

(a) The shape of the XeF_4 molecule is square planar.

(b) The electronic configuration of Mn^{2+} ion ($\text{Mn}24$) is $[\text{Ar}] 3d^5$.

© Lattice energy is the energy required to break apart an ionic compound into its gaseous ions. It's also defined as the energy released when gaseous ions combine to form an ionic compound.

(d) The IUPAC name of $[\text{Co}(\text{NH}_3)_5\text{H}_2\text{O}]\text{Cl}_3$ is **pentaammineaquacobalt(III) chloride**¹.

(e) Lanthanide contraction refers to the gradual decrease in atomic and ionic radii of lanthanide elements as we move from left to right in the periodic table. This is due to the poor shielding effect of 4f electrons.

(f) The order of increasing acidity is $\text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$. This is because acidity increases with the size of the central atom in the hydride series of group 16 elements.

(g) The inert pair effect refers to the reluctance of the s-electrons (ns^2) to participate in bonding, which is particularly noticeable down a group in the p-block of the periodic table.

(h) CO_2 is a non-polar molecule because it is linear in shape, and the two polar $\text{C}=\text{O}$ bonds are equal in magnitude but opposite in direction, cancelling each other out.

(i) The melting point of CuCl is lower than that of KCl because CuCl has covalent character due to polarization of anion (Cl^-) by the Cu^+ ion, which weakens the lattice and hence, lowers the melting point.

(j) The equivalent conductance of an electrolyte solution is the conductance of all the ions produced by one gram equivalent of the electrolyte when present in a solution.

(k) The mixture in aqueous solution that would act as a buffer solution is $\text{CH}_3\text{COOH} + \text{NaOH}$ (2 : 1 molar ratio). This is because it forms a weak acid (acetic acid) and its conjugate base (acetate ion), which is the requirement for a buffer solution.

(l) An aqueous solution of sodium acetate is basic in nature because it is the salt of a weak acid (acetic acid) and a strong base (sodium hydroxide). In water, it hydrolyzes to produce acetate ions, which react with water to produce OH^- ions, making the solution basic.

(m) A calomel electrode is a type of reference electrode used in electrochemical measurements to establish a stable reference potential. It is made up of a mercury-mercurous chloride ($\text{Hg}/\text{Hg}_2\text{Cl}_2$) electrode in contact with a solution of potassium chloride (KCl)².

(n) The pH scale is a logarithmic scale used to specify the acidity or basicity of an aqueous solution. It is defined as the negative logarithm (base 10) of the activity of the hydrogen ion (H^+).

(o) Dry ether is used as a solvent during the preparation of Grignard reagent because it can solvate the Grignard reagent, forming a stable complex, and it is non-acidic (aprotic), so it does not react with the Grignard reagent³.

(p) The active electrophile in the nitration reaction of benzene with mixed acid is the nitronium ion (NO_2^+)⁴.

(q) Benzene can be prepared from phenol through its reduction. In this process, vapors of phenol are passed over heated zinc dust, which reduces them to form benzene⁵.

® Cyanobenzene can be prepared from aniline using the Sandmeyer reaction. In this reaction, aniline is first diazotized to form a diazonium salt, which is then treated with copper(I) cyanide to replace the diazonium group with a cyanide group, forming cyanobenzene⁶.

(s) Anhydrous AlCl_3 must be used in Friedel-Crafts reactions because it acts as a Lewis acid, accepting a chloride ion from the incoming electrophile and making the electrophile more electrophilic, which facilitates the attack on the aromatic ring⁷.

(t) Benzene can be brominated by treating it with bromine in the presence of a Lewis acid catalyst such as FeBr_3 . The bromine replaces one of the hydrogen atoms on the benzene ring in an electrophilic aromatic substitution reaction⁸.

(u) The hybridization state of 'S' in SF_6 molecule is sp^3d^2 ⁹.

(v) Kohlrausch's law of independent migration of ions states that the limiting molar conductivity of an electrolyte at infinite dilution is equal to the sum of the individual limiting molar conductivities of the cations and anions that make up the electrolyte¹⁰.

(w) Among the given compounds, $(\text{C}_2\text{H}_5)_2\text{Zn}$ is not an organometallic compound. Organometallic compounds are generally defined as compounds which contain at least one metal-carbon (M-C) bond where the carbon is part of an organic group.

(x) The unit of cell constant is cm^{-1} . It is the reciprocal of the cell's geometric factor, which is the ratio of the distance between the electrodes to the area of the electrodes.

2.

(a) (a) According to Werner's theory, the central metal atom in coordination compounds exhibits two types of valencies: primary and secondary¹²³⁴⁵.

