBH_4$. Sodium borohydride is a mild reducing agent and is generally unreactive toward aromatic nitro groups under normal conditions. It does not yield aniline. (Typically, Sn/HCl or H_2/Pd is used).

D. N-Phenylacetamide (Acetanilide, $Ph-NH-COCH_3$) boiled with aqueous HCl undergoes acid-catalyzed amide hydrolysis. The amide bond cleaves to form Aniline ($Ph-NH_2$) and acetic acid (CH_3COOH).

Reactions B and D yield aniline.

Step 4: Final Answer:

The correct options are B and D only.

Quick Tip: Hoffmann bromamide degradation is an excellent step-down reaction for synthesizing aromatic amines directly from primary amides. Amide hydrolysis is the standard method for unprotecting an amine.

59. Two moles of an ideal gas undergo free expansion from 10 L to 100 L at 300 K. The values of ΔS_{system} and $\Delta S_{\text{surroundings}}$ are

(R is universal gas constant)

- (A) $\Delta S_{\text{system}} = 4.606R$; $\Delta S_{\text{surroundings}} = 0$
(B) $\Delta S_{\text{system}} = 0$; $\Delta S_{\text{surroundings}} = 0$
(C) $\Delta S_{\text{system}} = 4.606R$; $\Delta S_{\text{surroundings}} = -4.606R$
(D) $\Delta S_{\text{system}} = 0$; $\Delta S_{\text{surroundings}} = 4.606R$

Correct Answer: (A) $\Delta S_{\text{system}} = 4.606R$; $\Delta S_{\text{surroundings}} = 0$

Solution:

Step 1: Understanding the Question:

We need to calculate the entropy change for both the system and the surroundings when an ideal gas undergoes free expansion (expansion into a vacuum).

Step 2: Key Formula or Approach:

Entropy is a state function. For the isothermal expansion of an ideal gas, the system's entropy change depends only on the initial and final states:

$$\Delta S_{\text{sys}} = nR \ln \left(\frac{V_2}{V_1} \right)$$

For free expansion, the external pressure is zero ($P_{\text{ext}} = 0$), hence work done $W = 0$. Since it's an ideal gas undergoing isothermal free expansion, internal energy change $\Delta U = 0$. By the first law ($q = \Delta U - W$), heat exchanged $q = 0$.

Therefore, the surroundings exchange no heat: $\Delta S_{\text{surr}} = \frac{-q_{\text{actual}}}{T} = 0$.

Step 3: Detailed Explanation:

Calculate ΔS_{sys} :

Given $n = 2$ moles, $V_1 = 10$ L, $V_2 = 100$ L.

$$\Delta S_{\text{sys}} = 2 \times R \times \ln \left(\frac{100}{10} \right) = 2R \ln(10)$$

Since $\ln(10) \approx 2.303$,

$$\Delta S_{\text{sys}} = 2 \times 2.303 \times R = 4.606R$$

Calculate ΔS_{surr} :

Because it is a free expansion, the process is adiabatic ($q = 0$) with respect to the surroundings.

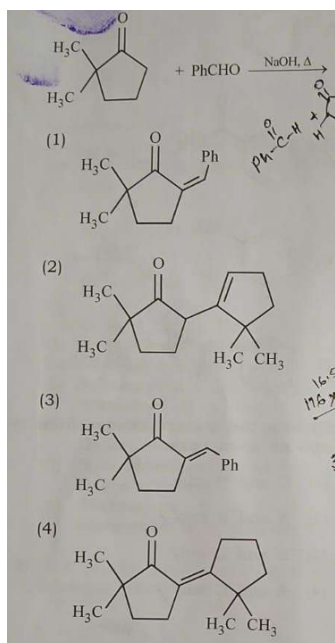
$$\Delta S_{\text{surr}} = 0$$

Step 4: Final Answer:

The values are $\Delta S_{\text{sys}} = 4.606R$ and $\Delta S_{\text{surr}} = 0$.

Quick Tip: Free expansion is highly irreversible. The entropy of the universe must increase ($\Delta S_{\text{total}} > 0$). Here, $4.606R + 0 > 0$, validating our calculation.

60. The compound that CANNOT be obtained from the aldol condensation reaction shown below, is



Correct Answer: (D) [A self-aldol product where the double bond connects C5 to C1 of a 3-methylcyclopentyl ring]

Solution:

Step 1: Understanding the Question:

The reaction is a base-catalyzed crossed aldol condensation between 2-methylcyclopentanone and benzaldehyde. We need to identify which of the four given structures is chemically impossible to form, even as a side product.

Step 2: Key Formula or Approach:

Analyze the possible enolates and their nucleophilic attack targets.

1. Enolate forms primarily at C5 (less sterically hindered) and attacks benzaldehyde to form cross-aldol products (E and Z isomers).
2. Enolate can also attack another molecule of 2-methylcyclopentanone (self-aldol). Since the attacked carbonyl carbon (C1) is directly adjacent to the C2 methyl group, any self-aldol product must feature a methyl group immediately adjacent to the newly formed inter-ring double bond.

Step 3: Detailed Explanation:

- **Option (A) and (C):** Both show 2-benzylidene-5-methylcyclopentanone, formed by the C5 enolate attacking benzaldehyde. They are merely E/Z stereoisomers and are completely valid products.
- **Option (B):** Shows a self-aldol product. The double bond connects the two rings. On the right-hand ring (the one that was attacked), the methyl group is located at the top vertex, which is directly adjacent to the double bond. This preserves the 2-methylcyclopentanone skeleton.
- **Option (D):** Shows a self-aldol product. However, on the right-hand ring, the methyl group is located at the bottom-right vertex (two carbons away from the double bond). This skeleton corresponds to an attack on **3-methylcyclopentanone**, not the 2-methylcyclopentanone starting material provided. Since the carbon skeleton is fundamentally wrong, this product cannot be formed.

Step 4: Final Answer:

The compound with the wrong skeleton (Option 4) cannot be obtained.

Quick Tip: When dealing with "CANNOT be formed" questions in condensation reactions, aggressively check the carbon skeleton of the reactant versus the products. Side-products like self-aldols are valid, but migrating a methyl group is impossible without rearrangement!

61. The complex which has facial and meridional isomers is

(Given : py = pyridine and en = $H_2N - CH_2 - CH_2 - NH_2$)

- (A) $[Ni(en)_2(H_2O)_2]^{2+}$
- (B) $[Cr(py)_3(Cl)_3]$
- (C) $[Cr(H_2O)_6]^{3+}$
- (D) $[Co(NH_3)_4(H_2O)_2]^{3+}$

Correct Answer: (B) $[Cr(py)_3(Cl)_3]$

Solution:

Step 1: Understanding the Question:

Identify which of the given coordination complexes exhibits facial (*fac*) and meridional (*mer*) geometrical isomerism.

Step 2: Key Formula or Approach:

Facial (*fac*) and meridional (*mer*) isomerism is exclusively shown by octahedral coordination complexes of the general formula $[Ma_3b_3]$, where 'a' and 'b' are two different unidentate ligands, each present in a quantity of three.

Step 3: Detailed Explanation:

Let's evaluate the generic formula of each option:

(A) $[Ni(en)_2(H_2O)_2]^{2+}$: Type $[M(AA)_2a_2]$. Shows *cis-trans* isomerism and optical isomerism (for the *cis* form), but not *fac/mer*.

(B) $[Cr(py)_3(Cl)_3]$: Type $[Ma_3b_3]$. Three pyridine (py) ligands and three chloride (Cl) ligands. This complex perfectly satisfies the condition for *fac/mer* isomerism.

(C) $[Cr(H_2O)_6]^{3+}$: Type $[Ma_6]$. All ligands are identical. No geometrical isomerism is possible.

(D) $[Co(NH_3)_4(H_2O)_2]^{3+}$: Type $[Ma_4b_2]$. Shows *cis-trans* geometrical isomerism, but not *fac/mer*.

Step 4: Final Answer:

The complex with *fac* and *mer* isomers is $[Cr(py)_3(Cl)_3]$.

Quick Tip: Memorize the specific isomerism formulas: $[Ma_4b_2] \rightarrow cis/trans$. $[Ma_3b_3] \rightarrow fac/mer$.
 $[M(AA)_2a_2] \rightarrow cis$ (chiral) / *trans* (achiral).

62. The numbers 17.0145 and 21.0235 were rounded to three figures after the decimal point. The resulting numbers, respectively, are

- (A) 17.015 and 21.024
- (B) 17.014 and 21.023
- (C) 17.015 and 21.023
- (D) 17.014 and 21.024

Correct Answer: (D) 17.014 and 21.024

Solution:

Step 1: Understanding the Question:

We need to apply standard significant figure rules for rounding numbers that end exactly in the digit 5.

