

# NIOS Class 12 Chemistry Sample Paper – 9

Duration: 180 Minutes

Maximum Marks: 80

## Instructions

- This paper contains **43** Questions. The paper is divided into two sections: **Section A – 40** marks, **Section B – 40** marks.
- **Section A** consists of
  - **Q.No. 1 to 16** – Multiple Choice type questions (MCQs) carrying 1 mark each. Select and write the most appropriate option out of the four options given in each of these questions. An internal choice has been provided in some of these questions. You have to attempt only one of the given choices in such questions.
  - **Q. No. 17 to 28** – Objective type questions. Q. No. 17 to 28 carry 02 marks each (with 2 sub- parts of 1 mark each). Attempt these questions as per the instructions given for each of the questions 17 –28.
- **Section B** consists of
  - **Q.No. 29 to 37** – Very Short questions carrying 02 marks each to be answered in the range of 30 to 50 words.
  - **Q.No. 38 to 41** – Short Answer type questions carrying 03 marks each to be answered in the range of 50 to 80 words.
  - **Q.No. 42 and 43** – Long Answer type questions carrying 05 marks each to be answered in the range of 80 to 120 words.
- There is **No Negative marking**.
- Use of mobile phones, smartwatches, calculators, or any electronic gadgets is strictly prohibited.

## Section: A

**Q1.** How many molecules are present in 4.4 g of carbon dioxide? (Molar mass of  $\text{CO}_2 = 44 \text{ g mol}^{-1}$ ,  $N_A = 6.022 \times 10^{23}$ ) (1)

(A)  $6.022 \times 10^{22}$

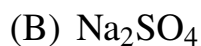


(B)  $3.011 \times 10^{23}$

(C)  $6.022 \times 10^{23}$

(D)  $1.204 \times 10^{24}$

**Q2.** A compound has the composition: Na = 32.4%, S = 22.5%, O = 45.1%. Its empirical formula is: (Atomic masses: Na = 23, S = 32, O = 16) **(1)**



**Q3.** The azimuthal quantum number for a *d*-orbital is: **(1)**

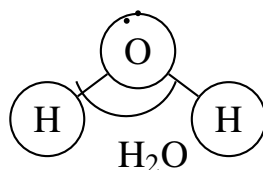
(A) 0

(B) 1

(C) 2

(D) 3

**Q4.** The bond angle in water (H<sub>2</sub>O) is approximately: **(1)**



(A) 120°

(B) 109.5°

(C) 104.5°

(D) 90°

**Q5.** A gas at 2 atm pressure and 300 K occupies 5 L. What will be its pressure if the volume is reduced to 2 L at constant temperature? **(1)**



- (A) 1 atm
- (B) 3 atm
- (C) 5 atm
- (D) 10 atm

**Q6.** The osmotic pressure of a solution increases with: (1)

- (A) Decrease in temperature
- (B) Decrease in concentration
- (C) Increase in temperature
- (D) Increase in volume of solvent

**Q7.** According to Hess's law, the enthalpy change of a reaction: (1)

- (A) Depends on the path of the reaction
- (B) Is independent of the path of the reaction
- (C) Is always positive
- (D) Cannot be measured experimentally

**Q8.** For which of the following processes is the entropy change positive? (1)

- (A) Condensation of steam
- (B) Freezing of water
- (C) Sublimation of dry ice
- (D) Deposition of iodine vapour

**Q9.** The standard electrode potential  $E^\circ$  for  $\text{Zn}^{2+}/\text{Zn}$  is  $-0.76\text{ V}$  and for  $\text{Cu}^{2+}/\text{Cu}$  is  $+0.34\text{ V}$ . The EMF of the Daniell cell is: (1)

- (A) 0.42 V
- (B) 1.10 V
- (C)  $-1.10\text{ V}$



(D)  $-0.42\text{ V}$

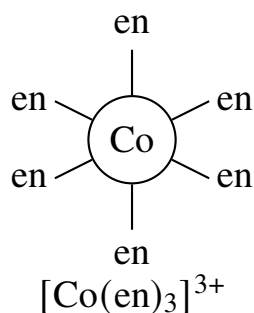
**Q10.** The half-life of a second-order reaction is: **(1)**

- (A) Independent of initial concentration
- (B) Directly proportional to initial concentration
- (C) Inversely proportional to initial concentration
- (D) Inversely proportional to the square of initial concentration

**Q11.** Which of the following oxides is amphoteric in nature? **(1)**

- (A)  $\text{Na}_2\text{O}$
- (B)  $\text{SO}_2$
- (C)  $\text{Al}_2\text{O}_3$
- (D)  $\text{P}_4\text{O}_{10}$

**Q12.** The coordination number of the central metal ion in  $[\text{Co}(\text{en})_3]^{3+}$  is: **(1)**



- (A) 3
- (B) 4
- (C) 6
- (D) 9

**Q13.** Which of the following pairs are functional group isomers? **(1)**

- (A) Propanal and propanone
- (B) Butane and 2-methylpropane



- (C) Pent-1-ene and pent-2-ene
- (D) 1-chloropropane and 2-chloropropane

**Q14.** Which reagent is used to distinguish between primary, secondary and tertiary alcohols? (1)

- (A) Tollens' reagent
- (B) Fehling's solution
- (C) Lucas reagent
- (D) Benedict's reagent

**Q15.** Deficiency of which vitamin causes scurvy? (1)

- (A) Vitamin A
- (B) Vitamin B
- (C) Vitamin C
- (D) Vitamin D

**Q16.** Terfenadine is used as a/an: (1)

- (A) Analgesic
- (B) Antihistamine
- (C) Antibiotic
- (D) Antacid

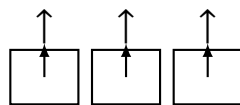
**Note:** Q. No. 17 to 28 are the objective type questions of 2 marks each.

**Q17.** Read the passage given below and answer the following questions:

The distribution of electrons in various atomic orbitals is governed by three fundamental rules: the Aufbau principle, Pauli exclusion principle and Hund's rule of maximum multiplicity. According to the Aufbau principle, electrons occupy orbitals in the order of increasing energy. Pauli's exclusion principle states that no two electrons in an atom can have the same set of four quantum



numbers. Hund’s rule states that in a set of degenerate orbitals, electrons occupy different orbitals with parallel spins before any pairing occurs. (2)



Hund’s rule: 2*p* orbitals

1. State the Pauli exclusion principle and explain why an orbital can hold a maximum of two electrons.
2. What is the electronic configuration of chromium (atomic number 24) and why is it an exception to the Aufbau principle?

**Q18.** Complete the following by using the options given below:

(bonding, antibonding, non-bonding, sigma, pi) (2)

1. In molecular orbital theory, the molecular orbital formed by constructive interference of atomic orbitals is called a ..... molecular orbital.
2. The molecular orbital formed by destructive interference has higher energy and is called an ..... molecular orbital.

**Q19.** Write TRUE (T) for the correct statement and FALSE (F) for the incorrect statement: (2)

1. The vapour pressure of a liquid increases with an increase in temperature.
2. According to Dalton’s law of partial pressures, the total pressure exerted by a mixture of non-reacting gases is equal to the difference of their individual partial pressures.

**Q20.** Complete the following by using the options given below:

(elevation of boiling point, depression of freezing point, osmotic pressure, relative lowering of vapour pressure) (2)

1. The colligative property used in the determination of molar mass of a non-volatile solute by the Beckmann method is .....



2. The phenomenon used in reverse osmosis for desalination of sea water is based on .....

**Q21.** Complete the following by using the options given below:

(anode, cathode, oxidation, reduction, electrolyte) (2)

1. In electrolysis, the process occurring at the anode is .....
2. The substance which in aqueous solution or in molten state conducts electricity and undergoes chemical decomposition is called an .....

**Q22.** Read the passage given below and answer the following questions:

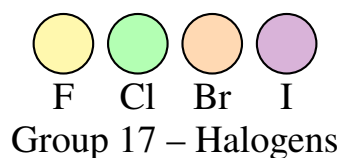
Green chemistry is the design of chemical products and processes that reduce or eliminate the use and generation of hazardous substances. The principles of green chemistry encourage the use of safer solvents, renewable feedstocks, energy-efficient processes, and biodegradable products. For example, instead of using toxic organic solvents, chemists now increasingly use water or supercritical carbon dioxide as reaction media. Catalysts are preferred over stoichiometric reagents to minimise waste. (2)

1. What is meant by green chemistry? Mention one of its important principles.
2. Why are catalysts preferred over stoichiometric reagents from a green chemistry perspective?

**Q23.** Read the passage given below and answer the following questions:

Halogens are group 17 elements with the general electronic configuration  $ns^2np^5$ . Fluorine is the most electronegative element and shows anomalous behaviour due to its very small size, high electronegativity and absence of *d*-orbitals. The halogens form interhalogen compounds of the types  $XX'$ ,  $XX'_3$ ,  $XX'_5$  and  $XX'_7$ , where X is the larger halogen. The acidic strength of hydrogen halides increases down the group:  $HF < HCl < HBr < HI$ . However, HF is the weakest acid because of strong H–F bond. (2)





1. Why does fluorine show anomalous behaviour among halogens?
2. Arrange HCl, HBr and HI in increasing order of their acidic strength.

**Q24.** Match the items given in Column I with the most appropriate items in Column II: (2)

Column I	Column II
(a) Wurtz reaction	(i) $2RX + 2Na \xrightarrow{\text{dry ether}} R - R + 2NaX$
(b) Grignard reagent preparation	(ii) $RX + Mg \xrightarrow{\text{dry ether}} RMgX$
(c) Kolbe's electrolysis	(iii) $2RCOONa + 2H_2O \xrightarrow{\text{Electrolysis}} R - R + 2CO_2 + 2NaOH + H_2$
(d) Friedel-Crafts alkylation	(iv) $C_6H_6 + RCl \xrightarrow{\text{anhyd. AlCl}_3} C_6H_5R + HCl$

**Q25.** Complete the following reaction equations: (2)

1.  $CH_3CH_2CH_2OH \xrightarrow[573\text{ K}]{Cu} +H_2$
2.  $CH_3COOH + PCl_5 \rightarrow +POCl_3 + HCl$

**Q26.** Read the passage given below and answer the following questions:

Isomerism is the phenomenon in which two or more compounds have the same molecular formula but different arrangements of atoms in space or different structural formulas. Structural isomerism includes chain isomerism, position isomerism, functional group isomerism and metamerism. Stereoisomerism includes geometrical isomerism and optical isomerism. Geometrical isomerism arises due to restricted rotation about a double bond or in a ring system. Optical isomerism arises when a molecule is chiral, i.e., non-superimposable on its mirror image. (2)



1. What is geometrical isomerism? Which of the following will show geometrical isomerism: but-1-ene or but-2-ene?
2. Define optical isomerism and state the condition necessary for a molecule to be optically active.

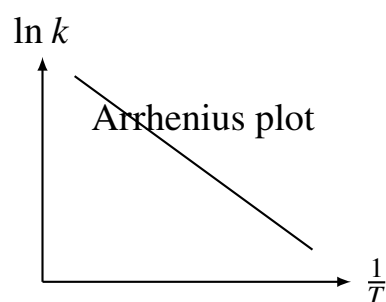
**Q27.** Write TRUE (T) for the correct statement and FALSE (F) for the incorrect statement: (2)

1. The empirical formula of benzene ( $C_6H_6$ ) is CH.
2. One mole of any gas at STP occupies exactly 22.4 litres irrespective of the nature of the gas.

