Question Set 4

GIVE REASONS

Q. Give reasons : ***(1 mark each)***

[**Note :** Write the answer in points or different paragraphs. Write balanced equations for the reactions if necessary.]

Chapter 1. Solid State

(1) Why does a crystalline solid has a sharp melting point ?

Ans. (1) Crystalline solid is a homogeneous solid and it has long range order of regular pattern of arrangement which repeats periodically over entire crystal.

(2) The interatomic or intermolecular forces are identical, hence the thermal energy required to break the regular structure by overcoming the intermolecular forces is uniform throughout.

(3) Hence the heat and temperature needed to melt the solid are same, and therefore solids have sharp melting points.

Chapter 2. Solutions

(2) Why does the solubility of a gas decrease with increase in temperature ?

Ans. (1) The gases are soluble in water and other liquids.

(2) According to Charles' law, the volume of a given mass of a gas increases with the increase in temperature at constant pressure.

(3) Hence, the volume of the dissolved gas increases with the increase in temperature.

(4) This enormous increase in volume of the gases cannot be accommodated by the solvent molecules, hence excess of the gases escape out in the form of bubbles.

Therefore, the solubility of gases in liquids decreases with temperature.

(3) Why does the solubility of a gas increase with increase in pressure?

Ans. (1) With the increase in pressure, more gas molecules are accommodated in the vacant spaces or holes of a liquid.

(2) Therefore with the increase in pressure, the solubility of a gas in a liquid increases.

(4) The osmotic pressure of a solution of an electrolyte is higher than theoretical value. Explain.

Ans. (1) Due to the dissociation of an electrolyte in a solution, the number of particles like ions is increased.

(2) Osmotic pressure of a solution is a colligative property.

(3) Hence, osmotic pressure of an electrolytic solution is higher than theoretical value.

Chapter 3. Ionic Equilibria

(5) Why are cations Lewis acids and anions Lewis bases?

Ans. (1) Since cations are deficient of electrons, they accept a pair of electrons, hence they are Lewis acids.

(2) Since anions are rich in electrons, they donate a pair of electrons, hence they are Lewis bases.

(6) Aqueous solution of sodium carbonate is alkaline whereas aqueous solution of ammonium chloride is acidic. Explain.

Ans.

(A) (i) Sodium carbonate is a salt of weak acid and strong base.

(ii) In aqueous solution it undergoes hydrolysis.

$$\underset{\text{salt}}{Na_2CO_{3(aq)}} + 2H_2O_{(l)} \rightleftharpoons \underset{\text{strong base}}{2NaOH_{(aq)}} + \underset{\text{weak acid}}{H_2CO_{3(aq)}}$$

$$2Na^{+}_{(aq)} + CO^{2-}_{3(aq)} + 2H_2O_{(l)} \rightleftharpoons 2Na^{+}_{(aq)} + 2OH^{-}_{(aq)} + H_2CO_{3(aq)}$$

(iii) Strong base dissociates completely while weak acid dissociates partially hence, $[OH^-] > [H_3O^+]$ and the solution is basic.

(B) (i) Ammonium chloride is a salt of strong acid and weak base.

(ii) In aqueous solution it undergoes hydrolysis

$$\underset{\text{salt}}{NH_4Cl_{(aq)}} + H_2O_{(l)} \rightleftharpoons \underset{\text{weak base}}{NH_4OH_{(aq)}} + \underset{\text{strong acid}}{HCl_{(aq)}}$$

$$NH^{+}_{4(aq)} + Cl^{-}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^{+}_{(aq)} + Cl^{-}_{(aq)}$$

(iii) Since $[H^+]$ or $[H_3O^+] > [OH^-]$ the solution is acidic.

(7) Why is KCl solution neutral to litmus ?

Ans. (1) Since KCl is a salt of strong base KOH and strong acid HCl, it does not undergo hydrolysis in its aqueous solution.

(2) Due to strong acid and strong base, concentrations $[H_3O^+] = [OH^-]$ and the solution is neutral.

(8) Homemade jams or jellies spoil in a few days whereas commercial jams and jellies have a long life. Explain.

Ans. (1) To maintain the pH constant, sodium benzoate is added to commercial jams and jellies which also acts as a preservative.