Step 2: Key Formula or Approach:

When rounding off a number, if the digit to be dropped is exactly 5 (with no following non-zero digits), the "round to even" rule is applied:

- If the preceding digit is even, it is left unchanged.
- If the preceding digit is odd, it is increased by 1.

Step 3: Detailed Explanation:

For 17.0145: We need three decimal places, so we drop the '5'. The preceding digit is '4', which is **even**. Therefore, the number remains unchanged.

Result: 17.014.

For 21.0235: We drop the '5'. The preceding digit is '3', which is **odd**. Therefore, we increase it by 1.

Result: 21.024.

Step 4: Final Answer:

The rounded numbers are 17.014 and 21.024.

Quick Tip: The "round to even" rule prevents statistical bias when analyzing large datasets. Always check if the digit before '5' is odd or even!

63. The amount of carbon dioxide evolved upon complete combustion of 116 g of *n*-butane is (Given: atomic mass in amu H = 1, C = 12 and O = 16)

- (A) 362 g
- (B) 352 g
- (C) 322 g
- (D) 176 g

Correct Answer: (B) 352 g

Solution:

Step 1: Understanding the Question:

We must calculate the mass of CO_2 produced from the complete combustion of a given mass of butane.

Step 2: Key Formula or Approach:

1. Write the balanced chemical equation for the combustion of butane.
2. Convert the given mass of butane to moles.

3. Use stoichiometry to find the moles of CO_2 produced.
4. Convert the moles of CO_2 back to grams.

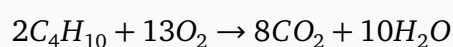
Step 3: Detailed Explanation:

The formula for *n*-butane is C_4H_{10} .

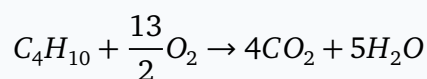
Molar mass of $C_4H_{10} = (4 \times 12) + (10 \times 1) = 48 + 10 = 58 \text{ g/mol}$.

Molar mass of $CO_2 = 12 + (2 \times 16) = 44 \text{ g/mol}$.

Balanced combustion equation:



Alternatively, for 1 mole:



This shows that 1 mole of butane produces 4 moles of CO_2 .

Calculate moles of butane in 116 g:

$$n = \frac{116 \text{ g}}{58 \text{ g/mol}} = 2 \text{ moles}$$

Moles of CO_2 produced:

$$n(CO_2) = 2 \text{ moles butane} \times 4 = 8 \text{ moles}$$

Mass of CO_2 evolved:

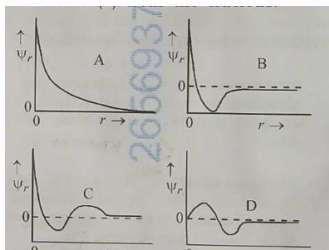
$$\text{Mass} = 8 \text{ moles} \times 44 \text{ g/mol} = 352 \text{ g}$$

Step 4: Final Answer:

The amount of carbon dioxide evolved is 352 g.

Quick Tip: For alkane combustion C_nH_{2n+2} , the moles of CO_2 formed will always be exactly n times the moles of alkane burned.

64. Consider the following schematic plots of orbital wavefunction (ψ_r) against distance (r) from the nucleus.



(A) D

(B) A

(C) B

(D) C

Correct Answer: (D) C

Solution:

Step 1: Understanding the Question:

We need to identify which wavefunction plot (ψ_r vs r) corresponds to an atomic orbital having exactly two radial nodes.

Step 2: Key Formula or Approach:

A radial node occurs where the radial wavefunction ψ_r changes sign (crosses the horizontal axis where $\psi_r = 0$).

The total number of radial nodes is given by the formula: $\text{Nodes} = n - l - 1$. We simply need to count the number of times the graph intersects and crosses the x-axis.

Step 3: Detailed Explanation:

Let's analyze the zero-crossings for each plot:

- **Plot A:** Starts at a high positive value and decays to zero asymptotically. It never crosses the x-axis. (0 radial nodes, e.g., 1s, 2p).
- **Plot B:** Starts at a high positive value, crosses the x-axis once, and then approaches zero asymptotically from the negative side. (1 radial node, e.g., 2s, 3p).

- **Plot C:** Starts at a high positive value, crosses the x-axis (first node), goes negative, crosses the x-axis again (second node), goes positive, and approaches zero. It crosses the axis **twice**. (2 radial nodes, e.g., 3s).
- **Plot D:** Starts at zero, rises to a maximum, crosses the x-axis (first node), goes negative to a minimum, and then approaches zero asymptotically from below. It crosses the axis **once**. (1 radial node, e.g., 4d, 5f).

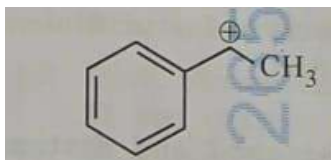
Only Plot C exhibits exactly two radial nodes.

Step 4: Final Answer:

The figure representing two radial nodes is C.

Quick Tip: Do not confuse the graph returning asymptotically to zero with a node. A radial node requires the wavefunction to fully cross from positive to negative, or vice versa.

65. The following carbocation is stabilized by the interaction of the empty p orbital with



- (A) empty σ and empty π orbitals
- (B) filled σ and filled π orbitals
- (C) empty σ and empty π orbitals
- (D) empty σ and filled π orbitals

Correct Answer: (B) filled σ and filled π orbitals

Solution:

Step 1: Understanding the Question:

We need to identify the molecular orbital interactions responsible for stabilizing the given

1-phenylethyl carbocation ($Ph - C^+(H) - CH_3$).

Step 2: Key Formula or Approach:

Carbocations are electron-deficient and possess an empty unhybridized 2p orbital. They are stabilized by the donation of electron density from adjacent filled orbitals.

1. **Hyperconjugation:** Involves the delocalization of electrons from a filled adjacent σ bond (like $C - H$ or $C - C$) into the empty p orbital.
2. **Resonance:** Involves the delocalization of electrons from a filled adjacent π system (like a benzene ring) into the empty p orbital.

Step 3: Detailed Explanation:

The carbocation center is flanked by a methyl group and a phenyl ring.

- The adjacent methyl group ($-CH_3$) stabilizes the empty p orbital through hyperconjugation. This involves the donation of electron density from the **filled** σ orbitals of the $C - H$ bonds.
 - The adjacent phenyl ring ($-C_6H_5$) stabilizes the empty p orbital through resonance. This involves the donation of electron density from the **filled** π orbitals of the aromatic ring.
- Therefore, the stabilization occurs via interaction with filled σ and filled π orbitals.

Step 4: Final Answer:

The stabilization is by filled σ and filled π orbitals.

Quick Tip: Remember that stabilization inherently means transferring electron density into the electron-deficient region. Only filled orbitals have electrons to give! Empty orbitals cannot donate electron density.

66. A 1:3 electrolyte in an aqueous solution is

- (A) $[Co(NH_3)_3(NO_2)_3]$
(B) $[CoCl_2(NH_3)_4]Cl$
(C) $[CoCl(NH_3)_5]Cl_2$
(D) $[Co(NH_3)_6]Cl_3$

Correct Answer: (D) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

Solution:

Step 1: Understanding the Question:

We need to identify which of the given coordination complexes acts as a 1:3 electrolyte, meaning it dissociates into one cation and three anions (or vice versa) in an aqueous solution.

Step 2: Key Formula or Approach:

The part of the complex enclosed in square brackets [...] is the coordination sphere and remains intact in solution. The counter ions outside the brackets dissociate in water.

Step 3: Detailed Explanation:

Let's analyze the dissociation of each complex:

(A) $[\text{Co}(\text{NH}_3)_3(\text{NO}_2)_3] \rightarrow$ Does not dissociate. It is a neutral complex and a non-electrolyte (0:0).

(B) $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl} \rightarrow [\text{CoCl}_2(\text{NH}_3)_4]^+ + \text{Cl}^-$. Yields 2 ions. It is a 1:1 electrolyte.

(C) $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2 \rightarrow [\text{CoCl}(\text{NH}_3)_5]^{2+} + 2\text{Cl}^-$. Yields 3 ions. It is a 1:2 electrolyte.

(D) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3 \rightarrow [\text{Co}(\text{NH}_3)_6]^{3+} + 3\text{Cl}^-$. Yields 4 ions (one complex cation and three chloride anions). It perfectly matches the 1:3 electrolyte ratio.

Step 4: Final Answer:

The 1:3 electrolyte is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.

Quick Tip: The primary valency (oxidation state) governs the number of counter ions, while the secondary valency (coordination number) governs the ligands inside the brackets. Only ions outside the brackets conduct electricity.