**Q28.** Read the passage given below and answer the following questions:

Chemical kinetics is the study of rates of chemical reactions and the factors that influence them. The rate of a reaction is expressed as the change in concentration of a reactant or product per unit time. According to the rate law, for a reaction  $aA + bB \rightarrow$  products, the rate  $= k[A]^m[B]^n$ , where  $m$  and  $n$  are the orders with respect to A and B respectively, and  $k$  is the rate constant. The activation energy is the minimum energy required for the reacting molecules to form products. The Arrhenius equation relates the rate constant to temperature:

$$k = Ae^{-E_a/RT}. \quad (2)$$



1. Write the Arrhenius equation in its logarithmic form and indicate how activation energy can be determined from it.
2. How does an increase in temperature affect the rate constant of a reaction? Explain using the Arrhenius equation.



## Section: B

**Q29.** Define the terms 'extensive property' and 'intensive property' in thermodynamics. Give one example of each. (2)

**Q30.** Explain why evaporation of a liquid is always accompanied by an increase in entropy. (2)

**Q31.** (i) Calculate the pH of a 0.005 M  $\text{H}_2\text{SO}_4$  solution assuming complete dissociation.

**OR**

(ii) Explain the common ion effect with a suitable example. How does it affect the solubility of a sparingly soluble salt? (2)

**Q32.** (i) Write the Nernst equation for a general electrode reaction:  $\text{M}^{n+} + n\text{e}^- \rightarrow \text{M}(\text{s})$ .

**OR**

(ii) Define specific conductance and cell constant. How are they related? (2)

**Q33.** State Faraday's second law of electrolysis. If the same quantity of electricity is passed through  $\text{CuSO}_4$  and  $\text{AgNO}_3$  solutions, how will the masses of Cu and Ag deposited compare? (Atomic masses: Cu = 63.5, Ag = 108) (2)

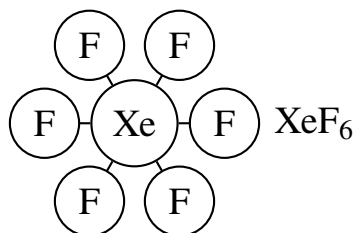
**Q34.** Derive the expression for the half-life of a first-order reaction:  $t_{1/2} = 0.693/k$ . A first-order reaction is 20% complete in 10 minutes. Calculate the rate constant. (2)

**Q35.** (i) Explain why interhalogen compounds are more reactive than halogens.

**OR**



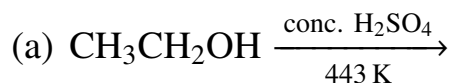
- (ii) Draw the structure of  $\text{XeF}_6$  and state its shape according to VSEPR theory. (2)



**Q36.** How will you convert the following?

- (i) Propene to propan-2-ol  
 (ii) Benzene to acetophenone (2)

**Q37.** Complete the following reaction equations: (2)



**Q38.** Define the following terms with one example each:

- A. Raoult's law  
 B. Azeotropic mixture  
 C. Colligative property (3)

**Q39.** (i) A solution is prepared by dissolving 1.8 g of glucose ( $\text{C}_6\text{H}_{12}\text{O}_6$ , molar mass =  $180\text{ g mol}^{-1}$ ) in 100 g of water. Calculate the boiling point of the solution. ( $K_b$  for water =  $0.52\text{ K kg mol}^{-1}$ , boiling point of water =  $373.15\text{ K}$ )

**OR**

(ii) Calculate the osmotic pressure of a 0.1 M urea solution at 300 K. ( $R = 0.0821\text{ L atm K}^{-1}\text{ mol}^{-1}$ ) (3)

**Q40.** State Kohlrausch's law of independent migration of ions. How is this law used to determine the limiting molar conductivity of a weak electrolyte? Illustrate with the example of acetic acid. (3)



- Q41.** (i) Using Valence Bond Theory, explain the hybridisation, shape and magnetic properties of  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ .

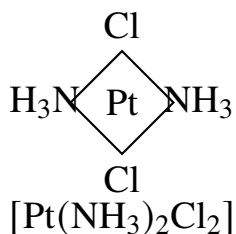
**OR**

- (ii) (a) What is the cause of lanthanoid contraction?  
 (b) Why do Zr and Hf have nearly identical atomic radii? (3)

- Q42.** (i) (a) Explain the hybridisation, shape and magnetic behaviour of  $[\text{CoF}_6]^{3-}$  using Valence Bond Theory.  
 (b) Write the IUPAC name of  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ .  
 (c) Which type of isomerism is shown by  $[\text{Pt}(\text{NH}_3)_2\text{Cl}_2]$ ?

**OR**

- (ii) (a) How is chlorine prepared in the laboratory? Write the chemical equation.  
 (b) Explain the bleaching action of chlorine.  
 (c) Write two uses of chlorine. (5)



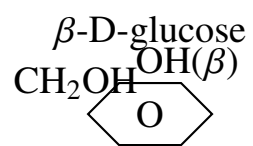
- Q43.** (i) (a) Explain the  $\text{S}_{\text{N}}1$  mechanism for the hydrolysis of tert-butyl bromide.  
 (b) How will you prepare ethanol from ethanal? Write the reaction.  
 (c) Why are phenols more acidic than alcohols?

**OR**

- (ii) (a) What are anomers? Explain with reference to glucose.  
 (b) What is the difference between DNA and RNA in terms of their sugar units and nitrogenous bases?



(c) What are enzymes? Why are they called biocatalysts? (5)



## Detailed Solutions

Q1.

## Solution

**Concept:** The mole concept serves as a bridge between the microscopic world of atoms or molecules and the macroscopic world of grams. One mole of any chemical substance contains exactly Avogadro's number of fundamental entities, defined as  $6.022 \times 10^{23}$  particles. To calculate the total number of particles present in a given mass of a substance, one must first determine the amount of substance in moles. This is achieved using the formula:  $\text{moles} = \frac{\text{mass}}{\text{molar mass}}$ . Once the number of moles is known, multiplying this value by Avogadro's constant yields the absolute number of molecules or atoms in the sample.

**Step 1** — Determine the number of moles of carbon dioxide ( $\text{CO}_2$ ). The given mass of the  $\text{CO}_2$  sample is 4.4 g. The molar mass of carbon dioxide is calculated by adding the atomic masses of one carbon atom and two oxygen atoms ( $12.011 + 2 \times 15.999 \approx 44 \text{ g/mol}$ ). Applying the mole formula gives:

$$\text{Moles of CO}_2 = \frac{4.4 \text{ g}}{44 \text{ g/mol}} = 0.10 \text{ mol}$$

**Step 2** — Calculate the absolute number of molecules using Avogadro's number. By multiplying the calculated 0.10 mol by the number of molecules per mole, we get:

$$\text{Number of molecules} = 0.10 \text{ mol} \times 6.022 \times 10^{23} \text{ molecules/mol} = 6.022 \times 10^{22} \text{ molecules}$$

**Step 3** — Analyze the choices to determine the matching alternative. Option A perfectly matches the calculated value of  $6.022 \times 10^{22}$  molecules. Looking at the other distractors, Option B ( $3.011 \times 10^{23}$ ) represents a sample containing 0.5 mol, Option C represents exactly 1.0 mol, and Option D corresponds to 2.0 mol of the substance.

**Final Answer:**  $6.022 \times 10^{22}$  molecules (Option A)

**Answer:** (A)

[Go Back to Question 1](#)



Q2.

**Solution**

**Concept:** The empirical formula represents the simplest, irreducible whole-number ratio of the various atoms present in a chemical compound. Determining this formula from elemental weight percentages involves a systematic multi-step process. First, the percentage composition is converted directly into a mass composition by assuming a standard base mass of exactly 100 g for the sample. Next, these masses are divided by their respective relative atomic masses to establish the molar amounts. Finally, the relative ratio is simplified into small integers by dividing each molar value by the lowest number of moles obtained in the set.

**Step 1** — Convert the percentage composition of the sample into moles assuming a total mass of 100 g. Under this condition, the mass of Sodium (Na) is 32.4 g, Sulfur (S) is 22.5 g, and Oxygen (O) is 45.1 g. Using the atomic weights (Na = 23, S = 32, O = 16), the moles are:

$$\text{Moles of Na} = \frac{32.4}{23} = 1.409 \text{ mol}$$

$$\text{Moles of S} = \frac{22.5}{32} = 0.703 \text{ mol}$$

$$\text{Moles of O} = \frac{45.1}{16} = 2.819 \text{ mol}$$

**Step 2** — Convert these molar values to the simplest ratio by dividing all values by the smallest value among them, which is 0.703 mol:

$$\text{Ratio for Na} = \frac{1.409}{0.703} \approx 2.0, \quad \text{Ratio for S} = \frac{0.703}{0.703} = 1.0, \quad \text{Ratio for O} = \frac{2.819}{0.703} \approx 4.0$$

**Step 3** — Combine these whole-number integers as subscripts to express the empirical formula. The resulting ratio Na : S : O = 2 : 1 : 4 gives the empirical formula  $\text{Na}_2\text{SO}_4$ , which matches option B.

**Final Answer:**  $\text{Na}_2\text{SO}_4$  (Option B)

**Answer: (B)**

[Go Back to Question 2](#)



Q3.

**Solution**

**Concept:** Quantum numbers describe the values of conserved quantities in the quantum system of an atom, defining the distribution and characteristics of electrons. The azimuthal quantum number, denoted by the letter  $l$ , is also known as the orbital angular momentum quantum number. It determines the specific orbital angular momentum and describes the geometric shape of the subshell where an electron resides. The value of  $l$  depends strictly on the principal quantum number  $n$  and ranges from 0 up to  $(n - 1)$ . By convention, specific integers of  $l$  correspond directly to particular subshell letters:  $l = 0$  corresponds to  $s$ ,  $l = 1$  corresponds to  $p$ ,  $l = 2$  corresponds to  $d$ , and  $l = 3$  corresponds to  $f$ .

**Step 1** — Analyze the orbital given in the question, which is a  $d$ -orbital. According to the established rules of quantum mechanics and standard spectroscopic notation, the shape and angular properties of any  $d$ -subshell are explicitly defined by an azimuthal quantum number of 2.

**Step 2** — Evaluate the constraints on the magnetic quantum number  $m_l$  and the principal quantum number  $n$ . For a  $d$ -orbital to exist, the principal quantum number  $n$  must be at least 3. Under this condition, the magnetic quantum number can take any of the  $(2l + 1) = 5$  possible orientation values from  $-2, -1, 0, +1, +2$ . Because the value of  $l$  is specifically fixed at 2 for all types of  $d$ -orbitals, it matches option C.

**Final Answer:** 2 (Option C)

**Answer:** (C)

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Q4.