1. **Primary Valency:** These are the valencies that a metal exhibits in the formation of simple salts, such as CoCl_3 , NaCl , CuSO_4 , etc. In modern terminology, it represents the oxidation number of the metal. The primary valencies are ionizable, non-directional, and do not contribute to the geometry of the complex compound¹²³⁴⁵. For example, in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, the number of primary valencies is 3, corresponding to an oxidation state of $+3^1$.
2. **Secondary Valency:** These are the valencies satisfied by negative ions or neutral molecules, or both. In modern terminology, it represents the coordination number of the metal. Secondary valencies are non-ionizable, directional, and give definite geometry to the complex¹²³⁴⁵. For example, in $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, the coordination number is 6^1 .

So, in a coordination complex, the primary valency corresponds to the charge on the complex ion, while the secondary valency corresponds to the number of ligands attached to the central metal atom¹²³⁴⁵.

(b)

(i) **BCl_3 (Boron Trichloride):** According to the VSEPR theory, BCl_3 possesses a trigonal planar molecular geometry¹². The central atom, boron, forms three σ sp-p bonds with the three chlorine atoms surrounding it. Each chlorine atom uses its half-filled p-orbital for the σ -bond formation. Thus, the Cl-B-Cl bond angle is 120° degrees¹².

(ii) **NH_3 (Ammonia):** In the NH_3 molecule, there are 8 electrons (four electron pairs) in the valence shell of the nitrogen atom i.e., five nitrogen atoms and one of each of three H atoms. The expected geometry of the molecule is tetrahedral with a bond angle of $109^\circ 28'$ ⁴³. However, due to the presence of a lone pair of electrons on the nitrogen atom, the actual shape of NH_3 is trigonal pyramidal⁴⁵. The lone pair-bond pair repulsion is more than bond pair-bond pair repulsion, which results in a slightly smaller H-N-H bond angle of about 107° ⁴⁵.

(d)

(d) The degree of hydrolysis (h) of a 0.1 M sodium acetate solution can be calculated using the formula:

$$h = \sqrt{\frac{K_h}{C}}$$

where K_h is the hydrolysis constant and C is the concentration of the solution ¹.

The hydrolysis constant K_h for a salt of a weak acid and a strong base is given by:

$$K_h = \frac{K_w}{K_a}$$

where K_w is the ion product of water (1×10^{-14} at 25°C) and K_a is the acid dissociation constant ¹. Given that K_a for acetic acid is 1, we can calculate K_h as follows:

$$K_h = \frac{1 \times 10^{-14}}{1} = 1 \times 10^{-14}$$

Substituting $K_h = 1 \times 10^{-14}$ and $C = 0.1$ M into the formula for h , we get:

$$h = \sqrt{\frac{1 \times 10^{-14}}{0.1}} = \sqrt{1 \times 10^{-15}} = 1 \times 10^{-7.5}$$

So, the degree of hydrolysis of a 0.1 M sodium acetate solution at 25°C is $1 \times 10^{-7.5}$ ¹.

(e) (e) Among electrophilic substitution and nucleophilic substitution reactions, electrophilic substitution is the most common for an aromatic system¹²³⁴.

Aromatic compounds, such as benzene, are rich in electrons due to the delocalization of the electrons in the pi bond. Therefore, they can donate electrons to an electrophile, which is an atom or a molecule that does not contain electrons¹². This makes aromatic compounds nucleophilic, tending to attract the positive center of the electrophile, which has fewer electrons².

In contrast, nucleophilic aromatic substitution is less common because it requires the aromatic compound to be electron-deficient, hence electrophilic². This is usually achieved by the presence of electron-withdrawing groups in the ring, which is not a typical characteristic of most aromatic compounds².

Therefore, electrophilic aromatic substitution is more common for an aromatic system¹²³⁴.

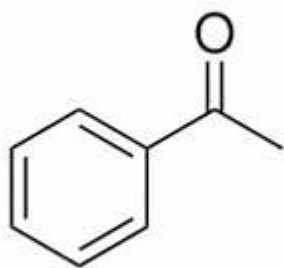
(f) The Reformatsky reaction, named after Russian chemist Sergey Nikolaevich Reformatsky, is an organic reaction that condenses aldehydes or ketones with α -halo esters using metallic zinc to form β -hydroxy-esters¹²³⁴.

The organozinc reagent, also known as a 'Reformatsky enolate', is prepared by treating an alpha-halo ester with zinc dust¹²³⁴. This reaction allows the generation of an enolate without using a Bronsted base, which would normally condense with the ketone or aldehyde itself².

The reaction begins with the oxidative addition of the zinc metal to the carbon-halogen bond of the α -haloester¹²³⁴. After insertion, the compounds coordinate with each other, leading to the formation of a dimer. This compound further undergoes a rearrangement, resulting in the formation of two zinc enolates².