67. The standard electrode potential (E°) for the half-cell reaction $\text{Fe}^{3+} + e^- \rightarrow \text{Fe}^{2+}$ at 298 K is (Given: $E^\circ(\text{Fe}^{3+}/\text{Fe}) = -0.04 \text{ V}$ and $E^\circ(\text{Fe}^{2+}/\text{Fe}) = -0.44 \text{ V}$ at 298 K)

(A) +0.92 V

- (B) +0.40 V
(C) +0.76 V
(D) -0.48 V

Correct Answer: (C) +0.76 V

Solution:

Step 1: Understanding the Question:

We need to find the standard electrode potential for the Fe^{3+} to Fe^{2+} reduction using the given standard reduction potentials for Fe^{3+} to Fe and Fe^{2+} to Fe .

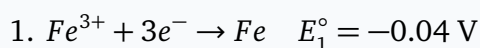
Step 2: Key Formula or Approach:

Standard electrode potentials (E°) are intensive properties and cannot be added directly. We must convert them to standard Gibbs free energy changes (ΔG°), which are extensive and additive:

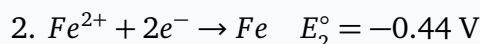
$$\Delta G^\circ = -nFE^\circ$$

Step 3: Detailed Explanation:

Write down the half-reactions and their ΔG° values:

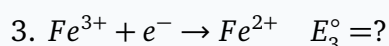


$$\Delta G_1^\circ = -3 \times F \times (-0.04) = +0.12F$$

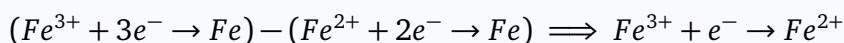


$$\Delta G_2^\circ = -2 \times F \times (-0.44) = +0.88F$$

We need the ΔG° for the target reaction:



We can obtain reaction (3) by subtracting reaction (2) from reaction (1):



Therefore, the Gibbs free energy for the target reaction is:

$$\Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$$

$$\Delta G_3^\circ = 0.12F - 0.88F = -0.76F$$

Relate ΔG_3° back to E_3° :

$$\Delta G_3^\circ = -n_3 F E_3^\circ$$

Since $n_3 = 1$ (one electron is transferred):

$$-0.76F = -1 \times F \times E_3^\circ$$

$$E_3^\circ = +0.76 \text{ V}$$

Step 4: Final Answer:

The standard electrode potential is +0.76 V.

Quick Tip: Never add or subtract E° values directly unless the number of electrons transferred in both half-reactions is exactly the same and cancel out to form a full cell reaction. Always route through ΔG° .

68. In potash alum, the ratio of K^+ and SO_4^{2-} ions is

- (A) 3:2
- (B) 1:2
- (C) 2:1
- (D) 2:3

Correct Answer: (B) 1:2

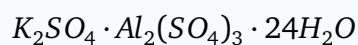
Solution:

Step 1: Understanding the Question:

We must identify the chemical formula of potash alum and determine the stoichiometric ratio of potassium ions to sulfate ions.

Step 2: Key Formula or Approach:

The chemical formula of potash alum (potassium aluminum sulfate dodecahydrate) is:



(or equivalently written as $KAl(SO_4)_2 \cdot 12H_2O$).

Step 3: Detailed Explanation:

Let's count the ions in one formula unit of $K_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$:

- Number of Potassium ions (K^+) = 2
- Number of Sulfate ions (SO_4^{2-}) = 1 (from potassium sulfate) + 3 (from aluminum sulfate) = 4 total sulfate ions.

The ratio of K^+ to SO_4^{2-} is:

$$\text{Ratio} = 2 : 4$$

Simplifying the ratio gives 1 : 2.

(If we use the simplified empirical formula $KAl(SO_4)_2 \cdot 12H_2O$, we directly see 1 K^+ and 2 SO_4^{2-} , giving the same 1:2 ratio).

Step 4: Final Answer:

The ratio of K^+ and SO_4^{2-} ions is 1:2.

Quick Tip: Alums are double salts with the general formula $M_2SO_4 \cdot M'_2(SO_4)_3 \cdot 24H_2O$, where M is a monovalent cation and M' is a trivalent cation. They completely dissociate into their constituent ions in water.

69. Consider the following statements about the solutions formed by mixing two liquids.
- A. An ideal solution thus formed obeys Raoult's law throughout the composition range.
 - B. Mixture of chloroform and acetone shows negative deviation from Raoult's law.
 - C. Mixture of aniline and phenol shows positive deviation from Raoult's law.

- (A) A and C only
- (B) A and B only
- (C) B and C only
- (D) A only

Correct Answer: (B) A and B only

Solution:

Step 1: Understanding the Question:

We need to assess the validity of three thermodynamic statements regarding the behavior of ideal and non-ideal liquid-liquid solutions.

Step 3: Detailed Explanation:

Statement A: By definition, an ideal solution rigorously obeys Raoult's law across all concentrations and temperatures. This statement is correct.

Statement B: A mixture of chloroform (CHCl_3) and acetone (CH_3COCH_3) features a strong intermolecular hydrogen bond between the polarized hydrogen of chloroform and the carbonyl oxygen of acetone. Because A-B interactions are stronger than A-A and B-B interactions, the escaping tendency of molecules decreases, causing a negative deviation from Raoult's law. This statement is correct.

Statement C: A mixture of aniline and phenol forms very strong intermolecular hydrogen bonds between the amine and hydroxyl groups. Similarly, since the A-B attractive forces are stronger than the pure A-A and B-B forces, it exhibits a **negative** deviation from Raoult's law, not positive. This statement is incorrect.

Step 4: Final Answer:

Statements A and B only are correct.

Quick Tip: Positive deviation occurs when newly formed interactions are *weaker* (e.g., ethanol + acetone). Negative deviation occurs when interactions are *stronger* (e.g., acid + water, or any combination prone to strong H-bonding).

70. For a salt XY, which is a strong electrolyte, the plot of Λ_m versus $\sqrt{c}$ has a slope of $-90.0 \text{ S cm}^2 \text{ mol}^{-3/2} \text{ L}^{1/2}$ at 298 K. At 0.01 M concentration of XY, the value of Λ_m is $145.0 \text{ S cm}^2 \text{ mol}^{-1}$. The limiting molar conductivity of Y^- ion ($\lambda_{Y^-}^\circ$, in $\text{S cm}^2 \text{ mol}^{-1}$) at 298 K will be (Given: $\lambda_{X^+}^\circ = 74.0 \text{ S cm}^2 \text{ mol}^{-1}$)

- (A) 76.0
- (B) 80.0
- (C) 100.0
- (D) 90.0

Correct Answer: (B) 80.0

Solution:

Step 1: Understanding the Question:

We need to calculate the limiting molar conductivity of the anion Y^- using the Debye-Hückel-Onsager equation and Kohlrausch's law of independent migration of ions.

Step 2: Key Formula or Approach:

For a strong electrolyte, the variation of molar conductivity with concentration is:

$$\Lambda_m = \Lambda_m^\circ - A\sqrt{c}$$

where Λ_m° is the limiting molar conductivity, and $-A$ is the slope of the plot.

Kohlrausch's law states:

$$\Lambda_m^\circ(XY) = \lambda_{X^+}^\circ + \lambda_{Y^-}^\circ$$

Step 3: Detailed Explanation:

From the given data:

$$\text{Slope } -A = -90.0 \implies A = 90.0$$

$$\text{Concentration } c = 0.01 \text{ M} \implies \sqrt{c} = \sqrt{0.01} = 0.1$$

$$\text{Molar conductivity } \Lambda_m = 145.0 \text{ S cm}^2 \text{ mol}^{-1}$$

Plug these values into the Debye-Hückel-Onsager equation to find Λ_m° :

$$145.0 = \Lambda_m^\circ - (90.0 \times 0.1)$$

$$145.0 = \Lambda_m^\circ - 9.0$$

$$\Lambda_m^\circ = 145.0 + 9.0 = 154.0 \text{ S cm}^2 \text{ mol}^{-1}$$

Now, apply Kohlrausch's law to find $\lambda_{Y^-}^\circ$:

$$\Lambda_m^\circ(XY) = \lambda_{X^+}^\circ + \lambda_{Y^-}^\circ$$

$$154.0 = 74.0 + \lambda_{Y^-}^\circ$$

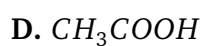
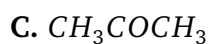
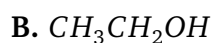
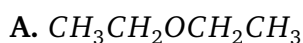
$$\lambda_{Y^-}^\circ = 154.0 - 74.0 = 80.0 \text{ S cm}^2 \text{ mol}^{-1}$$

Step 4: Final Answer:

The limiting molar conductivity of the Y^- ion is 80.0.