**Solution**

**Concept:** Valence Shell Electron Pair Repulsion (VSEPR) theory provides a systematic framework for predicting the three-dimensional geometric structures of molecules. The theory dictates that the geometry around a central atom is governed by minimizing the electrostatic repulsion between all valence electron pairs. A key tenet of VSEPR theory is the relative order of repulsive strength: lone pair–lone pair (lp–lp) repulsions are significantly stronger than lone pair–bond pair (lp–bp) repulsions, which in turn are stronger than bond pair–bond pair (bp–bp) repulsions. Lone pairs occupy more spatial volume around the nucleus, forcing adjacent bonding pairs closer together.

**Step 1** — Examine the central oxygen atom in a water ( $\text{H}_2\text{O}$ ) molecule. Oxygen possesses six valence electrons. Two of these electrons form single covalent  $\sigma$ -bonds with two hydrogen atoms, leaving four non-bonding valence electrons that organize into two distinct lone pairs. The steric number is 4 (2 bond pairs + 2 lone pairs), which establishes a basic tetrahedral electronic geometry.

**Step 2** — Account for structural distortions caused by the two lone pairs. In a perfect, unperturbed tetrahedral geometry (such as methane,  $\text{CH}_4$ ), the ideal bond angle is exactly  $109.5^\circ$ . However, the strong lp–lp repulsion between the non-bonding pairs on the oxygen atom compresses the internal H – O – H bond angle. This compression reduces the measured angle down to approximately  $104.5^\circ$ , directly corresponding to option C.

**Final Answer:**  $104.5^\circ$  (Option C)

**Answer:** (C)

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Q5.

**Solution**

**Concept:** Boyle's law is a fundamental gas law that describes the precise mathematical relationship between the pressure and volume of an ideal gas. It states that at a constant temperature and for a fixed mass of gas, the absolute pressure exerted by the gas is inversely proportional to the volume it occupies. Mathematically, this relationship is expressed as  $P \propto \frac{1}{V}$ , or as the product of pressure and volume being a constant value ( $PV = k$ ). When a gas undergoes a transition from an initial state to a final state without a change in temperature or amount, this law can be rewritten as:

$$P_1V_1 = P_2V_2$$

**Step 1** — Extract the given parameter values from the problem statement to define the initial state of the system. The initial pressure ( $P_1$ ) is 2 atm and the initial volume ( $V_1$ ) is 5 L. The final state parameters specify that the gas is compressed or expanded until its final volume ( $V_2$ ) reaches exactly 2 L.

**Step 2** — Substitute these known values into the algebraic expression of Boyle's law to solve for the unknown final pressure ( $P_2$ ):

$$2 \text{ atm} \times 5 \text{ L} = P_2 \times 2 \text{ L}$$

$$10 = 2 \cdot P_2 \implies P_2 = \frac{10}{2} = 5 \text{ atm}$$

This calculated final pressure value matches option C.

**Final Answer:** 5 atm (Option C)

**Answer:** (C)

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Q6.

**Solution**

**Concept:** Osmotic pressure is a colligative property defined as the minimum external pressure that must be applied to a solution to completely halt the inward flow of its pure solvent across a semipermeable membrane. For dilute solutions, this behavior mimics ideal gas behavior and is quantified by the van 't Hoff equation:  $\pi = CRT$ , where  $\pi$  represents the osmotic pressure,  $C$  is the molar concentration of solute particles,  $R$  is the universal gas constant, and  $T$  is the absolute temperature measured in Kelvin. This equation indicates that at a constant concentration, osmotic pressure is directly proportional to the absolute temperature ( $\pi \propto T$ ).

**Step 1** — Analyze the functional dependency of  $\pi$  on temperature based on the equation  $\pi = CRT$ . Because  $C$  and  $R$  are positive scaling values, any change in  $T$  causes a linear modification in  $\pi$ . When the absolute temperature increases, the kinetic energy of the solvent molecules rises, leading to more frequent collisions against the membrane barrier, which increases the osmotic pressure.

**Step 2** — Evaluate the given options in light of this proportional relationship. An increase in temperature leads directly to an increase in osmotic pressure, matching option C. Conversely, decreasing the system temperature or lowering the concentration would lead to a reduction in  $\pi$ .

**Final Answer:** Increase in temperature (Option C)

Answer: (C)

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Q7.

**Solution**

**Concept:** Hess's law of constant heat summation is a cornerstone of thermochemistry derived from the law of conservation of energy. It asserts that the total enthalpy change ( $\Delta H$ ) during a chemical reaction remains identical regardless of whether the reaction takes place in a single step or through a series of sequential intermediate steps. Enthalpy ( $H$ ) is a thermodynamic state function, meaning its absolute value depends solely on the current state of the system (such as pressure, temperature, composition) and not on its historical path. Therefore, the net enthalpy change is always the difference between the total enthalpy of products and reactants:  $\Delta H = H_{\text{products}} - H_{\text{reactants}}$ .

**Step 1** — Relate the state function property directly to the pathway of the chemical conversion. Because enthalpy is path-independent, we can mathematically add, subtract, or manipulate intermediate chemical equations and their corresponding  $\Delta H$  values to find the net enthalpy change of an overall reaction.

**Step 2** — Match this fundamental definition with the given answer choices. The premise that the net change in heat is independent of the specific chemical path taken confirms that option B is correct. Other paths or mechanisms do not alter the final net energy balance of the transformation.

**Final Answer:** Is independent of the path of the reaction (Option B)

Answer: (B)

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Q8.

**Solution**

**Concept:** Entropy, denoted by the symbol  $S$ , is a fundamental thermodynamic quantity that measures the degree of randomness, disorder, or statistical multiplicity within a physical or chemical system. According to the Second Law of Thermodynamics, processes that occur spontaneously tend toward an increase in the total entropy of the universe. In terms of states of matter, the gaseous phase exhibits significantly higher entropy than the liquid phase, which in turn has higher entropy than a structured crystalline solid phase. Consequently, any phase change or chemical reaction that transforms a highly ordered solid phase into a highly disordered gaseous phase will result in a positive entropy change ( $\Delta S > 0$ ).

**Step 1** — Analyze the phase transitions listed in the options. Sublimation represents the direct physical transition of a substance from the solid phase directly into the gaseous phase without passing through an intermediate liquid state.

**Step 2** — Apply the entropy principle to the sublimation of dry ice (solid  $\text{CO}_2$ ). As solid  $\text{CO}_2$  sublimates into gaseous  $\text{CO}_2$ , the particles escape their rigid lattice and gain immense translational freedom, causing a sharp increase in structural disorder ( $\Delta S > 0$ ). On the other hand, processes like condensation (gas  $\rightarrow$  liquid), freezing (liquid  $\rightarrow$  solid), or deposition (gas  $\rightarrow$  solid) all constrain particle motion, leading to a decrease in system entropy ( $\Delta S < 0$ ). This identifies option C as the correct answer.

**Final Answer:** Sublimation of dry ice (Option C)

**Answer:** (C)

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Q9.

**Solution**

**Concept:** The electromotive force (EMF) of an electrochemical cell, denoted as  $E_{\text{cell}}^{\circ}$  under standard state conditions, measures the potential difference between two half-cells. This value represents the driving force pushing electrons through an external circuit. Standard cell potential is calculated using standard reduction potentials with the formula:

$$E_{\text{cell}}^{\circ} = E_{\text{cathode}}^{\circ} - E_{\text{anode}}^{\circ}$$

By IUPAC convention, the cathode is the electrode where reduction takes place (higher reduction potential), and the anode is the electrode where oxidation occurs (lower reduction potential). In a classic galvanic system like the Daniell cell, zinc undergoes oxidation while copper ions undergo reduction.

**Step 1** — Identify the role of each half-reaction using their standard reduction potentials. The given potentials are  $E^{\circ}(\text{Cu}^{2+}/\text{Cu}) = +0.34 \text{ V}$  and  $E^{\circ}(\text{Zn}^{2+}/\text{Zn}) = -0.76 \text{ V}$ . Because copper has the higher reduction potential, it acts as the cathode. Zinc has the lower reduction potential, so it acts as the anode.

**Step 2** — Substitute these values into the standard EMF equation to determine the total cell voltage:

$$E_{\text{cell}}^{\circ} = (+0.34 \text{ V}) - (-0.76 \text{ V}) = 0.34 + 0.76 = 1.10 \text{ V}$$

This calculated potential value matches option B.

**Final Answer:** 1.10 V (Option B)

**Answer: (B)**

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Q10.

**Solution**

**Concept:** The half-life of a chemical reaction, denoted as  $t_{1/2}$ , is defined as the time required for the initial reactant concentration to decrease to exactly half of its starting value. The mathematical expression for half-life depends fundamentally on the overall kinetic order of the reaction. For a zero-order reaction, the half-life is directly proportional to the initial concentration. For a first-order reaction, it is entirely independent of concentration. For a second-order reaction involving a single reactant, the integrated rate law yields a half-life formula that is expressed as:

$$t_{1/2} = \frac{1}{k[A]_0}$$

Here,  $k$  represents the second-order rate constant and  $[A]_0$  represents the initial molar concentration of the reactant.

**Step 1** — Evaluate the mathematical relationship shown in the second-order half-life formula. Because the initial concentration term  $[A]_0$  is located in the denominator of the fraction,  $t_{1/2}$  and  $[A]_0$  have an inverse relationship.

**Step 2** — Deduce the physical behavior of the system. As the initial concentration  $[A]_0$  increases, the denominator grows larger, which causes the value of  $t_{1/2}$  to decrease. Doubling the starting concentration cuts the half-life in half. This inverse proportionality matches option C.

**Final Answer:** Inversely proportional to initial concentration (Option C)

**Answer:** (C)

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Q11.

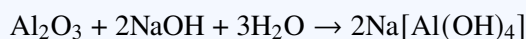
**Solution**

**Concept:** Chemical oxides are classified as acidic, basic, neutral, or amphoteric based on their behavior when reacting with acids and bases. Amphoteric oxides possess unique chemical properties that allow them to neutralize both strong acids and strong bases to yield salt and water. Aluminium oxide ( $\text{Al}_2\text{O}_3$ ) is a prime example of an amphoteric metal oxide, situated diagonally on the periodic table near the metalloid boundary. In contrast, sodium oxide ( $\text{Na}_2\text{O}$ ) is a strongly basic alkali oxide, whereas non-metal oxides such as sulfur dioxide ( $\text{SO}_2$ ) and tetraphosphorus decaoxide ( $\text{P}_4\text{O}_{10}$ ) are strictly acidic because they react exclusively with water or bases to produce acidic solutions or salts.

**Step 1** — Demonstrate the amphoteric nature of aluminium oxide through balanced chemical equations. When reacted with a strong monobasic mineral acid like hydrochloric acid (HCl), aluminium oxide acts as a chemical base, forming aluminium chloride salt and water:



**Step 2** — Demonstrate its reactivity with a strong base. When treated with an aqueous solution of sodium hydroxide (NaOH), aluminium oxide acts as an acid, dissolving to produce a soluble tetrahydroxoaluminate coordination complex:



This dual reactivity confirms its identity, making Option C the correct choice.

**Final Answer:**  $\text{Al}_2\text{O}_3$  (Option C)

**Answer:** (C)

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Q12.