(2) Such preservatives are not added in homemade jams and jellies.

(3) Therefore, homemade jams and jellies spoil in a few days while commercial products have a long life.

(9) Why is it necessary to add H_2SO_4 while preparing the solution of $CuSO_4$?

Ans. $CuSO_4$ is a salt of strong acid H_2SO_4 and weak base $Cu(OH)_2$. $CuSO_4$ in aqueous solution undergoes hydrolysis and forms a precipitate of $Cu(OH)_2$ and solution becomes turbid.

$$CuSO_4 + 2H_2O \rightleftharpoons Cu(OH)_2\downarrow + H_2SO_4 \qquad \text{OR}$$

$$CuSO_4 + 4H_2O \rightleftharpoons \underset{\text{turbidity}}{Cu(OH)_2} + 2H_3O^+ + SO_4^{2-}$$

When H_2SO_4 is added, the hydrolysis equilibrium is shifted to left hand side and $Cu(OH)_2$ dissolves giving clear solution.

Chapter 4. Chemical Thermodynamics

(10) Comment on the statement : No work is involved in an expansion of a gas in vacuum.

Ans. (1) When a gas expands against an external pressure P_{ex}, changing the volume from V_1 to V_2, the work obtained is given by

$W = -P_{ex}\ (V_2 - V_1)$.

(2) Hence the work is performed by the system when it experiences the opposing force or pressure.

(3) Greater the opposing force, more is the work.

(4) In free expansion, the gas expands in vacuum where it does not experience opposing force, (P = 0). Since external pressure is zero, no work is obtained.

$$\begin{aligned} \therefore\ W &= -P_{ex}\ (V_2 - V_1) \\ &= -0 \times (V_2 - V_1) \\ &= 0 \end{aligned}$$

(5) Since during expansion in vacuum no energy is expended, it is called free expansion.

(11) In the conversion of a solid into a liquid and further into a vapour, entropy increases. Explain.

Ans. (1) When a solid is heated it melts and forms a liquid and further vapour.

(2) When solid melts forming a liquid or when a liquid vaporises, the constituents are separated and are in random motion imparting maximum disorder.

(3) Since entropy is a measure of disorder, the entropy of the system increases.

Chapter 5. Electrochemistry

(12) Explain the effect of dilution of solution on conductivity.

Ans. (1) The conductance of a solution is due to the presence of ions in the solution. More the ions, higher is the conductance of the solution.

(2) Conductivity or the specific conductance is the conductance of unit volume (1 cm^3) of the electrolytic solution.

(3) The conductivity of the electrolytic solution always decreases with the decrease in the concentration of the electrolyte or the increase in dilution of the solution.

(4) On dilution, the concentration of the solution decreases, hence the number of (current carrying) ions per unit volume decreases. Therefore the conductivity of the solution decreases, with the decrease in concentration or increase in dilution.

(13) What are the functions of a salt bridge?

Ans. The functions of a salt bridge are :

(1) It maintains the electrical contact between the two electrode solutions of the half cells.

(2) It prevents the mixing of electrode solutions.

(3) It maintains the electrical neutrality in both the solutions of two half cells by a flow of ions.

(4) It eliminates the liquid junction potential.

(14) Explain on the basis of standard reduction potentials, fluorine is a strong oxidising agent while potassium is a strong reducing agent.

Ans. (1) Fluorine has very high standard reduction potential (positive standard reduction potential).

(2) It has a strong tendency to accept electrons and get reduced.

(3) Hence, fluorine is a strong oxidising agent.

(4) Potassium has very low reduction potential (negative standard reduction potential).

(5) It has a strong tendency to donate electrons and get oxidised.

(6) Hence, potassium is a strong reducing agent.

Chapter 6. Chemical Kinetics

(15) Decomposition of $NH_{3(g)}$ on platinum surface at high temperature is a zero order reaction. Explain.

Ans. (1) The decomposition of $NH_{3(g)}$ on platinum surface is represented as,

$$2NH_{3(g)} \xrightarrow[\text{Pt}]{1130\text{ K}} N_{2(g)} + 3H_{2(g)}$$

(2) Since it is a heterogeneous catalysed reaction, gaseous molecules of NH_3 at high pressure are adsorbed on the metal surface covering the surface area.