Quick Tip: The slope A depends on the type of electrolyte (e.g., 1-1, 2-1) and the solvent properties. Always double-check if you need to subtract or add the $A\sqrt{c}$ term; since conductivity drops as concentration rises, Λ_m° must be strictly greater than Λ_m .

71. Arrange the following compounds in the increasing order of polarity



Choose the correct answer from the options given below.

(A) $A < C < B < D$

(B) $A < B < C < D$

(C) $C < A < D < B$

(D) $C < A < B < D$

Correct Answer: (A) $A < C < B < D$

Solution:

Step 1: Understanding the Question:

We are asked to rank four organic compounds (an ether, an alcohol, a ketone, and a carboxylic acid) based on their relative polarities.

Step 2: Key Formula or Approach:

Solvent polarity is determined by the presence and strength of dipole moments and the ability to engage in hydrogen bonding.

Order of functional group polarity: Alkanes < Ethers < Esters < Ketones/Aldehydes < Alcohols < Carboxylic acids.

Step 3: Detailed Explanation:

- **A (Diethyl ether):** Has a small net dipole moment due to the bent $C - O - C$ bond but cannot donate hydrogen bonds. It is the least polar.
- **C (Acetone):** Has a strong, highly polarized $C = O$ double bond, giving it a high dipole moment, making it more polar than ethers but less polar than H-bonding solvents.
- **B (Ethanol):** Has an $-OH$ group, which provides a strong dipole and allows it to act as both a strong hydrogen bond donor and acceptor, making it highly polar.
- **D (Acetic acid):** Contains both a $C = O$ group and an $-OH$ group. It forms exceptionally strong dimeric hydrogen bonds and has the highest dielectric interaction capacity among the listed compounds. It is the most polar.

The increasing order of polarity is: Ether (A) < Ketone (C) < Alcohol (B) < Acid (D).

Step 4: Final Answer:

The correct sequence is $A < C < B < D$.

Quick Tip: In chromatography (like TLC), this exact polarity sequence determines the R_f value. Non-polar substances elute faster (high R_f), while carboxylic acids stick strongly to silica gel (low R_f).

72. According to crystal field theory, the correct order of ligands with respect to their decreas-

ing order of field strength is

- (A) $Cl^- > NH_3 > H_2O > CO$
- (B) $CO > NH_3 > H_2O > Cl^-$
- (C) $CO > H_2O > NH_3 > Cl^-$
- (D) $Cl^- > H_2O > NH_3 > CO$

Correct Answer: (B) $CO > NH_3 > H_2O > Cl^-$

Solution:

Step 1: Understanding the Question:

The question asks for the correct decreasing order of ligand field strength (crystal field splitting energy, Δ_o) according to the spectrochemical series.

Step 2: Key Formula or Approach:

The spectrochemical series arranges ligands in order of increasing crystal field splitting. A simplified order from weak field to strong field is:

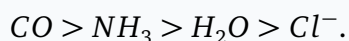
Halides (e.g., I^- , Br^- , Cl^- , F^-) < Oxygen donors (e.g., OH^- , H_2O , ox^{2-}) < Nitrogen donors (e.g., NH_3 , en) < Carbon donors (e.g., CN^- , CO).

Step 3: Detailed Explanation:

Comparing the given ligands:

- CO (Carbon monoxide) is a strong π -acceptor ligand and sits at the very top of the spectrochemical series.
- NH_3 (Ammonia) is a strong σ -donor nitrogen ligand, forming intermediate to strong fields.
- H_2O (Water) is a typical oxygen donor and acts as a weak field ligand.
- Cl^- (Chloride) is a π -donor halide and exhibits a very weak field.

Arranging them in decreasing order (strongest to weakest):



Step 4: Final Answer:

The correct sequence is $CO > NH_3 > H_2O > Cl^-$.

Quick Tip: An easy rule of thumb for ligand strength based on the donor atom: $C > N > O > \text{Halogens}$.

73. The amino acid that gives a red-blood colour on treating its sodium fusion extract with sodium nitroprusside is

- (A) serine
- (B) leucine
- (C) threonine
- (D) methionine

Correct Answer: (D) methionine

Solution:

Step 1: Understanding the Question:

We need to identify the amino acid that produces a red/violet/blood-red coloration in the sodium nitroprusside test, which is a qualitative laboratory test for a specific element.

Step 2: Key Formula or Approach:

The sodium nitroprusside test ($\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}]$) is the definitive test for the presence of **Sulphur** in organic compounds. During sodium fusion, the sulfur is converted to sodium sulfide (Na_2S).

Addition of sodium nitroprusside to the extract yields a deep purple or blood-red complex: $[\text{Fe}(\text{CN})_5\text{NOS}]^{4-}$.

Step 3: Detailed Explanation:

We must identify which of the provided amino acids contains a sulfur atom in its side chain.

- **Serine:** Contains a hydroxyl group ($-\text{OH}$).
- **Leucine:** Contains an isobutyl alkyl chain.
- **Threonine:** Contains a secondary hydroxyl group.
- **Methionine:** Contains a thioether group ($-\text{CH}_2 - \text{CH}_2 - \text{S} - \text{CH}_3$).

Since methionine is the only sulfur-containing amino acid among the choices, it will form sodium sulfide in the Lassaigne's extract and give a positive nitroprusside test.

Step 4: Final Answer:

Methionine gives the red-blood colour.

Quick Tip: The only two standard amino acids that contain sulfur are Methionine and Cysteine. If a question mentions a positive test for sulfur (nitroprusside or lead acetate), look for one of these two!

74. In an acidic medium, 10 mL of 0.25 M oxalic acid is titrated with $KMnO_4$ solution. If the volume of $KMnO_4$ solution required to reach end point is 10 mL, the strength of the $KMnO_4$ solution is

- (A) 0.15 M
- (B) 0.10 M
- (C) 0.20 M
- (D) 0.25 M

Correct Answer: (B) 0.10 M

Solution:

Step 1: Understanding the Question:

A standard redox titration between potassium permanganate ($KMnO_4$) and oxalic acid ($H_2C_2O_4$) in acidic medium. We need to find the molarity of the $KMnO_4$ solution.

Step 2: Key Formula or Approach:

At the equivalence point, the equivalents of the oxidizing agent equal the equivalents of the reducing agent:

$$N_1 V_1 = N_2 V_2$$

Normality (N) is related to Molarity (M) by the n-factor: $N = M \times \text{n-factor}$.

Step 3: Detailed Explanation:

Determine the n-factors for both reactants in an acidic medium:

1. **Potassium Permanganate ($KMnO_4$):** Mn goes from +7 to +2. The change in oxidation state is 5.

$$\text{n-factor}_1 = 5.$$

2. **Oxalic Acid ($H_2C_2O_4$):** Carbon goes from +3 to +4 (in CO_2). Since there are 2 carbon atoms per molecule, the total change is $2 \times 1 = 2$.

$$\text{n-factor}_2 = 2.$$

Apply the equivalence equation:

$$(M_1 \times \text{n-factor}_1) \times V_1 = (M_2 \times \text{n-factor}_2) \times V_2$$

$$(M_1 \times 5) \times 10 \text{ mL} = (0.25 \text{ M} \times 2) \times 10 \text{ mL}$$

Cancel the 10 mL from both sides:

$$5M_1 = 0.50$$

$$M_1 = \frac{0.50}{5} = 0.10 \text{ M}$$

Step 4: Final Answer:

The strength of the $KMnO_4$ solution is 0.10 M.

Quick Tip: Permanganate titration n-factors to memorize: Acidic medium = 5 (Mn^{2+}), Neutral/faintly alkaline = 3 (MnO_2), Strongly alkaline = 1 (MnO_4^{2-}).

75. The correct statement is

- (A) Aluminium has five valence orbitals.
- (B) Boron has a maximum covalency of four.
- (C) Beryllium has three valence orbitals.

(D) Magnesium has a maximum covalency of four.

Correct Answer: (B) Boron has a maximum covalency of four.

Solution:

Step 1: Understanding the Question:

Evaluate statements regarding the valence orbitals and maximum covalency (maximum number of covalent bonds) of various s and p-block elements.