**Solution**

**Concept:** In coordination chemistry, the coordination number of a central metal atom or ion is defined as the total number of ligand donor atoms that form direct coordinate covalent (dative) bonds with it. Ligands are categorized by their denticity, which indicates the number of donor atoms a single ligand molecule uses to bind to the metal. Monodentate ligands bind through one atom, whereas bidentate ligands contain two distinct donor atoms positioned to bind simultaneously. Ethylenediamine, abbreviated as 'en' ( $\text{H}_2\text{N} - \text{CH}_2 - \text{CH}_2 - \text{NH}_2$ ), is a neutral bidentate ligand that coordinates through the lone pairs on its two separate nitrogen atoms, forming stable five-membered chelate rings.

**Step 1** — Analyze the structural components of the given homoleptic coordination complex,  $[\text{Co}(\text{en})_3]^{3+}$ . The central transition metal core is a cobalt ion in a +3 oxidation state, which is surrounded by three individual ethylenediamine molecules.

**Step 2** — Calculate the total number of coordinate bonds using the denticity of the ligand. Since each ethylenediamine ligand contributes exactly two nitrogen donor atoms to the cobalt center, three such ligands provide a total of:

$$\text{Total donor atoms} = 3 \text{ ligands} \times 2 \text{ donor atoms/ligand} = 6$$

Therefore, the coordination number of the central cobalt ion is 6, establishing an octahedral geometry. This matches Option C.

**Final Answer:** 6 (Option C)

**Answer:** (C)

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Q13.

**Solution**

**Concept:** Isomerism is a phenomenon where two or more chemical compounds share an identical molecular formula but possess distinct structural arrangements or spatial orientations. Functional group isomers are a specific category of structural isomers that have the same molecular formula but contain completely different functional groups. This structural divergence drastically alters their chemical reactivities, physical states, and spectroscopic properties. For instance, aliphatic aldehydes and ketones containing the same number of carbon atoms are classic examples of functional group isomers, as they share the general structural formula  $C_nH_{2n}O$  but differ in carbonyl placement.

**Step 1** — Evaluate the molecular structures and formulas for the compounds given in Option A. Propanal is a three-carbon aldehyde represented by the structural formula  $CH_3CH_2CHO$ , while propanone is a three-carbon ketone represented by  $CH_3COCH_3$ . Counting the atoms reveals that both compounds possess exactly 3 carbon atoms, 6 hydrogen atoms, and 1 oxygen atom, giving them the identical molecular formula  $C_3H_6O$ .

**Step 2** — Contrast Option A with the remaining pairs to rule out other isomer classes. The pairs in Options B, C, and D represent chain isomers, position isomers, and position isomers respectively, leaving Option A as the only true functional group isomer pair.

**Final Answer:** Propanal and propanone (Option A)

**Answer:** (A)

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Q14.

**Solution**

**Concept:** Qualitative analysis of organic compounds involves specific chemical reagents to distinguish between different classes of functional groups or sub-classes of alcohols. Lucas reagent consists of a solution of anhydrous zinc chloride ( $\text{ZnCl}_2$ ) dissolved in concentrated hydrochloric acid (HCl). This test differentiates primary, secondary, and tertiary monohydric alcohols based on their varying rates of nucleophilic substitution ( $\text{S}_{\text{N}}1$ ) to form insoluble alkyl chlorides. The mechanism depends on carbocation stability; tertiary carbocations form rapidly, secondary carbocations form at a moderate rate, and primary carbocations are highly unstable and form very slowly under standard conditions.

**Step 1** — Analyze the reaction rates and physical indicators of the Lucas test. When mixed with Lucas reagent, tertiary alcohols react instantly at room temperature to form an insoluble layer of alkyl chloride, observed as immediate cloudiness or turbidity. Secondary alcohols produce distinct turbidity within five to ten minutes, often requiring gentle heating. Primary alcohols do not produce turbidity at room temperature, showing a reaction only upon prolonged heating.

**Step 2** — Review the alternative choices. Tollens' and Fehling's tests are used to identify reducing aldehydes, while Benedict's reagent is used to detect reducing carbohydrates. Therefore, Lucas reagent (Option C) is the correct chemical test.

**Final Answer:** Lucas reagent (Option C)

**Answer:** (C)

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Q15.

**Solution**

**Concept:** Vitamins are essential micronutrients that human organisms require in small quantities to perform vital metabolic functions, maintain cellular integrity, and regulate biochemical processes. Because the body cannot synthesize most vitamins in sufficient quantities, they must be obtained through a balanced diet. A prolonged deficiency of any specific vitamin leads to distinct clinical deficiency syndromes. Vitamin C, chemically known as ascorbic acid, is a water-soluble vitamin that acts as a powerful antioxidant and serves as an essential cofactor for the enzymatic hydroxylation of proline and lysine residues during collagen biosynthesis.

**Step 1** — Examine the structural consequences of Vitamin C deficiency. Without ascorbic acid, defective collagen synthesis weakens connective tissues throughout the body, leading to scurvy. This condition is clinically characterized by spongy, bleeding gums, subcutaneous hemorrhages, severe joint pain, anemia, and delayed wound healing.

**Step 2** — Compare this with the deficiency profiles of the other choices. A lack of Vitamin A results in night blindness; a deficiency in Vitamin B components (like thiamine) causes beriberi; and insufficient Vitamin D causes rickets in children. Thus, scurvy is caused by a Vitamin C deficiency, which corresponds to Option C.

**Final Answer:** Vitamin C (Option C)

**Answer:** (C)

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Q16.

**Solution**

**Concept:** Medicinal chemistry involves the study, discovery, and development of synthetic or natural chemical substances that interact with biological systems to treat, prevent, or alleviate diseases. Synthetic drugs are classified into broad therapeutic categories based on their primary pharmacological action and the specific biological receptors they target. Histamine is a naturally occurring biogenic amine that triggers inflammatory responses, bronchoconstriction, and allergic reactions when it binds to cellular H<sub>1</sub> receptors. Drugs designed to competitively block these receptors and counter allergic reactions are called antihistamines.

**Step 1** — Identify the specific drug molecule mentioned in the problem. Terfenadine (commercially known as Seldane) is a prominent synthetic drug molecule developed to act as a potent, non-sedating blocker of peripheral H<sub>1</sub> histamine receptors, providing relief from allergy symptoms like hay fever and urticaria.

**Step 2** — Contrast this mechanism with the alternative choices. Analgesics function primarily to relieve physiological pain; antibiotics are targeted agents used to eliminate bacterial infections; and antacids neutralize excess gastric acid. Since Terfenadine acts by blocking histamine pathways, it is classified as an antihistamine, matching Option B.

**Final Answer:** Antihistamine (Option B)

**Answer: (B)**

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Q17.

**Solution**

**Concept:** The distribution of electrons within the electronic subshells of an atom is governed by quantum mechanical principles: the Aufbau principle, the Pauli exclusion principle, and Hund's rule of maximum multiplicity. The Pauli exclusion principle dictates that no two electrons within a single atom can possess an identical set of all four quantum numbers ( $n, l, m_l, m_s$ ). Because an orbital is defined by the first three quantum numbers, it can accommodate a maximum of two electrons, which must have opposite spin orientations ( $m_s = +\frac{1}{2}$  and  $-\frac{1}{2}$ ). Transition metals like Chromium show anomalies in these rules because half-filled or fully filled  $d$ -subshells provide enhanced thermodynamic stability.

**Step 1** — State the Pauli exclusion principle based on its quantum parameters. Since each orbital has fixed  $n, l$ , and  $m_l$  values, adding a third electron would force it to duplicate a spin quantum number, violating the principle. Thus, an orbital can hold at most two electrons with antiparallel spins.

**Step 2** — Rationalize the anomalous configuration of Chromium ( $Z = 24$ ). The expected Aufbau configuration is  $[\text{Ar}]3d^44s^2$ . However, the actual ground-state configuration is  $[\text{Ar}]3d^54s^1$ . Shifting an electron from the  $4s$  orbital to the  $3d$  subshell creates a symmetrical, half-filled  $3d^5$  subshell, which maximizes exchange energy and minimizes electron-electron repulsion.

**Final Answer:** (i) No two electrons can have identical four quantum numbers; maximum 2 electrons per orbital. (ii) Cr:  $[\text{Ar}] 3d^54s^1$  due to extra stability of half-filled  $d^5$  configuration.

**Answer:** (See above)

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Q18.

**Solution**

**Concept:** Molecular Orbital (MO) theory describes the electronic structure of molecules by treating electrons as moving under the influence of all nuclei. Molecular orbitals form through the Linear Combination of Atomic Orbitals (LCAO). When two atomic wave functions combine, they interfere either constructively or destructively. In-phase combination results in constructive interference, which increases electron probability density in the internuclear region, drawing the nuclei together and lowering the potential energy. Out-of-phase combination results in destructive interference, decreasing electron density between the nuclei and creating a nodal plane, which destabilizes the system.

**Step 1** — Define the properties of a bonding molecular orbital. Formed by the constructive addition of atomic orbital wave functions ( $\psi_A + \psi_B$ ), it concentrates electron density between the bonded nuclei, shielding them from mutual repulsion. This orbital has lower energy than the parent atomic orbitals, stabilizing the molecule.

**Step 2** — Define the properties of an antibonding molecular orbital. Formed by destructive subtraction ( $\psi_A - \psi_B$ ), it features a zero-density node between the nuclei, exposing them to mutual electrostatic repulsion. This orbital has higher energy than the parent atomic orbitals and is designated with an asterisk (\*).

**Final Answer:** bonding; antibonding

**Answer:** (See above)

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Q19.

**Solution**

**Concept:** Liquid-vapor equilibrium is regulated by kinetic factors that depend on temperature, intermolecular forces, and partial pressures. The vapor pressure of a pure liquid is the pressure exerted by its vapor when the liquid and vapor phases are in dynamic equilibrium at a specific temperature. Dalton's law of partial pressures applies to mixtures of non-reacting gases, stating that the total pressure exerted by a gas mixture equals the sum of the individual pressures that each gas would exert if it occupied the volume alone.

**Step 1** — Assess the first statement regarding vapor pressure and temperature. Raising the temperature increases the average kinetic energy of the liquid molecules. A larger fraction of molecules can overcome the intermolecular attractive forces within the bulk liquid and escape into the gas phase, increasing the equilibrium vapor pressure. Thus, Statement 1 is true.

**Step 2** — Assess the second statement regarding Dalton's law. Dalton's law is mathematically defined as  $P_{\text{total}} = P_1 + P_2 + P_3 + \dots$ , meaning the total pressure is the mathematical sum of the partial pressures, not their difference. Therefore, Statement 2 is false.

**Final Answer:** T; F

**Answer:** (See above)

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Q20.

**Solution**

**Concept:** Colligative properties are physical properties of solutions that depend solely on the total number of solute particles dissolved in a given volume of solvent, rather than the chemical identity or nature of those particles. These properties include relative lowering of vapor pressure, elevation of boiling point, depression of freezing point, and osmotic pressure. Experimental techniques leverage these properties to determine the molar masses of unknown, non-volatile solutes. For example, cryoscopic methods measure the decrease in freezing point, while membrane transport methods exploit osmotic pressure differentials across semipermeable barriers.

**Step 1** — Identify the colligative property associated with Beckmann's method. Beckmann's method utilizes a specialized, highly sensitive Beckmann thermometer to measure the precise depression of freezing point ( $\Delta T_f$ ) that occurs when a non-volatile solute is added to a solvent, allowing the calculation of molecular weight.