(3) The number of NH_3 molecules adsorbed is small compared to NH_3 molecules in the gaseous phase.

(4) Only the molecules adsorbed on the surface get decomposed. Hence, the rate of the decomposition becomes independent of the concentration (pressure) of NH_3. Therefore, the decomposition reaction is a zero order reaction.

(16) Inversion of cane sugar (sucrose) is a pseudo-first order reaction. Explain.

Ans. The inversion of cane sugar (sucrose) is an acid catalysed hydrolysis reaction which can be represented as,

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11(aq)}} + H_2O_{(l)} \longrightarrow \underset{\text{glucose}}{C_6H_{12}O_{6(aq)}} + \underset{\text{fructose}}{C_6H_{12}O_{6(aq)}}$$

This is a bimolecular reaction. Hence, the true rate law for the reaction should be, Rate $= k[C_{12}H_{22}O_{11}][H_2O]$. This shows that the reaction should be second order.

Since water (H_2O) is in large excess, its concentration remains constant and the rate depends only upon the concentration of cane sugar.

$\therefore$ Rate $= k[C_{12}H_{22}O_{11}]$

Therefore, the second order true rate law becomes first order rate law. Hence, the inversion of cane sugar is a pseudo-first order reaction.

(17) The catalysed decomposition of nitrous oxide (N_2O) to nitrogen and oxygen is a zero order reaction. Explain.

Ans. (1) The decomposition of $N_2O_{(g)}$ on platinum can be represented as, $2N_2O_{(g)} \xrightarrow{Pt} 2N_{2(g)} + O_{2(g)}$

(2) Since it is a heterogeneous catalysed reaction, N_2O gaseous molecules are adsorbed on the metal surface covering the surface area.

(3) The number of N_2O molecules adsorbed is small compared to N_2O molecules in the gaseous phase.

(4) Only the molecules adsorbed on the metal surface get decomposed. Hence rate of decomposition becomes independent of the concentration (pressure) of N_2O. Therefore the decomposition of N_2O is a zero order reaction.

Chapter 7. Elements of Groups 16, 17 and 18

(18) The first ionisation enthalpies of S, Cl and Ar are 1000, 1256 and 1520 kJ mol^{-1}, respectively. Explain the observed trend.

Ans. (1) The atomic number increases as,

${}_{16}S < {}_{17}Cl < {}_{18}Ar$.

(2) Due to decrease in atomic size and increase in effective nuclear charge, Cl binds valence electrons strongly.

(3) Hence ionisation enthalpy of Cl (1256 kJ mol^{-1}) is higher than that of S (1000 kJ mol^{-1}).

(4) Ar has electronic configuration $3s^2 3p^6$. Since all electrons are paired and octet is complete, it has the highest ionisation enthalpy, (1520 kJ mol^{-1}).

(19) Why oxygen has less negative electron gain enthalpy than sulphur ?

Ans. (1) Oxygen has a smaller atomic size than sulphur.

(2) It is more electronegative than sulphur.

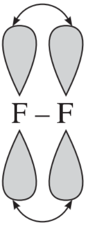
(3) It has a larger electron density.

(4) Due to high electron density, oxygen does not accept the incoming electron easily and therefore has less electron gain enthalpy than sulphur.

(20) Why is bond dissociation enthalpy of F_2 (158.8 kJ mol^{-1}) lower than that of Cl_2 (242.6 kJ mol^{-1}) ?

Ans. Fluorine has small atomic size than chlorine. The lone pairs on each F atom in F_2 molecule are so close together that they strongly repel each other, and make the F – F bond weak. Thus, it requires less amount of energy to break the F – F bond. In Cl_2 molecule the lone pairs on each Cl atom are at a larger distance and the repulsion is less. Thus, Cl – Cl bond is comparatively stronger.

Therefore, bond dissociation enthalpy of F_2 is lower than that of Cl_2.



lone pair – lone pair repulsion

(21) Why does fluorine show anomalous behaviour ?

Ans. Fluorine exhibits anomalous behaviour as compared to other halogens in the group.