Step 3: Detailed Explanation:

Let's verify each option:

(A) Aluminium (Period 3) has valence orbitals 3s, 3p, and 3d. This provides $1(s) + 3(p) + 5(d) = 9$ valence orbitals. Not five. (Incorrect)

(B) Boron (Period 2) has a valence shell electron configuration of $2s^2 2p^1$. Because it belongs to the second period, it lacks vacant d-orbitals. The maximum number of orbitals available for bonding is four (one 2s and three 2p orbitals). Thus, it can form a maximum of 4 covalent bonds (e.g., BF_4^-). (Correct)

(C) Beryllium (Period 2) has valence orbitals 2s and 2p. Similar to Boron, it has a total of 4 valence orbitals, not three. (Incorrect)

(D) Magnesium (Period 3) has empty 3d orbitals available. Therefore, it can expand its octet and achieve a covalency greater than four (typically up to 6, as seen in complex ions like $[Mg(H_2O)_6]^{2+}$). (Incorrect)

Step 4: Final Answer:

The correct statement is (B).

Quick Tip: Elements of the 2nd period (Li to Ne) are strictly restricted to a maximum covalency of 4 because they do not have accessible d-orbitals to expand their octet.

76. Among the following, the compound having conjugated double bonds is

(A) hepta-1,6-diene

- (B) hepta-1,3-diene
(C) hepta-1,4-diene
(D) hepta-1,5-diene

Correct Answer: (B) hepta-1,3-diene

Solution:

Step 1: Understanding the Question:

We need to identify the diene where the two carbon-carbon double bonds are conjugated.

Step 2: Key Formula or Approach:

Conjugation occurs when double bonds are separated by exactly one single bond, creating an alternating pattern ($C = C - C = C$). If they are separated by two or more single bonds, they are termed "isolated."

Step 3: Detailed Explanation:

Let's draw the skeleton for each isomer:

- (A) hepta-1,6-diene: $C = C - C - C - C - C = C$ (separated by 3 single bonds; isolated)
- (B) hepta-1,3-diene: $C = C - C = C - C - C - C$ (separated by exactly 1 single bond; **conjugated**)
- (C) hepta-1,4-diene: $C = C - C - C = C - C - C$ (separated by 2 single bonds; isolated)
- (D) hepta-1,5-diene: $C = C - C - C - C = C - C$ (separated by 3 single bonds; isolated)

Step 4: Final Answer:

The compound with conjugated double bonds is hepta-1,3-diene.

Quick Tip: For any diene named *alk-x,y-diene*, it is conjugated if and only if $y = x + 2$.

77. $2A \rightarrow B$ is a zero-order reaction, where $k = 1.0 \text{ mol L}^{-1} \text{ min}^{-1}$. If the initial concentration of A is 2 M, then the time taken to complete 75% of the reaction will be

- (A) 2.0 min

- (B) 1.5 min
(C) 0.75 min
(D) 1.0 min

Correct Answer: (B) 1.5 min

Solution:

Step 1: Understanding the Question:

Calculate the time required for a zero-order reaction to reach 75% completion.

Step 2: Key Formula or Approach:

The integrated rate equation for a zero-order reaction (following typical textbook conventions where k directly represents the rate of reactant consumption) is:

$$[A]_t = [A]_0 - kt$$

Where $[A]_0$ is the initial concentration, and $[A]_t$ is the concentration remaining at time t .

Step 3: Detailed Explanation:

Given:

Initial concentration, $[A]_0 = 2 \text{ M}$

Rate constant, $k = 1.0 \text{ mol L}^{-1} \text{ min}^{-1}$

The reaction is 75% complete. This means 75% of A has been consumed.

Amount of A consumed $= 0.75 \times 2 \text{ M} = 1.5 \text{ M}$

Remaining concentration of A, $[A]_t = 2.0 - 1.5 = 0.5 \text{ M}$

Substitute into the rate equation:

$$0.5 = 2.0 - 1.0 \times t$$

$$1.0 \times t = 2.0 - 0.5$$

$$t = 1.5 \text{ min}$$

Step 4: Final Answer:

The time taken is 1.5 min.

Quick Tip: For a zero-order reaction, the time for completion is directly proportional to the percentage reacted. If 100% reaction takes time $t_{100} = [A]_0/k$, then 75% completion takes exactly $0.75 \times t_{100}$. Here, $t_{100} = 2/1 = 2$ min. $0.75 \times 2 = 1.5$ min.

78. The correct order of solubility of the given salts in water at 298 K is

Salt	K_{sp} at 298 K
$AgBr$	5.0×10^{-13}
$Zn(OH)_2$	1.0×10^{-15}
Hg_2Cl_2	1.3×10^{-18}

- (A) $Zn(OH)_2 > AgBr > Hg_2Cl_2$
(B) $Hg_2Cl_2 > Zn(OH)_2 > AgBr$
(C) $AgBr > Zn(OH)_2 > Hg_2Cl_2$
(D) $Hg_2Cl_2 > AgBr > Zn(OH)_2$

Correct Answer: (A) $Zn(OH)_2 > AgBr > Hg_2Cl_2$

Solution:**Step 1: Understanding the Question:**

We must calculate and compare the molar solubility (s) for three sparingly soluble salts using their provided K_{sp} values.

Step 2: Key Formula or Approach:

The relationship between K_{sp} and molar solubility (s) depends on the stoichiometry of the salt:

- For a 1:1 salt (AB): $K_{sp} = s^2 \implies s = \sqrt{K_{sp}}$
- For a 1:2 salt (AB_2): $K_{sp} = (s)(2s)^2 = 4s^3 \implies s = \sqrt[3]{K_{sp}/4}$
- For Hg_2Cl_2 , the mercury(I) cation is a diatomic ion $[Hg_2]^{2+}$. It dissociates as $Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$, giving 3 ions total. $K_{sp} = (s)(2s)^2 = 4s^3 \implies s = \sqrt[3]{K_{sp}/4}$

Step 3: Detailed Explanation:

1. $AgBr$ (1:1 salt):

$$s = \sqrt{5.0 \times 10^{-13}} = \sqrt{0.5 \times 10^{-12}} \approx 0.707 \times 10^{-6} = 7.1 \times 10^{-7} \text{ M}$$

2. $Zn(OH)_2$ (1:2 salt):

$$4s^3 = 1.0 \times 10^{-15} \implies s^3 = 0.25 \times 10^{-15} = 250 \times 10^{-18}$$

$$s = \sqrt[3]{250} \times 10^{-6} \approx 6.3 \times 10^{-6} \text{ M}$$

3. Hg_2Cl_2 (1:2 salt type behavior):

$$4s^3 = 1.3 \times 10^{-18} \implies s^3 = 0.325 \times 10^{-18}$$

$$s = \sqrt[3]{0.325} \times 10^{-6} \approx 0.69 \times 10^{-6} = 6.9 \times 10^{-7} \text{ M}$$

Comparing the molar solubilities:

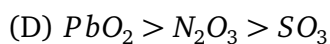
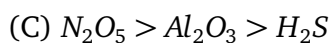
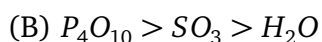
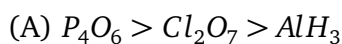
$$Zn(OH)_2 (6.3 \times 10^{-6}) > AgBr (7.1 \times 10^{-7}) > Hg_2Cl_2 (6.9 \times 10^{-7}).$$

Step 4: Final Answer:

The correct order is $Zn(OH)_2 > AgBr > Hg_2Cl_2$.

Quick Tip: Never compare K_{sp} values directly unless the salts have the exact same ion ratio (e.g., both 1:1). A salt with a smaller K_{sp} can be more soluble if it produces more ions upon dissociation!

79. The correct decreasing order of oxidation state of the underlined atom in each molecule is



Correct Answer: (C) $N_2O_5 > Al_2O_3 > H_2S$

Solution:

Step 1: Understanding the Question:

We need to calculate the oxidation state of the first (primary) atom in each given molecule and identify the option where the sequence is strictly decreasing.

Step 2: Key Formula or Approach:

Sum of all oxidation states in a neutral molecule equals zero. Standard states: Oxygen is usually -2, Hydrogen is usually +1 (but -1 with metals).

Step 3: Detailed Explanation:

Let's evaluate the oxidation states for the central atoms in each option:

(A) $P_4O_6 \rightarrow P = +3$; $Cl_2O_7 \rightarrow Cl = +7$; $AlH_3 \rightarrow Al = +3$. Order: +3, +7, +3. (Not decreasing)

(B) $P_4O_{10} \rightarrow P = +5$; $SO_3 \rightarrow S = +6$; $H_2O \rightarrow H = +1$. Order: +5, +6, +1. (Not decreasing)

(C) $N_2O_5 \rightarrow N = +5$; $Al_2O_3 \rightarrow Al = +3$; $H_2S \rightarrow S = -2$. Order: +5, +3, -2. (**Strictly decreasing**)

(D) $PbO_2 \rightarrow Pb = +4$; $N_2O_3 \rightarrow N = +3$; $SO_3 \rightarrow S = +6$. Order: +4, +3, +6. (Not decreasing)

Step 4: Final Answer:

The correct option is $N_2O_5 > Al_2O_3 > H_2S$.