**Step 2** — Identify the principle behind reverse osmosis. Osmosis is the natural flow of solvent into a concentrated solution. If an external pressure greater than the osmotic pressure ( $\pi$ ) is applied to the concentrated side, solvent molecules are forced backward through the semipermeable membrane into the dilute side. This process is based on osmotic pressure.

**Final Answer:** depression of freezing point; osmotic pressure

**Answer:** (See above)

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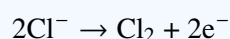


Q21.

**Solution**

**Concept:** Electrolysis is a fundamental chemical process driven by an external electrical current, forcing non-spontaneous oxidation-reduction reactions to occur within an electrochemical cell. An electrolytic cell consists of an external power source and two conducting rods called electrodes, which are immersed in a conducting fluid known as an electrolyte. The electrical power source drives an excess of electrons onto the negative electrode, called the cathode, while pulling electrons away from the positive electrode, called the anode. By standard electrochemical definition, chemical oxidation is the fundamental process wherein a chemical species loses one or more electrons. Therefore, oxidation reactions take place exclusively at the anode surface, where anions migrate to surrender their valence electrons to the external circuit.

**Step 1** — Analyze the oxidation process at the anode. When an electrical potential is established, negatively charged ions (anions) are electrostatically attracted to the positively charged anode. Upon contact, these anions release their excess electrons to the electrode material. For instance, during the electrolysis of molten sodium chloride, chloride ions undergo oxidation to produce diatomic chlorine gas:



**Step 2** — Define the properties and role of the electrolyte. An electrolyte is a chemical substance containing free, mobile ions that allows the medium to conduct electricity when in a liquid or aqueous solution phase. Solid salts are non-conductive because their ions are locked in a rigid crystal lattice. However, when melted or dissolved in water, the ions become free to move, facilitating the transport of charge through chemical decomposition. Classic examples include molten sodium chloride (NaCl) and aqueous sulfuric acid (H<sub>2</sub>SO<sub>4</sub>).

**Final Answer:** oxidation; electrolyte

**Answer:** (See above)

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Q22.

**Solution**

**Concept:** Green chemistry, also known as sustainable chemistry, focuses on designing chemical products and manufacturing processes that minimize or completely eliminate the use and generation of hazardous chemical substances. This field is governed by twelve core principles that guide chemical engineers toward sustainable manufacturing. A primary goal of green chemistry is to maximize atom economy, which measures the efficiency of a chemical reaction by tracking how many reactant atoms end up in the desired final product. Traditional synthetic methodologies often rely heavily on stoichiometric reagents, which are consumed fully in a one-to-one ratio, generating vast quantities of chemical waste and hazardous by-products that require intensive disposal procedures.

**Step 1** — Outline the primary objectives and methodologies of green chemistry. This approach aims to reduce environmental hazards at their source by substituting toxic organic solvents with benign solvents like water or supercritical carbon dioxide (CO<sub>2</sub>). It emphasizes designing chemical processes where all starting materials are fully incorporated into the final product, lowering toxicity profiles and reducing energy consumption throughout the chemical life cycle.

**Step 2** — Evaluate the role of catalysts in green chemical engineering. Catalysts are substances that increase the rate of a chemical reaction by lowering its activation energy without being consumed in the process. Unlike traditional stoichiometric reagents, catalysts are required only in sub-stoichiometric amounts and can be recovered and reused for multiple reaction cycles. They provide high selectivity, steering reactions toward the desired target molecule and minimizing the formation of unwanted side-products.

**Final Answer:** (i) Green chemistry minimises hazardous substances; e.g., use safer solvents. (ii) Catalysts are reusable, reduce waste, and give higher atom economy.

**Answer: (See above)**

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Q23.

**Solution**

**Concept:** Periodic trends and atomic structures govern the chemical behavior, bond strengths, and relative reactivities of the halogen family (Group 17). Fluorine, the topmost element in this group, exhibits unique, anomalous chemical properties compared to its heavier congeners. This divergence stems from its exceptionally small atomic radius, high electron density, high ionization enthalpy, and absence of vacant *d*-orbitals in its valence shell. These distinct properties alter its bonding behavior and limit its oxidation states. Additionally, when halogens bond with hydrogen to form binary hydrogen halides (HX), their relative acidic strengths follow a steady trend determined by the covalent bond properties down the group.

**Step 1** — Rationalize the anomalous behavior of elemental fluorine. Because fluorine lacks accessible *d*-orbitals, it cannot expand its valence octet, restricting it to a single oxidation state of  $-1$  and allowing it to form only one oxoacid (HOF). Furthermore, due to severe lone-pair repulsions caused by the tight spacing of electrons around its small nucleus, the F – F covalent bond has an unexpectedly low dissociation energy, making elemental fluorine highly reactive.

**Step 2** — Explain the trend in acidic strength among the hydrogen halides (HCl, HBr, and HI). As you move down the halogen group from chlorine to iodine, the valence orbitals grow larger and more diffuse, resulting in less effective orbital overlap with the small *1s* orbital of hydrogen. This weaker overlap steadily reduces the H – X bond dissociation energy, making it much easier for the molecule to deprotonate and release free  $H^+$  ions in water. Consequently, the acidic strength increases down the group:



**Final Answer:** (i) Small size, high electronegativity, no *d*-orbitals. (ii)  $HCl < HBr < HI$ .

**Answer:** (See above)

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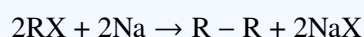


Q24.

**Solution**

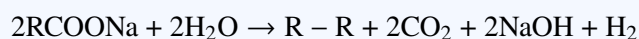
**Concept:** Organic chemistry relies on classic named reactions that carry out specific functional group transformations. These chemical reactions feature unique mechanisms, reaction conditions, and reagents to convert specific starting materials into predictable target molecules. Understanding these fundamental steps allows chemists to build complex carbon frameworks. Key named transformations include the Wurtz coupling reaction for extending carbon chains, the preparation of highly reactive organometallic Grignard reagents, Kolbe's electrochemical decarboxylation pathway for synthesizing symmetrical alkanes, and Friedel-Crafts electrophilic aromatic substitution for introducing alkyl groups onto an aromatic ring.

**Step 1** — Analyze the transformations given in the matching exercise. In the Wurtz reaction, two molecules of an alkyl halide are coupled by heating with metallic sodium in a dry ether solvent, yielding a symmetrical alkane with twice the carbon content:

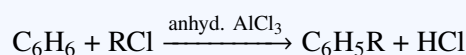


This step matches item (ii). Next, the preparation of a Grignard reagent involves reacting an alkyl halide directly with magnesium turnings in dry ether, forming an organomagnesium halide (RMgX), matching item (i).

**Step 2** — Evaluate the remaining reaction steps. Kolbe's electrolytic method involves the electrolysis of an aqueous solution of an alkali metal carboxylate salt, leading to decarboxylation and free-radical coupling at the anode to produce an alkane:



This matches item (iii). Finally, Friedel-Crafts alkylation involves treating an aromatic ring with an alkyl halide in the presence of a Lewis acid catalyst like anhydrous  $AlCl_3$  to yield an alkylbenzene, matching item (iv):



**Final Answer:** (a)-(ii), (b)-(i), (c)-(iii), (d)-(iv)

**Answer:** (See above)

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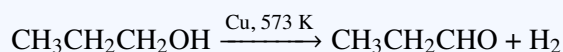


Q25.

**Solution**

**Concept:** Functional group transformations form the core of synthetic organic chemistry, enabling the conversion of one organic family into another through oxidation, reduction, substitution, or elimination reactions. Alcohols and carboxylic acids serve as versatile starting materials in these synthetic pathways. When primary aliphatic alcohols are exposed to transition metal catalysts at high temperatures, they undergo selective catalytic dehydrogenation, losing hydrogen atoms to yield carbonyl compounds. Carboxylic acids, on the other hand, contain a hydroxyl group within their carboxyl unit that can be targeted by halogenating reagents like phosphorus pentachloride ( $\text{PCl}_5$ ), which substitutes the hydroxyl group with a chlorine atom to produce highly reactive acyl chlorides.

**Step 1** — Examine the dehydrogenation of propan-1-ol. When vaporized propan-1-ol ( $\text{CH}_3\text{CH}_2\text{CH}_2\text{OH}$ ), a primary alcohol, is passed over a heated copper catalyst at a temperature of 573 K, it undergoes a selective loss of hydrogen from the oxygen and the primary carbon atom. This elimination process forms a carbon-oxygen double bond, converting the alcohol into its corresponding aldehyde, propanal:



**Step 2** — Examine the chlorination of ethanoic acid. When ethanoic acid ( $\text{CH}_3\text{COOH}$ ) reacts with phosphorus pentachloride ( $\text{PCl}_5$ ), a nucleophilic substitution occurs at the carbonyl carbon. The hydroxyl group ( $-\text{OH}$ ) is replaced by a chlorine atom, converting the acid into an acyl chloride known as ethanoyl chloride (or acetyl chloride), alongside phosphorus oxychloride and hydrochloric acid by-products:



**Final Answer:** (i)  $\text{CH}_3\text{CH}_2\text{CHO}$  (propanal); (ii)  $\text{CH}_3\text{COCl}$  (ethanoyl chloride)

**Answer:** (See above)

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Q26.

**Solution**

**Concept:** Stereoisomerism occurs when molecules share the same molecular formula and structural connectivity but differ in the spatial orientation of their component atoms. Stereoisomers are broadly split into geometrical (*cis-trans*) isomers and optical isomers. Geometrical isomerism requires structural rigidity—such as a carbon-carbon double bond ( $C = C$ ) or a cyclic ring framework—that prevents free rotation. For a double bond to exhibit geometrical isomerism, each carbon atom involved must be bonded to two entirely different chemical groups. Optical isomerism, by contrast, depends on molecular asymmetry, which typically requires a central carbon atom bonded to four completely different substituents.

**Step 1** — Analyze the requirements for geometrical isomerism using but-1-ene and but-2-ene. In but-1-ene ( $CH_2 = CH - CH_2 - CH_3$ ), the terminal carbon (C-1) is bonded to two identical hydrogen atoms. Because swapping these positions yields an identical molecule, but-1-ene cannot show geometrical isomerism. In contrast, but-2-ene ( $CH_3 - CH = CH - CH_3$ ) features a central double bond where each carbon is bonded to one hydrogen atom and one methyl group. This arrangement allows for two distinct spatial orientations: the *cis* isomer, where both methyl groups sit on the same side of the double bond, and the *trans* isomer, where they sit on opposite sides.

**Step 2** — Define the requirements for optical isomerism. A molecule exhibits optical isomerism when its 3D structure cannot be superimposed onto its mirror image, a property known as chirality. The most common cause of chirality is an asymmetric or chiral carbon center, which is a tetrahedral carbon atom bonded to four chemically distinct groups. The absence of an internal plane or center of symmetry ensures that the mirror images, called enantiomers, can rotate plane-polarized light in opposite directions.

**Final Answer:** (i) Geometrical isomerism from restricted rotation; but-2-ene shows it. (ii) Optical isomerism requires a chiral carbon with four different groups.

**Answer:** (See above)

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Q27.