The reasons for anomalous behaviour of fluorine are as follows :

(1) the smallest size of fluorine

(2) the highest electronegativity

(3) low bond dissociation enthalpy of F–F bond

(4) non-availability of *d*-orbitals in its valence shell.

(22) Chlorine acts as a powerful oxidising agent. Explain.

Ans. (1) Chlorine acts as a powerful bleaching agent due to its oxidising nature.

(2) In moist condition or in the presence of water it forms unstable hypochlorous acid, HOCl which decomposes giving nascent oxygen which

oxidises the vegetable colouring matter of green leaves, flowers, litmus, indigo, etc.

$Cl_2 + H_2O \longrightarrow HCl + HOCl$

$HOCl \longrightarrow HCl + [O]$

Vegetable coloured matter + [O] $\longrightarrow$ colourless matter.

Chapter 8. Transition and Inner Transition Elements

(23) Why is manganese more stable in the $+2$ state than the $+3$ state ?

Ans. (1) The electronic configuration of Mn is $_{25}Mn$ [Ar] $3d^5\ 4s^2$.

(2) In $+2$ and $+3$ oxidation states, the electronic configuration of Mn is, Mn^{2+} [Ar] $3d^5$ and Mn^{3+} [Ar] $3d^4$.

(3) Since half-filled *d*-orbital ($3d^5$) has more stability and lower energy than $3d^4$, Mn^{2+} is more stable than Mn^{3+}.

(24) Iron exhibits $+2$ and $+3$ oxidation states. Write their electronic configuration. Which will be more stable ? Why ?

Ans. The electronic configuration of Fe^{2+} and Fe^{3+} :

Fe^{2+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6$

Fe^{3+} : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5$

Due to loss of two electrons from the 4*s*-orbital and one electron from 3*d*-orbital, iron attains $+3$ oxidation state. Since in Fe^{3+}, the 3*d*-orbital is half filled, it gets extra stability, hence, Fe^{3+} is more stable than Fe^{2+}.

(25) Why do the *d*-block elements form coloured compounds ?

Ans. (1) Compounds (or ions) of many *d*-block elements or transition metals are coloured.

(2) This is due to the presence of one or more unpaired electrons in $(n-1)$ *d*-orbital. The transition metals have incompletely filled $(n-1)$ *d*-orbitals.

(3) The energy required to promote one or more electrons within the *d*-orbitals involving *d*-*d* transitions is very low.

(4) The energy changes for *d*-*d* transitions lie in visible region of electromagnetic radiation.

(5) Therefore transition metal ions absorb the radiation in the visible region and appear coloured.

(6) Colour of ions of *d*-block elements depends on the number of unpaired electrons in $(n-1)$ *d*-orbital. The ions having equal number of unpaired electrons have similar colour.

(7) The colour of metal ions is complementary to the colour of the radiation absorbed.

(26) Why are zinc salts colourless?

Ans. (1) Colour of the ions of *d*-block elements depends on the number of unpaired electrons in $(n-1)$ *d*-orbitals.

(2) Zinc forms salts of Zn^{2+} ions.

(3) The electronic configuration of Zn^{+2} is [Ar] $3d^{10}$.

(4) Since Zn^{+2} does not have unpaired electrons in 3*d*-orbital, $d \rightarrow d$ transition cannot take place, hence, Zn^{+2} ions form colourless salts.

(27) *d*-block elements are good catalysts. Explain.

Ans. (1) *d*-block elements or transition metals and their compounds or complexes influence the rate of a chemical reaction and hence act as catalysts.

(2) In homogeneous catalysis a catalyst forms an unstable intermediate compound which decomposes into products and regenerates the catalyst. But transition metals involve heterogeneous catalysis.

(3) The transition metals have incompletely filled *d*-subshells which adsorb reactants on the surface and provide large surface area for the reactants to react.

(4) Since transition metals have variable oxidation states they are very good catalysts.

(5) Hence, compounds of Fe, Co, Ni, Pt, Pd, Cr, etc. are used as catalysts in many reactions.

(28) Why is Sc^{3+} colourless ?

Ans. (1) The electronic configuration of $_{21}Sc$ is, [Ar] $3d^{1}4s^{2}$ and Sc^{3+} [Ar] d^{0}.