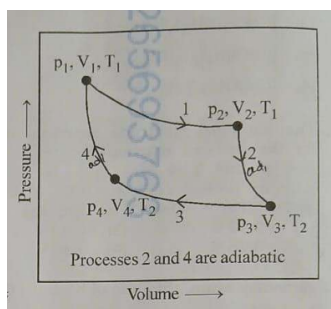
Quick Tip: Hydrogen is +1 when bonded to nonmetals (like Sulfur in H_2S) and -1 when bonded to active metals or metalloids acting as metals (like Al in AlH_3).

80. Consider the reversible processes for 1.0 mol of an ideal gas as shown in the figure.

w_1 , w_2 , w_3 and w_4 represent work done (in calories) in the processes 1, 2, 3 and 4, respectively;

ΔU_2 and ΔU_4 are changes in the internal energy for the processes 2 and 4, respectively.

use $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$



The correct option is

- (A) $w_1 + w_2 + w_3 + w_4 = 0$
- (B) $w_1 + w_3 = -2T_1 \ln \frac{V_2}{V_1} - 2T_2 \ln \frac{V_4}{V_3}$
- (C) $w_2 + w_4 = \Delta U_2 - \Delta U_4$
- (D) $w_1 + w_2 = 2T_1 \ln \frac{V_2}{V_1}$

Correct Answer: (B) $w_1 + w_3 = -2T_1 \ln \frac{V_2}{V_1} - 2T_2 \ln \frac{V_4}{V_3}$

Solution:

Step 1: Understanding the Question:

The graph represents a standard Carnot cycle consisting of two isothermal processes (1 and 3) and two adiabatic processes (2 and 4). We need to identify the correct thermodynamic expression for the work done.

Step 2: Key Formula or Approach:

Using the standard chemistry convention (Work done **on** the system):

- For an isothermal reversible process: $w = -nRT \ln(V_f/V_i)$
- For an adiabatic process: $q = 0$, so by the first law, $w = \Delta U$.

Step 3: Detailed Explanation:

Given $n = 1.0 \text{ mol}$ and $R = 2 \text{ cal K}^{-1} \text{ mol}^{-1}$:

- **Process 1 (Isothermal expansion from V_1 to V_2 at T_1):**

$$w_1 = -nRT_1 \ln\left(\frac{V_2}{V_1}\right) = -2T_1 \ln\left(\frac{V_2}{V_1}\right)$$

- **Process 3 (Isothermal compression from V_3 to V_4 at T_2):**

$$w_3 = -nRT_2 \ln\left(\frac{V_4}{V_3}\right) = -2T_2 \ln\left(\frac{V_4}{V_3}\right)$$

Adding w_1 and w_3 together gives:

$$w_1 + w_3 = -2T_1 \ln\left(\frac{V_2}{V_1}\right) - 2T_2 \ln\left(\frac{V_4}{V_3}\right)$$

This matches Option (B) exactly.

Let's briefly check the others:

(A) The net work in a cyclic cycle is the area inside the curve, which is non-zero.

(C) Since $w = \Delta U$ for adiabatic steps, $w_2 + w_4 = \Delta U_2 + \Delta U_4$, not a subtraction.

(D) Does not mathematically conform to any single thermodynamic combination of steps 1 and 2.

Step 4: Final Answer:

The correct equation is $w_1 + w_3 = -2T_1 \ln \frac{V_2}{V_1} - 2T_2 \ln \frac{V_4}{V_3}$.

Quick Tip: Always check the sign convention! In chemistry, expansion work is negative because the system loses energy doing work on the surroundings. In physics, expansion work is often defined as positive.

81. Assertion A : For an ideal solution formed by mixing liquids P and Q, $\Delta_{mix}H = 0$ and $\Delta_{mix}V = 0$

Reason R : No interactions occur between P and Q

In the light of the above statements, choose the *most appropriate* answer from the options given below.

(A) A is not correct but R is correct

(B) Both A and R are correct and R is the correct explanation of A

(C) Both A and R are correct but R is NOT the correct explanation of A

(D) A is correct but R is not correct

Correct Answer: (D) A is correct but R is not correct

Solution:

Step 1: Understanding the Question:

We must evaluate the truth of an Assertion regarding the thermodynamic properties of ideal solutions, and a Reason proposing the molecular cause of this behavior.

Step 2: Detailed Explanation:

Assertion A: For an ideal liquid-liquid solution, there is no enthalpy change upon mixing ($\Delta_{mix}H = 0$) and no change in total volume upon mixing ($\Delta_{mix}V = 0$). This is the fundamental thermodynamic definition of an ideal solution. The Assertion is **correct**.

Reason R: The requirement for an ideal solution is *not* that "no interactions occur." Liquids exist precisely because of strong intermolecular forces. An ideal solution forms when the intermolecular interactions between unlike molecules (P-Q) are exactly identical in strength and nature to the interactions between like molecules (P-P and Q-Q). Because the interactions are identical, there is no net energy change or volume change. The claim that "no interactions occur" is physically absurd for liquid mixtures. The Reason is **incorrect**.

Step 4: Final Answer:

Assertion A is correct but Reason R is not correct.

Quick Tip: An ideal gas implies no intermolecular interactions. An ideal solution implies *perfectly uniform* intermolecular interactions ($P-P \approx Q-Q \approx P-Q$). Do not confuse the two definitions!

82. Among the species given below, the spin-only magnetic moment is highest for
(Given : Atomic number of Ti = 22, Mn = 25, Fe = 26 and Co = 27)

- (A) $[Ti(H_2O)_6]^{3+}$
- (B) $[Mn(CN)_6]^{3-}$
- (C) $[Fe(CN)_6]^{3-}$
- (D) $[Co(NH_3)_6]^{3+}$

Correct Answer: (B) $[Mn(CN)_6]^{3-}$

Solution:

Step 1: Understanding the Question:

The question asks to identify the coordination complex with the highest spin-only magnetic moment. The magnetic moment depends on the number of unpaired electrons in the central metal ion's d-orbitals.

Step 2: Key Formula or Approach:

The spin-only magnetic moment is calculated using the formula:

$$\mu = \sqrt{n(n+2)} \text{ B.M.}$$

where n is the number of unpaired electrons. A higher number of unpaired electrons results in a higher magnetic moment. We need to determine the oxidation state, the d-electron configuration, and the effect of the ligand field (strong vs. weak) for each complex.

Step 3: Detailed Explanation:

Let's analyze each complex: 1. $[Ti(H_2O)_6]^{3+}$: Titanium oxidation state = +3. Electronic configuration of Ti ($Z=22$) is $[Ar]3d^24s^2$. For Ti^{3+} , it is $[Ar]3d^1$. Number of unpaired electrons, $n = 1$.

2. $[Mn(CN)_6]^{3-}$: Manganese oxidation state = +3. Electronic configuration of Mn ($Z=25$) is $[Ar]3d^54s^2$. For Mn^{3+} , it is $[Ar]3d^4$. CN^- is a strong field ligand, so pairing occurs. The t_{2g} level fills first: $t_{2g}^4e_g^0$. Number of unpaired electrons, $n = 2$.

3. $[Fe(CN)_6]^{3-}$: Iron oxidation state = +3. Electronic configuration of Fe ($Z=26$) is $[Ar]3d^64s^2$. For Fe^{3+} , it is $[Ar]3d^5$. CN^- is a strong field ligand, causing pairing: $t_{2g}^5e_g^0$. Number of unpaired electrons, $n = 1$.

4. $[Co(NH_3)_6]^{3+}$: Cobalt oxidation state = +3. Electronic configuration of Co ($Z=27$) is $[Ar]3d^74s^2$. For Co^{3+} , it is $[Ar]3d^6$. NH_3 acts as a strong field ligand for Co^{3+} , causing complete pairing: $t_{2g}^6e_g^0$. Number of unpaired electrons, $n = 0$.

The highest number of unpaired electrons is $n = 2$ for $[Mn(CN)_6]^{3-}$.

Step 3: Final Answer:

The complex with the highest spin-only magnetic moment is $[Mn(CN)_6]^{3-}$.

Quick Tip: Always remember that NH_3 acts as a strong field ligand for Co^{3+} (resulting in a diamagnetic low-spin complex), even though it is generally a moderate field ligand for other +2 transition metals.