**Solution**

**Concept:** Chemical stoichiometry relies on fundamental relationships that link molecular formulas to macroscopic measurements. The empirical formula represents the simplest, irreducible whole-number ratio of the different atoms present in a chemical compound, whereas the molecular formula shows the exact number of atoms in a single molecule. Additionally, Avogadro's hypothesis establishes a direct relationship between gas volume and molar amounts, showing that equal volumes of gases under identical temperature and pressure conditions contain equal numbers of molecules. At Standard Temperature and Pressure (STP), defined as 0°C (273.15 K) and 1 atm pressure, one mole of any ideal gas occupies a fixed volume.

**Step 1** — Evaluate the first statement regarding the empirical formula of benzene. Benzene has a molecular formula of  $C_6H_6$ , indicating that each molecule contains six carbon atoms and six hydrogen atoms. To find its empirical formula, the subscripts are divided by their greatest common divisor, which is 6. This reduces the ratio to 1 : 1, yielding the empirical formula CH. Therefore, Statement 1 is true.

**Step 2** — Evaluate the second statement regarding molar gas volume at STP. According to ideal gas behavior, the volume occupied by a gas depends solely on temperature, pressure, and the number of gas moles, independent of the gas's chemical identity or molecular mass. One mole of any ideal gas at 273.15 K and 1 atm occupies a molar volume of approximately 22.414 L (commonly rounded to 22.4 L). This confirms that Statement 2 is true.

**Final Answer:** T; T

**Answer:** (See above)

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Q28.

**Solution**

**Concept:** Chemical kinetics examines the variables that influence reaction rates, primarily focusing on how temperature and activation energy dictate the rate constant ( $k$ ). This relationship is mathematically quantified by the Arrhenius equation:  $k = Ae^{-E_a/RT}$ , where  $A$  represents the pre-exponential frequency factor,  $E_a$  is the activation energy,  $R$  is the universal gas constant, and  $T$  is the absolute temperature in Kelvin. The exponential term  $e^{-E_a/RT}$  represents the fraction of reacting molecules that possess sufficient kinetic energy to overcome the energy barrier during a collision. Taking the natural logarithm transforms this exponential relation into a linear equation, making it easier to analyze experimental data.

**Step 1** — Derive the linear form of the Arrhenius expression. Taking the natural logarithm ( $\ln$ ) of both sides of the base equation yields:

$$\ln k = \ln \left( Ae^{-E_a/RT} \right) \implies \ln k = \ln A - \frac{E_a}{RT}$$

This matches the standard equation for a straight line ( $y = mx + b$ ). When experimental values of  $\ln k$  are plotted on the vertical axis against the reciprocal temperature ( $1/T$ ) on the horizontal axis, the resulting straight line has a negative slope equal to  $-\frac{E_a}{R}$ . The activation energy can then be calculated from this slope:

$$E_a = -\text{slope} \times R$$

**Step 2** — Explain why the reaction rate constant increases with temperature. As the absolute temperature  $T$  rises, the value of the reciprocal term  $1/T$  decreases. This makes the exponent  $-\frac{E_a}{RT}$  less negative, causing the value of the exponential term to grow. Physically, higher temperatures increase the average kinetic energy of the molecules, meaning a larger fraction of collisions occur with energy greater than or equal to the activation energy ( $E_a$ ), accelerating the reaction.

**Final Answer:** (i)  $\ln k = \ln A - E_a/RT$ ; slope of  $\ln k$  vs  $1/T$  plot gives  $-E_a/R$ . (ii) Rate constant increases with temperature as more molecules exceed  $E_a$ .

**Answer: (See above)**

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Q29.

**Solution**

**Concept:** Thermodynamics categorizes the macroscopic physical and chemical properties of matter into two primary classes based on how they scale with the size of the system: extensive properties and intensive properties. This distinction is vital when performing mathematical manipulations on thermodynamic variables and state functions during energy calculations. An extensive property is a property whose value depends directly on the total mass, volume, or quantity of matter present within the defined boundaries of the system. In contrast, an intensive property depends solely on the nature or composition of the substance and is entirely independent of the sample's total size or mass.

**Step 1** — Analyze the characteristics and examples of extensive properties. Because extensive properties scale linearly with the amount of matter, they are mathematically additive. For example, internal energy ( $U$ ), enthalpy ( $H$ ), mass ( $m$ ), and volume ( $V$ ) are extensive variables. If you combine two identical blocks of a substance, the total mass, volume, and total internal energy of the combined system will double.

**Step 2** — Analyze the characteristics and examples of intensive properties. Intensive properties do not change when the amount of matter is altered and are not additive. Examples include temperature ( $T$ ), pressure ( $P$ ), density ( $\rho$ ), and boiling point. If a large container of water at a uniform temperature of  $25^{\circ}\text{C}$  is divided into two separate flasks, the temperature of the water in each individual flask remains exactly  $25^{\circ}\text{C}$ . Interestingly, the ratio of two extensive properties always yields an intensive property, as seen in density (mass/volume).

**Final Answer:** Extensive property depends on amount of matter (e.g., internal energy); intensive property does not (e.g., temperature).

**Answer:** (See above)

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Q30.

**Solution**

**Concept:** Entropy ( $S$ ) is a fundamental thermodynamic state function that quantifies the degree of molecular disorder, randomness, or statistical microstate multiplicity within a system. The net change in entropy during a phase transition ( $\Delta S$ ) is determined by evaluating the structural arrangement and translational freedom of the particles before and after the transition. In a liquid phase, molecules are held close together by significant intermolecular attractive forces, restricting their movement to short-range vibrations and sliding motions within a fixed volume. In contrast, particles in the gaseous phase have completely overcome these intermolecular forces, moving rapidly and independently through a much larger volume.

**Step 1** — Evaluate the structural changes that occur during vaporization. When a liquid evaporates into a gas or vapor, the system undergoes a dramatic transition from a moderately ordered condensed state to a highly disordered gaseous state. The spatial volume available to each molecule increases by orders of magnitude, which significantly expands the number of possible positions and kinetic energy distributions (microstates) that the molecules can occupy.

**Step 2** — Relate these structural changes to the sign of the entropy change. Because entropy increases with rising disorder and microstate multiplicity, the entropy of the vapor phase ( $S_{\text{gas}}$ ) is always much greater than the entropy of the starting liquid phase ( $S_{\text{liquid}}$ ). The resulting change in entropy for vaporization, calculated as:

$$\Delta S_{\text{vap}} = S_{\text{gas}} - S_{\text{liquid}}$$

is always a positive value ( $\Delta S_{\text{vap}} > 0$ ). This confirms that evaporation is inherently an entropy-driven phase change.

**Final Answer:** Evaporation increases entropy because molecules in the gas phase have greater randomness and more accessible microstates than in the liquid phase.

**Answer:** (See above)

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Q31.

**Solution**

**Concept:** A strong diprotic acid completely dissociates in an aqueous solution, yielding two moles of hydrogen ions per mole of acid. Consequently, the hydronium ion concentration is exactly twice the analytical concentration of the acid. The common ion effect refers to the suppression of the degree of dissociation of a weak electrolyte upon the addition of a strong electrolyte that provides an ion identical to one produced by the weak electrolyte. This chemical phenomenon is a direct consequence of Le Chatelier's principle, which dictates that a system at equilibrium will shift to counteract a perturbation and restore equilibrium.

**Alternative (i):** Sulfuric acid ( $\text{H}_2\text{SO}_4$ ) undergoes complete, stepwise ionization in water. For a 0.005 M solution, assuming both protons dissociate fully, the stoichiometry yields a hydrogen ion concentration of:

$$[\text{H}^+] = 2 \times 0.005 \text{ M} = 0.01 \text{ M} = 10^{-2} \text{ M}$$

The pH of the solution is calculated using the negative base-10 logarithm of the hydrogen ion activity:

$$\text{pH} = -\log[\text{H}^+] = -\log(10^{-2}) = 2$$

**Alternative (ii):** The common ion effect shifts ionic equilibria. For example, adding sodium acetate ( $\text{CH}_3\text{COONa}$ ) to a solution of acetic acid ( $\text{CH}_3\text{COOH}$ ) introduces an excess of acetate ions ( $\text{CH}_3\text{COO}^-$ ). This shifts the weak acid dissociation equilibrium backward, lowering the concentration of hydronium ions. Similarly, for a sparingly soluble salt like silver chloride ( $\text{AgCl}$ ), adding sodium chloride ( $\text{NaCl}$ ) supplies a common chloride ion ( $\text{Cl}^-$ ), shifting the solubility equilibrium backward and decreasing the overall solubility of  $\text{AgCl}$ .

**Final Answer:** (i)  $\text{pH} = 2$ . (ii) Common ion effect suppresses dissociation of a weak electrolyte by adding a common ion, e.g.,  $\text{AgCl}$  solubility decreases in  $\text{NaCl}$  solution.

**Answer: (See above)**

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Q32.

### Solution

**Concept:** The Nernst equation describes how the reduction potential of an electrode depends on temperature, standard cell potential, and the activities of the oxidized and reduced chemical species. It connects thermodynamic properties with electrochemical cell parameters. Conductance measurements describe how a solution transmits an electric current. Specific conductance, denoted by kappa ( $\kappa$ ), represents the intrinsic conductivity of a solution contained between two parallel electrodes of unit cross-sectional area separated by a unit distance. The cell constant, designated as  $G^*$ , depends on the physical geometry of the cell and links specific conductance with measured electrolytic conductance.

**Alternative (i):** For a metal electrode undergoing reduction ( $M^{n+} + ne^- \rightarrow M$ ), the Nernst equation accounts for concentration changes. At a standard temperature of 298 K, substituting the values of the gas constant  $R$ , Faraday's constant  $F$ , and converting natural logs to base-10 logarithms yields the equation:

$$E_{M^{n+}/M} = E_{M^{n+}/M}^\circ - \frac{RT}{nF} \ln \frac{1}{[M^{n+}]} = E_{M^{n+}/M}^\circ + \frac{0.0591}{n} \log[M^{n+}]$$

**Alternative (ii):** The cell constant is defined as the ratio of the distance between the cell electrodes ( $l$ ) to their cross-sectional area ( $A$ ), expressed as  $G^* = \frac{l}{A}$ . The measured conductance ( $G$ ) of a solution is inversely proportional to its resistance. The specific conductance ( $\kappa$ ) accounts for cell geometry by multiplying the measured conductance by the cell constant:

$$\kappa = G \times \left(\frac{l}{A}\right) = G \times G^*$$

**Final Answer:** (i)  $E = E^\circ + (0.0591/n) \log[M^{n+}]$ . (ii)  $\kappa = G \times G^*$  where  $G^* = l/A$ .

**Answer:** (See above)

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Q33.

### Solution

**Concept:** Faraday's laws of electrolysis describe the quantitative relationships between the electrical charge passed through an electrolytic cell and the mass of chemical substances altered at the electrodes. Faraday's second law focuses on multi-cell systems, stating that when the same quantity of electricity is passed through different electrolytes connected in series, the masses of the substances liberated or deposited at the electrodes are directly proportional to their chemical equivalent weights. The chemical equivalent mass of an ion is defined as its relative atomic or molecular mass divided by its valence, which represents the total number of electrons gained or lost per atom.