Then, the oxygen of the ketone or aldehyde coordinates to the zinc, and a new rearrangement is formed where the two reagents now have a carbon-carbon bond between them². Following that, an acid workup splits the zinc and oxygen bond to generate zinc (II) salt and β -hydroxy ester as the final products².

The Reformatsky reaction is particularly useful because it can be conducted with highly hindered ketones, and it facilitates the successful addition of nucleophiles to the delta positive carbon atom of a ketone². The product α -hydroxy esters are important substances required for natural product synthesis and in pharmaceuticals².



(g)

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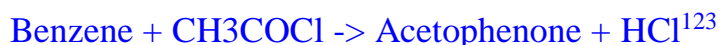
(g) Acetophenone can be prepared from benzene using a Friedel-Crafts acylation reaction¹²³. This is a type of electrophilic aromatic substitution reaction where

benzene reacts with acetyl chloride in the presence of anhydrous aluminum chloride¹²³.

The mechanism of this reaction involves the following steps:

1. **Formation of Acylium Ion:** The acetyl chloride (CH_3COCl) reacts with the Lewis acid catalyst, aluminum chloride (AlCl_3), to form an acylium ion (CH_3CO^+) and AlCl_4^- ³⁴⁵.
2. **Electrophilic Attack:** The benzene ring, acting as a nucleophile, attacks the electrophilic acylium ion. This forms a cyclohexadienyl cation, which is resonance-stabilized³⁴⁵.
3. **Deprotonation:** A base (AlCl_4^-) abstracts a proton from the cyclohexadienyl cation, restoring aromaticity to the benzene ring and regenerating the AlCl_3 catalyst³⁴⁵.

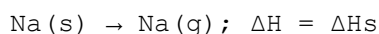
The overall reaction is:



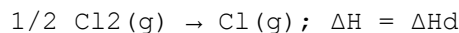
This results in the formation of acetophenone ($\text{C}_6\text{H}_5\text{COCH}_3$), with the acetyl group (CH_3CO) substituting one of the hydrogen atoms on the benzene ring¹²³.

(h) The Born-Haber cycle for the formation of NaCl involves several steps¹²:

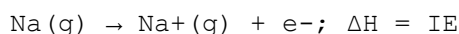
1. **Sublimation of Sodium:** Solid sodium (Na) is converted into gaseous sodium atoms. This step is endothermic and requires an input of energy, known as the enthalpy of sublimation (ΔH_s)².



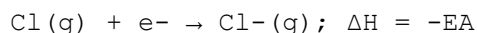
2. **Dissociation of Chlorine:** Chlorine molecules are dissociated into chlorine atoms. This step is also endothermic and requires an input of energy, known as the enthalpy of dissociation (ΔH_d)².



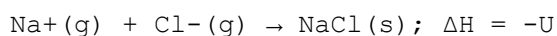
3. **Ionization of Sodium:** Gaseous sodium atoms are ionized to form sodium ions. This step is endothermic and requires an input of energy, known as the ionization energy (IE)².



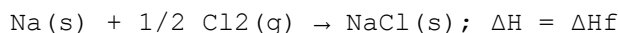
4. **Electron Affinity of Chlorine:** An electron is added to a chlorine atom to form a chloride ion. This step is exothermic and releases energy, known as the electron affinity (EA)².



5. **Formation of Sodium Chloride:** Sodium ions and chloride ions combine to form solid sodium chloride. This step is exothermic and releases energy, known as the lattice energy (U)².



The overall reaction is:



Where ΔH_f is the enthalpy of formation of sodium chloride². The sum of the enthalpies of all these steps equals the enthalpy of formation of sodium chloride². This is an application of Hess's Law³⁴.

- (i) The molecular orbital (MO) diagram of O₂ is as follows¹²³⁴.

$\sigma 1s^2$
 $\sigma^* 1s^2$
 $\sigma 2s^2$
 $\sigma^* 2s^2$
 $\sigma 2p_z^2$
 $\pi 2p_x^2$
 $\pi 2p_y^2$
 $\pi^* 2p_x^1$
 $\pi^* 2p_y^1$

In this configuration, the last two electrons are unpaired and occupy the $\pi 2p_x$ and $\pi 2p_y$ orbitals¹²³⁴. The presence of these unpaired electrons makes O₂ paramagnetic¹²³⁴. Paramagnetic substances are attracted to magnetic fields due to their unpaired electrons¹²³⁴. Therefore, O₂ is attracted to a magnetic field because of its two unpaired electrons¹²³⁴.

- (j) Both PCl₃ and PCl₅ compounds are formed because phosphorus (P) is a period 3 element and has access to the 3d orbitals. This allows phosphorus to expand its octet and form five bonds in PCl₅¹².