83. A protein undergoes reversible thermal denaturation from its initial state N to denatured state D according to $N \rightleftharpoons D$. At $60^\circ C$, the concentrations of both N and D are equal at equilibrium, and the standard enthalpy change of denaturation is 666 kJ mol^{-1} . The standard entropy change (ΔS° in $\text{kJ K}^{-1} \text{mol}^{-1}$) of the protein upon denaturation at $60^\circ C$ is closest to

- (A) 11.1
- (B) 2.0
- (C) 2000.0
- (D) 333.0

Correct Answer: (B) 2.0

Solution:

Step 1: Understanding the Question:

We are given a reversible protein denaturation process at equilibrium. We have the temperature, the standard enthalpy change, and the condition that the concentrations of the reactant and product are equal. We need to find the standard entropy change (ΔS°).

Step 2: Key Formula or Approach:

At equilibrium, the equilibrium constant $K = \frac{[D]}{[N]}$. Since concentrations are equal, $K = 1$. The standard Gibbs free energy change is related to K by:

$$\Delta G^\circ = -RT \ln K$$

Since $K = 1$, $\ln(1) = 0$, which means $\Delta G^\circ = 0$. The fundamental thermodynamic equation is:

$$\Delta G^\circ = \Delta H^\circ - T \Delta S^\circ$$

Setting $\Delta G^\circ = 0$ gives:

$$\Delta S^\circ = \frac{\Delta H^\circ}{T}$$

Step 3: Detailed Explanation:

Given: Temperature, $T = 60^\circ\text{C} = 60 + 273 = 333\text{ K}$ Standard enthalpy change, $\Delta H^\circ = 666\text{ kJ mol}^{-1}$

Substitute these values into the derived equation:

$$\Delta S^\circ = \frac{666\text{ kJ mol}^{-1}}{333\text{ K}}$$

$$\Delta S^\circ = 2.0\text{ kJ K}^{-1}\text{mol}^{-1}$$

Step 4: Final Answer:

The standard entropy change is $2.0\text{ kJ K}^{-1}\text{mol}^{-1}$.

Quick Tip: Whenever a reversible process is at equilibrium with equal concentrations of reactants and products, the standard free energy change ΔG° is exactly zero. This allows for direct calculation of ΔS° from ΔH° and T .

84. Given below are two statements : One is labelled as Assertion A and the other is labelled as Reason R.

Assertion A : Generally, $3d$ transition metals have high melting points.

Reason R : Involvement of $3d$ -electrons in addition to $4s$ -electrons in the interatomic metallic bonding.

In light of the above statements, choose the *most appropriate* answer from the options given below:

(A) A is not correct but R is correct.

(B) Both A and R are correct and R is the correct explanation of A.

- (C) Both A and R are correct and R is NOT the correct explanation of A.
(D) A is correct but R is not correct.

Correct Answer: (B) Both A and R are correct and R is the correct explanation of A.

Solution:

Step 1: Understanding the Question:

The question tests the conceptual understanding of the physical properties of transition metals, specifically their melting points, and the underlying atomic reasons for these properties.

Step 2: Detailed Explanation:

Assertion A: Transition metals are characterized by high melting and boiling points. This is a well-established factual statement. Thus, the Assertion is correct.

Reason R: The high melting points of transition metals are attributed to strong metallic bonding. This strong bonding arises because both the ns electrons (e.g., $4s$) and the unpaired $(n-1)d$ electrons (e.g., $3d$) are available to participate in the delocalized sea of electrons forming the metallic lattice. The greater the number of valence electrons contributed, the stronger the metallic bond, and the higher the melting point. Thus, the Reason is correct and it is the exact scientific explanation for the Assertion.

Step 3: Final Answer:

Both A and R are correct and R is the correct explanation of A.

Quick Tip: The strength of metallic bonding in transition metals roughly scales with the number of unpaired d-electrons. This is why elements near the middle of the d-block (like Cr, Mo, W) have the highest melting points in their respective series.

85. Given below are two statements : One is labelled as Assertion A and the other is labelled as Reason R.

Assertion A : The first ionization enthalpy of O is lower than that of N and F.

Reason R : The loss of an electron from O leads to stable half-filled p orbital.

In light of the above statements, choose the *most appropriate* answer from the options given

below:

- (A) A is not correct but R is correct.
- (B) Both A and R are correct and R is the correct explanation of A.
- (C) Both A and R are correct and R is NOT the correct explanation of A.
- (D) A is correct but R is not correct.

Correct Answer: (C) Both A and R are correct and R is NOT the correct explanation of A.

Solution:

Step 1: Understanding the Question:

We need to evaluate an assertion about the first ionization enthalpy trend among N, O, and F, and assess if the given reason correctly explains the entire assertion.

Step 2: Detailed Explanation:

Assertion A: The first ionization enthalpy of Oxygen (1314 kJ/mol) is indeed lower than that of Nitrogen (1402 kJ/mol) and Fluorine (1681 kJ/mol). The assertion is physically correct.

Reason R: The electronic configuration of Oxygen is $[He]2s^22p^4$. Losing one electron produces the O^+ ion with a $[He]2s^22p^3$ configuration. This resulting $2p^3$ state is exactly half-filled, which is unusually stable. Additionally, the paired electrons in the $2p^4$ configuration of oxygen experience inter-electronic repulsion, facilitating easier removal. Thus, the Reason is factually correct.

Evaluating the Link: While Reason R perfectly explains why Oxygen's ionization enthalpy is lower than Nitrogen's (anomalous trend), it does **not** explain why Oxygen's ionization enthalpy is lower than Fluorine's. Oxygen is lower than Fluorine primarily due to Fluorine's higher effective nuclear charge (Z_{eff}) and smaller atomic radius (the normal periodic trend). Because the reason provided only accounts for half of the phenomenon described in the assertion, it is typically considered NOT the complete or correct explanation for the assertion as a whole.

Step 3: Final Answer:

Both A and R are correct but R is NOT the correct explanation of A.

Quick Tip: In assertion-reason questions, if the reason only explains part of the assertion (e.g., explaining $O < N$ but ignoring $O < F$), it is classified as "NOT the correct explanation". The reason must cover the entire scope of the assertion.

86. Consider the following reaction sequences and choose the correct option.
Reaction Scheme:

Center: $Ph - C \equiv C - Me$

Left path: $\xrightarrow{Na/liq.NH_3} L \xrightarrow{HBr, benzoyl\ peroxide} N$

Right path: $\xrightarrow{H_2, Pd/C\ (Lindlar's\ Catalyst)} K \xrightarrow{HBr} M$

- (A) M and N are stereoisomers
- (B) K and L are geometrical isomers
- (C) K and L are enantiomers
- (D) M and N are geometrical isomers

Correct Answer: (B) K and L are geometrical isomers

Solution:

Step 1: Understanding the Question:

An internal alkyne undergoes partial reduction via two different methods to yield two alkenes (K and L). These alkenes subsequently undergo hydrobromination under different conditions to yield alkyl bromides (M and N). We must identify the structural relationship between the products.

Step 2: Detailed Explanation:

Formation of K and L:

- **Right Path (to K):** Reduction with H_2 over Lindlar's catalyst (Pd/C poisoned) undergoes syn-addition, yielding the *cis*-alkene. Product **K** is ***cis*-1-phenylprop-1-ene**.
- **Left Path (to L):** Birch reduction using Na in liquid NH_3 proceeds via a radical anion mechanism, yielding the more stable *trans*-alkene. Product **L** is ***trans*-1-phenylprop-1-ene**.

Since K and L are *cis* and *trans* isomers of the same compound, they are **geometrical isomers**.

Formation of M and N: - **To M:** Addition of HBr to *cis*-1-phenylprop-1-ene follows Markovnikov's rule. The protonation occurs to form the most stable carbocation, which is the resonance-stabilized benzylic carbocation at C1. Bromide ion attacks here. Product **M** is **1-bromo-1-phenylpropane**. - **To N:** Addition of HBr to *trans*-1-phenylprop-1-ene in the presence of benzoyl peroxide proceeds via a free-radical anti-Markovnikov mechanism. The bromine radical adds to the double bond to form the most stable intermediate carbon radical. Addition at C2 leaves the radical at C1 (benzylic, highly stabilized by resonance). Product **N** is **2-bromo-1-phenylpropane**. Since M and N differ in the position of the bromine atom, they are structural (positional) isomers, not stereoisomers or geometrical isomers.

Comparing the options, statement (B) is factually correct.

Step 3: Final Answer:

K and L are geometrical isomers.

Quick Tip: Lindlar's catalyst = *Syn* addition $\rightarrow$ *Cis* alkene. Birch reduction (Na/NH_3) = *Anti* addition $\rightarrow$ *Trans* alkene. This stereochemical divergence is a staple in competitive exams!

87. The highest occupied molecular orbital for Ne_2 is

- (A) σ^{2p}
- (B) π_{2p}
- (C) σ_{2p}
- (D) π^{2p}

Correct Answer: (A) σ^{2p}

Solution:

Step 1: Understanding the Question:

We need to determine the electronic configuration of the hypothetical Ne_2 molecule using

Molecular Orbital (MO) Theory and identify its Highest Occupied Molecular Orbital (HOMO).