**Step 1** — Express Faraday's second law mathematically for two different metals deposited in series:  $\frac{m_1}{m_2} = \frac{E_1}{E_2}$ , where  $m$  represents mass and  $E$  represents the equivalent mass. For a copper system containing divalent copper ions ( $\text{Cu}^{2+}$ ), the equivalent mass is calculated from its atomic mass:

$$E_{\text{Cu}} = \frac{\text{Atomic Mass}}{\text{Valency}} = \frac{63.5}{2} = 31.75 \text{ g/eq}$$

For a silver system containing monovalent silver ions ( $\text{Ag}^+$ ), its equivalent mass is:

$$E_{\text{Ag}} = \frac{108}{1} = 108 \text{ g/eq}$$

**Step 2** — Calculate the mass ratio by substituting these equivalent weights into the mathematical expression of the second law:

$$\frac{m_{\text{Cu}}}{m_{\text{Ag}}} = \frac{31.75}{108} \approx \frac{1}{3.4}$$

This means that when the same electrical charge passes through both cells, the mass of silver deposited on the cathode will be approximately 3.4 times greater than the mass of copper deposited.

**Final Answer:** Second law:  $m_1/m_2 = E_1/E_2$ . Mass of Ag deposited  $\approx$  3.4 times mass of Cu.

**Answer:** (See above)

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**Q34.**
**Solution**

**Concept:** Reaction kinetics studies the rates of chemical processes and how they depend on reactant concentrations. In a first-order chemical reaction, the rate depends linearly on the concentration of a single reactant. Integrating this differential rate law yields an equation that tracks concentration changes over time:  $\ln\left(\frac{[A]_0}{[A]_t}\right) = kt$ , where  $[A]_0$  is the initial concentration,  $[A]_t$  is the concentration at time  $t$ , and  $k$  is the first-order rate constant. The reaction half-life ( $t_{1/2}$ ) is the time required for the reactant concentration to decrease to exactly half its initial value ( $[A]_t = \frac{[A]_0}{2}$ ).

**Step 1** — Derive the expression for the half-life of a first-order reaction. Substituting the half-life conditions into the integrated rate law yields:

$$\ln\left(\frac{[A]_0}{[A]_0/2}\right) = kt_{1/2} \implies \ln(2) = kt_{1/2}$$

Solving for  $t_{1/2}$  reveals that the half-life is independent of the starting concentration:

$$t_{1/2} = \frac{\ln 2}{k} \approx \frac{0.693}{k}$$

**Step 2** — Calculate the rate constant using the given kinetic data. The reaction is 20% complete in 10 minutes, meaning 80% of the initial reactant remains ( $[A]_t = 0.80[A]_0$ ). Substituting these values into the rate equation gives:

$$\ln\left(\frac{[A]_0}{0.80[A]_0}\right) = k \times 10 \implies \ln(1.25) = 10k$$

$$0.2231 = 10k \implies k = \frac{0.2231}{10} = 0.02231 \text{ min}^{-1}$$

**Final Answer:**  $t_{1/2} = 0.693/k$ ;  $k = 0.02231 \text{ min}^{-1}$

**Answer: (See above)**

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Q35.

**Solution**

**Concept:** Interhalogen compounds are molecules formed by the direct combination of two different halogen elements, resulting in formulas like  $\text{ClF}$ ,  $\text{BrF}_3$ , or  $\text{IF}_5$ . These compounds show different chemical properties and reactivities compared to pure, homonuclear diatomic halogens. The valence shell electron pair repulsion (VSEPR) theory provides a geometric model to predict molecular structures by minimizing electron-pair repulsions around a central atom. Xenon hexafluoride ( $\text{XeF}_6$ ) is a noble gas coordination compound whose molecular geometry is strongly influenced by the presence of a non-bonding valence lone pair on the central xenon atom.

**Alternative (i):** Interhalogen compounds ( $\text{X} - \text{X}'$ ) are typically more reactive than their parent homonuclear halogens ( $\text{X} - \text{X}$ ), with the exception of fluorine. This higher reactivity stems from the electronegativity difference between the two different halogens, making the  $\text{X} - \text{X}'$  covalent bond polar. This polarization weakens the orbital overlap and lowers the bond dissociation energy compared to non-polar bonds, making interhalogens more susceptible to heterolytic cleavage and chemical attack.

**Alternative (ii):** Xenon hexafluoride ( $\text{XeF}_6$ ) contains a central xenon atom with eight valence electrons. Six of these electrons form covalent single bonds with six fluorine atoms, leaving two remaining valence electrons as a non-bonding lone pair. This gives a total steric number of seven (6 bond pairs + 1 lone pair). According to VSEPR theory, these seven electron pairs adopt a capped octahedral or distorted octahedral molecular geometry, where the lone pair distorts the regular octahedral angles.

**Final Answer:** (i) Weaker, more polar  $\text{X}-\text{X}'$  bonds make interhalogens more reactive. (ii)  $\text{XeF}_6$  has distorted octahedral shape.

**Answer: (See above)**

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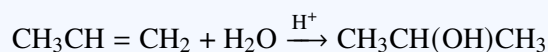


Q36.

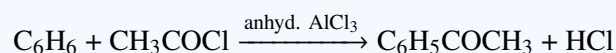
**Solution**

**Concept:** Organic synthesis relies on predictable reaction pathways to modify carbon frameworks and introduce specific functional groups. Alkenes can undergo electrophilic addition reactions across their carbon-carbon double bonds. In the presence of an acid catalyst, alkenes react with water via hydration. This addition follows Markovnikov's rule, which states that the hydrogen atom adds to the double-bonded carbon with more hydrogen atoms, while the nucleophilic hydroxyl group adds to the more substituted carbon atom. Aromatic hydrocarbons like benzene undergo electrophilic aromatic substitution, such as Friedel-Crafts acylation, to introduce acyl groups onto the ring.

**Step 1** — Analyze the acid-catalyzed hydration of propene ( $\text{CH}_3 - \text{CH} = \text{CH}_2$ ). The reaction begins with the protonation of the double bond, forming a stable secondary carbocation intermediate ( $\text{CH}_3 - \text{CH}^+ - \text{CH}_3$ ) rather than a less stable primary carbocation. Water then attacks this carbocation, followed by deprotonation to yield propan-2-ol:



**Step 2** — Analyze the Friedel-Crafts acylation of benzene. Benzene reacts with ethanoyl chloride ( $\text{CH}_3\text{COCl}$ ) in the presence of an anhydrous aluminium chloride ( $\text{AlCl}_3$ ) Lewis acid catalyst. The catalyst generates an electrophilic acylium ion ( $\text{CH}_3\text{CO}^+$ ), which attacks the aromatic benzene ring. Substitution of a ring hydrogen atom yields the aromatic ketone acetophenone:



**Final Answer:** (i) Propene +  $\text{H}_2\text{O}/\text{H}^+ \rightarrow$  propan-2-ol. (ii) Benzene +  $\text{CH}_3\text{COCl}/\text{AlCl}_3 \rightarrow$  acetophenone.

**Answer: (See above)**

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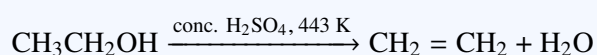


Q37.

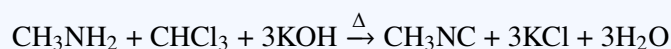
**Solution**

**Concept:** Eliminative and substitutive methods are foundational to organic functional group modifications. Dehydration of aliphatic alcohols is an elimination reaction where the elements of water are lost to form a carbon-carbon pi bond. The mechanism and reaction conditions depend on the structural class of the alcohol. Primary aliphatic amines undergo specific named base-catalyzed alpha-elimination pathways, such as the Hoffmann carbylamine reaction. This reaction serves as a sensitive qualitative test for primary amines, converting them into distinctive and foul-smelling isocyanide derivatives.

**Step 1** — Examine the acid-catalyzed dehydration of ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ). When ethanol is heated with concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) at 443 K, it undergoes intramolecular dehydration. The hydroxyl group is protonated to form a good leaving group ( $\text{H}_2\text{O}$ ), followed by elimination of a beta-hydrogen atom to form a double bond, producing ethene gas:



**Step 2** — Examine the carbylamine reaction using methanamine ( $\text{CH}_3\text{NH}_2$ ). When this primary amine is warmed with chloroform ( $\text{CHCl}_3$ ) and an alcoholic solution of potassium hydroxide ( $\text{KOH}$ ), it reacts with a highly reactive dichlorocarbene intermediate ( $:\text{CCl}_2$ ). This substitution and elimination sequence converts the amine group into an isocyanide group, yielding methyl isocyanide:



**Final Answer:** (a)  $\text{CH}_2=\text{CH}_2$  (ethene); (b)  $\text{CH}_3\text{NC}$  (methyl isocyanide)

**Answer:** (See above)

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Q38.

**Solution**

**Concept:** Physical chemistry classifies solutions based on the thermodynamic interactions between their components. For ideal liquid mixtures, Raoult's law states that the partial vapor pressure of each volatile component is directly proportional to its mole fraction in the liquid phase. However, real solutions often show deviations from ideality due to differences in intermolecular forces. At specific compositions, these non-ideal mixtures can form azeotropes—constant-boiling liquid mixtures that behave like a single pure substance during distillation. Colligative properties are a distinct class of solution properties that depend solely on the total concentration of dissolved solute particles.

**Step 1** — Define Raoult's law for an ideal solution. The law is mathematically expressed as  $p_i = p_i^\circ x_i$ , where  $p_i$  is the partial vapor pressure of component  $i$ ,  $p_i^\circ$  is the vapor pressure of the pure component, and  $x_i$  is its mole fraction. Mixtures with similar molecular structures and intermolecular forces, like benzene and toluene, follow this law.

**Step 2** — Explain an azeotropic mixture. An azeotrope forms when the liquid and vapor phases have the identical composition at a specific boiling temperature, preventing separation by fractional distillation. For example, a mixture of 95.6% ethanol and 4.4% water forms a minimum-boiling azeotrope that distills at 351.3 K.

**Step 3** — Define a colligative property. These physical properties change based on the number of solute particles in solution, regardless of their chemical identity. Examples include osmotic pressure and boiling point elevation.

**Final Answer:** A.  $p_i = p_i^\circ x_i$  (Raoult's law). B. Constant-boiling mixture (e.g., ethanol-water). C. Property dependent on particle number (e.g., osmotic pressure).

**Answer:** (See above)

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Q39.

### Solution

**Concept:** Dissolving a non-volatile solute in a liquid solvent alters its physical properties, resulting in colligative changes like boiling point elevation and the generation of osmotic pressure. The addition of solute particles lowers the chemical potential of the solvent, requiring a higher temperature to match atmospheric pressure during boiling. The elevation in boiling point is quantified by the ebullimetric equation:  $\Delta T_b = K_b \cdot m$ , where  $K_b$  is the molal boiling point elevation constant and  $m$  is the molality. Osmotic pressure ( $\pi$ ) describes the pressure required to stop solvent flow across a semipermeable membrane and is calculated using the van 't Hoff equation:  $\pi = CRT$ .