On the other hand, nitrogen (N) is a period 2 element and does not have access to d orbitals. Therefore, it follows the octet rule and can form a maximum of four bonds, which is why only NCl₃ is formed and NCl₅ does not exist¹². Nitrogen's inability to access d orbitals and expand its octet is due to the energy required to promote an electron to the 3d orbital being too high¹².

- (k) The mechanism of electrophilic substitution reaction of benzene generally involves three steps¹²³⁴:

1. **Generation of Electrophile:** In the presence of a Lewis acid, an electrophile is generated. The Lewis acid accepts the electron pair from the attacking reagent¹²³⁴.

2. **Formation of Arenium Ion:** The generated electrophile attacks the benzene ring to form a positively charged cyclohexadienyl cation, better known as an arenium ion, which contains one sp³ hybridized carbon atom¹²³⁴. The positive charge is effectively distributed over three carbon atoms by resonance, which makes it partially stable¹²³⁴. As the delocalization of electrons stops at an sp³ hybridized carbon atom, the arenium ion is not aromatic in nature¹²³⁴.
3. **Removal of Positive Charge from the Carbocation Intermediate:** The arenium ion finally loses its proton from the sp³ hybridized carbon to a Lewis base, restoring the aromaticity¹²³⁴.

This mechanism is applicable to various electrophilic aromatic substitution reactions such as nitration, sulfonation, halogenation, and Friedel-Crafts alkylation and acylation¹²³⁴.

(I) Faraday's laws of electrolysis are two scientific laws based on the electrochemical research of Michael Faraday from 1833¹²³⁴. These laws describe the relationship between the amount of substance deposited at electrodes and the quantity of electric charge or electricity passed¹²³⁴.

1. **Faraday's First Law of Electrolysis:** This law states that the mass of a substance deposited at any electrode is directly proportional to the amount of charge passed¹²³⁴. Mathematically, it can be expressed as follows⁴:

$$m \propto Q$$

where:

- m is the mass of a substance (in grams) deposited or liberated at an electrode,
 - Q is the amount of charge (in coulombs) or electricity passed through it.
2. **Faraday's Second Law of Electrolysis:** This law states that the amounts of chemical changes produced by the same quantity of electricity in different substances are proportional to their equivalent weights¹²³⁴.

These laws of electrolysis show that the amount of electricity needed for oxidation-reduction depends on the stoichiometry of the electrode reaction².

(m) Friedel-Crafts acylation is often preferred over Friedel-Crafts alkylation for several reasons¹²³:

- Better control over the reaction products: In acylation, the acylium ion is stabilized by resonance, so there are no chances of rearrangement¹²³.
- The ketones produced in acylation can be reduced to alkyl groups¹²³.

(n) A buffer solution is an aqueous solution that consists of a mixture of a weak acid and its salt (acid buffer) or a weak base with its salt (basic buffer). Its pH changes very little when a small amount of strong acid or base is added to it and is thus used to prevent a solution's pH change⁴⁵⁶⁷. An example of an acidic buffer is a mixture of acetic acid and its salt, sodium acetate.

(o) The relation between molar conductance (Λ_m) and specific conductance (K) is given by the formula⁸⁹¹⁰¹¹:

$$\Lambda_m = (K \times 1000) / c$$

where:

- Λ_m is the molar conductance,
- K is the specific conductance,
- C is the molar concentration.

(p) The complex $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$ can exist in two isomeric forms¹²¹³¹⁴¹⁵¹⁶:

- **cis isomer:** The two chloride ions are adjacent to each other on the cobalt atom.
- **trans isomer:** The two chloride ions are opposite to each other on the cobalt atom.

(q) The common ion effect refers to the decrease in solubility of an ionic precipitate by the addition to the solution of a soluble compound with an ion in common with the precipitate¹⁷¹⁸¹⁹²⁰. For example, if we have a solution of silver chloride (AgCl) and we add some sodium chloride (NaCl) to it, the chloride ions from the NaCl will cause the AgCl to precipitate out of solution because AgCl is less soluble in a solution that already contains chloride ions.

@ TiCl_2 is paramagnetic because titanium in its +2 oxidation state has two unpaired electrons in its d orbitals¹²³. On the other hand, TiO_2 is diamagnetic because titanium in its +4 oxidation state has all its d orbitals fully filled, with no unpaired electrons¹²³.

(s) Transition metals have a tendency to form complexes due to several reasons²¹²²²³²⁴²⁵:

- Small size and high nuclear charge of these metals.
- Availability of vacant d-orbitals of suitable energy to accommodate lone pairs of electrons donated by the ligands.