Step 2: Key Formula or Approach:

For homonuclear diatomic molecules with more than 14 electrons (like O_2 , F_2 , Ne_2), the filling order of molecular orbitals is: $\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < \pi_{2p_x} = \pi_{2p_y} < \pi_{2p_x}^* = \pi_{2p_y}^* < \sigma_{2p_z}^*$

Step 3: Detailed Explanation:

A single Neon atom has 10 electrons ($1s^2 2s^2 2p^6$). The diatomic molecule Ne_2 would have a total of $10 + 10 = 20$ electrons.

Let's fill the molecular orbitals with these 20 electrons: 1. σ_{1s} takes 2 2. σ_{1s}^* takes 2 3. σ_{2s} takes 2 4. σ_{2s}^* takes 2 5. σ_{2p_z} takes 2 6. π_{2p_x} and π_{2p_y} take 4 (2 each) 7. $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ take 4 (2 each) 8. $\sigma_{2p_z}^*$ takes 2

Total electrons filled = $2 + 2 + 2 + 2 + 2 + 4 + 4 + 2 = 20$. The last electrons are filled into the $\sigma_{2p_z}^*$ orbital. Therefore, this is the Highest Occupied Molecular Orbital (HOMO).

Step 4: Final Answer:

The highest occupied molecular orbital is σ_{2p}^* .

Quick Tip: Since Ne_2 has all bonding and antibonding orbitals completely filled, its bond order is exactly zero ($\frac{10-10}{2} = 0$). This is why noble gases exist as monoatomic species and do not form diatomic molecules.

88. Match the species in List I with their geometry in List II

List I	List II
A. PCl_5	I. Tetrahedral
B. BrF_5	II. Square Planar
C. BF_4^-	III. Trigonal bipyramidal
D. $[Ni(CN)_4]^{2-}$	IV. Square pyramidal

Choose the correct answer from the options given below:

- (A) A-III, B-II, C-I, D-IV
(B) A-IV, B-III, C-I, D-II

- (C) A-III, B-IV, C-I, D-II
(D) A-III, B-I, C-II, D-IV

Correct Answer: (C) A-III, B-IV, C-I, D-II

Solution:

Step 1: Understanding the Question:

We need to determine the molecular geometry of four chemical species based on VSEPR theory and Valence Bond Theory and match them with the correct shape.

Step 2: Detailed Explanation:

Let's analyze each species: **A. PCl_5 :** Phosphorus has 5 valence electrons. It forms 5 single bonds with Chlorine and has 0 lone pairs. Steric number = $5 + 0 = 5$ (sp^3d hybridization). The geometry is **Trigonal bipyramidal**. ($A \rightarrow III$) **B. BrF_5 :** Bromine has 7 valence electrons. It forms 5 single bonds with Fluorine, leaving 2 non-bonding electrons (1 lone pair). Steric number = $5 + 1 = 6$ (sp^3d^2 hybridization). The base geometry is octahedral, but with one lone pair, the molecular shape is **Square pyramidal**. ($B \rightarrow IV$) **C. BF_4^- :** Boron normally has 3 valence electrons, plus 1 for the negative charge = 4. It forms 4 single bonds with Fluorine and has 0 lone pairs. Steric number = $4 + 0 = 4$ (sp^3 hybridization). The geometry is **Tetrahedral**. ($C \rightarrow I$) **D. $[Ni(CN)_4]^{2-}$:** Nickel is in the +2 oxidation state ($3d^8$). CN^- is a strong field ligand, forcing the pairing of d-electrons and vacating one 3d orbital. This leads to dsp^2 hybridization. The geometry of dsp^2 complexes is **Square planar**. ($D \rightarrow II$)
Matching results: A-III, B-IV, C-I, D-II.

Step 3: Final Answer:

The correct option is (3) A-III, B-IV, C-I, D-II.

Quick Tip: For $3d^8$ metal complexes with coordination number 4: Strong field ligands (CN^- , CO) force pairing $\rightarrow dsp^2 \rightarrow$ Square planar. Weak field ligands (Cl^- , H_2O) don't pair $\rightarrow sp^3 \rightarrow$ Tetrahedral.

89. Match the vitamins in List I with their sources in List II

List I	List II
A. vitamin A	I. meat
B. vitamin B_{12}	II. sunflower oil
C. vitamin E	III. green leafy vegetables
D. vitamin K	IV. carrots

Choose the correct answer from the options given below.

- (A) A-III, B-I, C-IV, D-II
 (B) A-II, B-III, C-IV, D-I
 (C) A-IV, B-I, C-II, D-III
 (D) A-IV, B-II, C-I, D-III

Correct Answer: (C) A-IV, B-I, C-II, D-III

Solution:

Step 1: Understanding the Question:

The question asks to match specific vitamins to their major natural dietary sources.

Step 2: Detailed Explanation:

Let's pair each vitamin with its primary dietary source: **A. Vitamin A:** Retinol and its precursors (like beta-carotene) are highly concentrated in orange and yellow vegetables. **Carrots** are famously rich in Vitamin A. ($A \rightarrow IV$) **B. Vitamin B_{12} :** Cobalamin is naturally found almost exclusively in animal products. **Meat**, fish, and dairy are the primary sources. ($B \rightarrow I$) **C. Vitamin E:** Tocopherols are fat-soluble antioxidants primarily found in plant oils, nuts, and seeds. **Sunflower oil** is an excellent source. ($C \rightarrow II$) **D. Vitamin K:** Phylloquinone is heavily concentrated in photosynthetic plant tissues, making **green leafy vegetables** (like spinach and kale) the best source. ($D \rightarrow III$)

Matching results: A-IV, B-I, C-II, D-III.

Step 3: Final Answer:

The correct matching is A-IV, B-I, C-II, D-III.

Quick Tip: Vitamin B_{12} is unique among vitamins because it contains a metal ion (Cobalt) and is practically absent from plant-based foods, which is why vegans often require supplementation.

90. For the following reaction sequence, choose the correct option

Reaction scheme: Benzene $\xrightarrow{\text{i. } CH_3COCl, AlCl_3 \quad \text{ii. } NaOCl}$ P + Q

- (A) Both P and Q are carbonyl compounds.
(B) If P is the sodium salt of a carboxylic acid, Q is a primary alcohol.
(C) P and Q are aromatic compounds.
(D) If P gives a carboxylic acid on acidification, Q gives a poisonous gas on exposure to air and light.

Correct Answer: (D) If P gives a carboxylic acid on acidification, Q gives a poisonous gas on exposure to air and light.

Solution:

Step 1: Understanding the Question:

We need to determine the intermediate and final products of a two-step organic reaction sequence starting from benzene, and then evaluate four descriptive statements about the final products P and Q.

Step 2: Key Formula or Approach:

1. **Friedel-Crafts Acylation:** Benzene + Acetyl chloride (CH_3COCl) + Lewis acid ($AlCl_3$) yields Acetophenone ($Ph-CO-CH_3$). 2. **Haloform Reaction:** Acetophenone contains a methyl ketone group ($-CO-CH_3$). Treatment with sodium hypochlorite ($NaOCl$) undergoes the haloform reaction to yield the sodium salt of a carboxylic acid ($Ph-COONa$) and a haloform precipitate ($CHCl_3$).

Step 3: Detailed Explanation:

Step 1 product: Acetophenone. Step 2 products (P + Q): Sodium benzoate (C_6H_5COONa) and Chloroform ($CHCl_3$).

Let's evaluate the options based on these products: (A) Neither Sodium benzoate nor Chloroform is considered a standard "carbonyl compound" (ketone/aldehyde) in this context.

Chloroform certainly isn't. (False) (B) If P is sodium benzoate, Q is chloroform, which is a haloalkane, not a primary alcohol. (False) (C) Sodium benzoate is aromatic, but chloroform is aliphatic. Both are not aromatic. (False) (D) If P is sodium benzoate ($PhCOONa$), acidification yields benzoic acid ($PhCOOH$). If Q is chloroform ($CHCl_3$), exposure to oxygen and UV light oxidizes it to phosgene gas ($COCl_2$), which is highly poisonous. This perfectly matches the properties of the products. (True)

Step 4: Final Answer:

The correct statement is (4) If P gives a carboxylic acid on acidification, Q gives a poisonous gas on exposure to air and light.

Quick Tip: Chloroform is stored in dark amber bottles filled to the brim to prevent the formation of deadly phosgene gas ($2CHCl_3 + O_2 \xrightarrow{\text{light}} 2COCl_2 + 2HCl$).