**Alternative (i):** Calculate the boiling point elevation for the glucose solution. First, determine the moles of glucose (molar mass = 180 g/mol) dissolved in 100 g (0.100 kg) of water:

$$\text{Moles of glucose} = \frac{1.8 \text{ g}}{180 \text{ g/mol}} = 0.01 \text{ mol}$$

$$\text{Molality } (m) = \frac{0.01 \text{ mol}}{0.100 \text{ kg}} = 0.10 \text{ mol/kg}$$

Using the boiling point constant for water ( $K_b = 0.52 \text{ K kg/mol}$ ), the elevation is:

$$\Delta T_b = 0.52 \times 0.10 = 0.052 \text{ K}$$

The final boiling point of the solution at standard atmospheric pressure is:

$$T_b = 373.15 \text{ K} + 0.052 \text{ K} = 373.202 \text{ K}$$

**Alternative (ii):** Calculate the osmotic pressure ( $\pi$ ) for a 0.1 M solution at a temperature of 300 K. Substituting the values into the van 't Hoff equation yields:

$$\pi = CRT = 0.1 \text{ mol/L} \times 0.0821 \text{ L atm / (mol K)} \times 300 \text{ K} = 2.463 \text{ atm}$$

**Final Answer:** (i) B.P. = 373.202 K. (ii)  $\pi$  = 2.463 atm.

**Answer: (See above)**

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Q40.

### Solution

**Concept:** Electrolytic conductivity varies significantly depending on the concentration and degree of dissociation of the electrolyte. For strong electrolytes, molar conductivity increases linearly with the square root of concentration, allowing its limiting value at infinite dilution ( $\Lambda_m^\circ$ ) to be determined by direct extrapolation. However, weak electrolytes do not dissociate fully at higher concentrations, causing a sharp, non-linear increase in conductivity at high dilutions that prevents direct extrapolation. To address this, Kohlrausch's law of independent migration of ions states that at infinite dilution, each ion contributes a fixed amount to the total molar conductivity of an electrolyte, independent of the co-ion.

**Step 1** — State the mathematical form of Kohlrausch's law. For an electrolyte that dissociates into cations and anions, the total limiting molar conductivity ( $\Lambda_m^\circ$ ) is the sum of its individual limiting ionic conductivities:

$$\Lambda_m^\circ = \nu_+ \lambda_+^\circ + \nu_- \lambda_-^\circ$$

where  $\nu_+$  and  $\nu_-$  represent the stoichiometric coefficients of the cations and anions, and  $\lambda_+^\circ$  and  $\lambda_-^\circ$  are their respective limiting ionic conductivities.

**Step 2** — Apply this independent migration principle to determine the limiting molar conductivity of a weak electrolyte like acetic acid ( $\text{CH}_3\text{COOH}$ ). By combining experimental data from strong electrolytes ( $\text{HCl}$ ,  $\text{CH}_3\text{COONa}$ , and  $\text{NaCl}$ ), the individual ionic contributions can be algebraically isolated:

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = \Lambda_m^\circ(\text{HCl}) + \Lambda_m^\circ(\text{CH}_3\text{COONa}) - \Lambda_m^\circ(\text{NaCl})$$

$$\Lambda_m^\circ(\text{CH}_3\text{COOH}) = (\lambda_{\text{H}^+}^\circ + \lambda_{\text{Cl}^-}^\circ) + (\lambda_{\text{CH}_3\text{COO}^-}^\circ + \lambda_{\text{Na}^+}^\circ) - (\lambda_{\text{Na}^+}^\circ + \lambda_{\text{Cl}^-}^\circ) = \lambda_{\text{H}^+}^\circ + \lambda_{\text{CH}_3\text{COO}^-}^\circ$$

**Final Answer:**  $\Lambda_m^\circ = \lambda_+^\circ + \lambda_-^\circ$ . Weak electrolyte  $\Lambda_m^\circ$  is found by combining strong electrolyte data; e.g.,  $\text{CH}_3\text{COOH}$  via  $\text{HCl}$ ,  $\text{CH}_3\text{COONa}$  and  $\text{NaCl}$ .

**Answer:** (See above)

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Q41.

**Solution**

**Concept:** Valence Bond Theory (VBT) explains the geometric structures and magnetic properties of coordination complexes through the hybridisation of atomic orbitals on the central metal ion. The electronic configuration of the metal dictates which subshells participate in bonding. In the inner transition series, periodic properties are heavily influenced by the filling of the  $4f$  subshell. The lanthanoid contraction describes a steady decrease in atomic and ionic radii across the lanthanoid series, from lanthanum to lutetium. This contraction is caused by the poor shielding ability of  $4f$  electrons, which cannot effectively counter the increasing nuclear charge.

**Alternative (i):** Analyze the  $[\text{Zn}(\text{NH}_3)_4]^{2+}$  coordination complex. The central zinc ion has a +2 oxidation state, giving it a stable  $3d^{10}$  electronic configuration. Because the  $3d$  subshell is completely filled, inner  $d$ -orbitals cannot participate in hybridisation. To accommodate the four amine ligands, the metal ion hybridises one  $4s$  and three  $4p$  orbitals, forming four equivalent  $sp^3$  hybrid orbitals directed toward the corners of a tetrahedron. Since all ten electrons in the  $3d$  subshell remain paired, the complex has no net magnetic moment and is diamagnetic.

**Alternative (ii):** Explain the lanthanoid contraction and its structural consequences. The  $4f$  orbitals have a highly diffuse shape, resulting in poor shielding of the outer valence electrons from the growing nuclear charge. This causes the effective nuclear charge to increase across the series, pulling the electron shells closer to the nucleus and causing a contraction in size. A major consequence of this contraction is seen in the  $d$ -block elements of the fifth and sixth periods. For example, zirconium (Zr, 5th period) and hafnium (Hf, 6th period) have nearly identical atomic radii ( $\approx 160$  pm) and very similar chemical properties, because the intervening lanthanoid contraction counteracts the expected size increase from adding a principal electron shell.

**Final Answer:** (i)  $[\text{Zn}(\text{NH}_3)_4]^{2+}$ :  $sp^3$ , tetrahedral, diamagnetic. (ii) (a) Poor  $4f$  shielding causes contraction. (b) Lanthanoid contraction makes Zr and Hf nearly equal in size.

**Answer: (See above)**

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Q42.

**Solution**

**Concept:** Coordination complexes display distinct stereochemical arrangements and magnetic profiles depending on ligand field strength and coordination geometry. Weak-field ligands, like fluoride ions ( $F^-$ ), exert weak electrostatic repulsions and do not force electron pairing in the  $d$ -subshell, resulting in high-spin, outer-orbital complexes. Stronger coordinate interactions or specific square-planar geometries can lead to different electronic structures or give rise to geometrical isomerism, such as *cis* and *trans* forms. In industrial and laboratory chemistry, halogens like chlorine are prepared by oxidizing halide ions, and their oxidising properties make them effective bleaching and purifying agents.

**Alternative (i):** (a) In the hexafluoridocobaltate(III) complex,  $[CoF_6]^{3-}$ , the cobalt ion is in a +3 oxidation state with a  $3d^6$  configuration. Because fluoride is a weak-field ligand, it does not force electron pairing, leaving four unpaired electrons. The ion utilizes its outer  $4s$ ,  $4p$ , and  $4d$  orbitals to undergo  $sp^3d^2$  hybridisation, forming an outer-orbital octahedral complex that is strongly paramagnetic. (b) The IUPAC name for  $[Pt(NH_3)_2Cl_2]$  is diamminedichloridoplatinum(II). (c) This neutral, square-planar complex exhibits geometrical isomerism, forming a *cis* isomer when identical ligands are adjacent ( $90^\circ$  apart) and a *trans* isomer when they are opposite ( $180^\circ$  apart).

**Alternative (ii):** (a) Chlorine gas is prepared in the laboratory by heating manganese dioxide ( $MnO_2$ ) with concentrated hydrochloric acid, oxidizing chloride ions to elemental chlorine:



(b) The bleaching action of chlorine requires moisture. Chlorine reacts with water to produce unstable hypochlorous acid, which decomposes to release nascent oxygen ( $[O]$ ):



This nascent oxygen oxidizes colored organic pigments into permanent, colorless compounds. (c) Due to its strong oxidizing properties, chlorine is widely used for water purification, as a bleaching agent in paper pulp manufacturing, and as a starting material for producing polyvinyl chloride (PVC).

**Final Answer:** (i) (a)  $[CoF_6]^{3-}$ :  $sp^3d^2$ , octahedral, paramagnetic. (b) Diamminedichloridoplatinum(II). (c) Geometrical (*cis-trans*) isomerism. (ii) (a)  $MnO_2 + 4HCl \rightarrow MnCl_2 + Cl_2 + 2H_2O$ . (b) Nascent oxygen oxidises color. (c) Water purification, PVC manufacture.

**Answer: (See above)**

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Q43.

### Solution

**Concept:**  $S_N1$  proceeds via carbocation intermediate. Aldehydes reduce to alcohols. Phenols are more acidic due to resonance. Anomers differ at C-1. DNA/RNA differ in sugar and bases. Enzymes are protein catalysts.

**Alternative (i):** Step 1 – (a)  $S_N1$  mechanism for tert-butyl bromide: Step 1 (slow):  $(CH_3)_3CBr \rightarrow (CH_3)_3C^+ + Br^-$  (carbocation formation). Step 2 (fast):  $(CH_3)_3C^+ + H_2O \rightarrow (CH_3)_3COH_2^+$ . Step 3 (fast):  $(CH_3)_3COH_2^+ \rightarrow (CH_3)_3COH + H^+$ .

Step 2 – (b) Ethanal to ethanol:  $CH_3CHO \xrightarrow[NaBH_4]{\text{or } H_2/Ni} CH_3CH_2OH$  (reduction).

Step 3 – (c) Phenols are more acidic than alcohols because the phenoxide ion is resonance-stabilised (the negative charge is delocalised over the benzene ring through 4 resonance structures). Alkoxide ions lack such stabilisation.

**Alternative (ii):** Step 1 – (a) Anomers are cyclic stereoisomers that differ in configuration only at the anomeric carbon (C-1 in glucose).  $\alpha$ -D-glucose has  $-OH$  at C-1 below the ring plane;  $\beta$ -D-glucose has it above.

Step 2 – (b) DNA: deoxyribose sugar, bases A, G, C, T. RNA: ribose sugar, bases A, G, C, U (uracil instead of thymine).

Step 3 – (c) Enzymes are protein molecules that act as biological catalysts, speeding up biochemical reactions without being consumed. They are called biocatalysts because they lower the activation energy of biological reactions with high specificity.

**Final Answer:** (i) (a)  $S_N1$ : carbocation formation then nucleophilic attack. (b)  $CH_3CHO \xrightarrow{\text{red.}} CH_3CH_2OH$ . (c) Phenoxide ion is resonance-stabilised. (ii) (a) Anomers differ at anomeric C-1. (b) DNA: deoxyribose + A,G,C,T; RNA: ribose + A,G,C,U. (c) Enzymes are protein biocatalysts.

**Answer: (See above)**

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**Answer Key**

Q	Ans	Q	Ans	Q	Ans	Q	Ans	Q	Ans
1	A	2	B	3	C	4	C	5	C
6	C	7	B	8	C	9	B	10	C
11	C	12	C	13	A	14	C	15	C
16	B								