(2) Since there are no unpaired electrons in 3*d*-subshell, $d \rightarrow d$ transition is not possible.

(3) Therefore, Sc^{3+} ions do not absorb the radiations in the visible region. Hence salts of Sc^{3+} are colourless (or white).

(29) Why does copper show abnormal electronic configuration?

Ans. Copper ($_{29}Cu$) has electronic configuration,

$_{29}$Cu (Expected) : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$

(Observed) : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$

Explanation :

(1) The energy difference between 3*d*- and 4*s*-orbitals is very low.

(2) *d*-orbitals being degenerate, they acquire more stability when they are completely filled.

(3) Therefore, there arises a transfer of one electron from 4*s*-orbital to 3*d*-orbital in Cu giving completely filled more stable *d*-orbital.

Hence, the configuration of Cu is [Ar] $3d^{10}\ 4s^1$ and not [Ar] $3d^9\ 4s^2$.

(30) Why is Gd^{3+} colourless ?

Ans. (1) Gd^{3+} has electronic configuration, [Xe] $4f^7$.

(2) Due to extra stability of half-filled orbital, it does not allow $f \rightarrow f$ transition, and hence does not absorb radiations in the visible region.

Hence, Gd^{3+} is colourless.

Chapter 9. Coordination Compounds

(31) On the basis of Werner's theory explain, why cobalt amine complex, $CoCl_3 4NH_3$ when treated with $AgNO_3$ solution precipitates only one Cl^- ion even though there are three Cl^- ions.

Ans. The complex, $CoCl_3 4NH_3$ with $AgNO_3$ solution precipitates only one Cl^- ion.

$$CoCl_3 4NH_3 \xrightarrow{AgNO_3 \text{ soln}} \underset{\text{ppt}}{AgCl}$$

This indicates that, on ionisation the complex gives only one Cl^-. Hence according to Werner's theory, out of $3Cl^-$, there will be $2Cl^-$ in the coordination sphere as ligands and one Cl^- in the ionisation sphere or outer sphere.

Hence the formula of the complex must be $[Co(NH_3)_4Cl_2]Cl$.

$$[Co(NH_3)_4Cl_2]Cl \longrightarrow [Co(NH_3)_4Cl_2]^+ + Cl^-$$

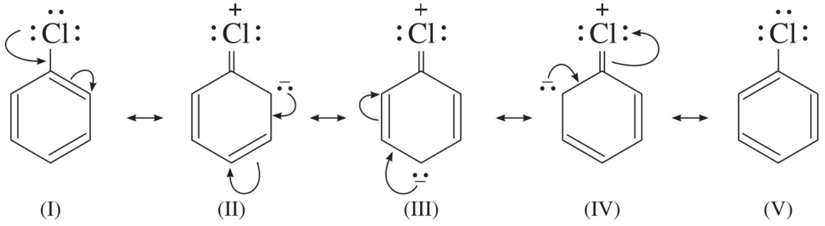
$$AgNO_3 + Cl^- \longrightarrow \underset{\text{ppt}}{AgCl} + NO_3^-$$

Chapter 10. Halogen Derivatives

(32) Haloarenes are less reactive than haloalkanes.

Ans. Haloarenes (Aryl halides) are less reactive than (alkyl halides) haloalkanes due to the following reasons :

(1) Resonance effect : In haloarenes, the electron pairs on halogen atom are in conjugation with π-electrons of the benzene ring. The delocalization of these electrons C–Cl bond acquires partial double bond character.



Due to partial double bond character of C–Cl bond in aryl halides, the bond cleavage in haloarene is difficult and are less reactive. On the other hand, in alkyl halides, carbon is attached to chlorine by a single bond and it can be easily broken.

(2) Aryl halides are stabilized by resonance but alkyl halides are not. Hence, the energy of activation for the displacement of halogen from aryl halides is much greater than that of alkyl halides.

(3) Different hybridization state of carbon atom in C–X bond :

(i) In alkyl halides, the carbon of C–X bond is sp^3-hybridized with less s-character and greater bond length of 178 pm, which requires less energy to break the C–X bond.

(ii) In aryl halides, the carbon of C–X bond is sp^2-hybridized with more s-character and shorter bond length which requires more energy to break C–X bond. Therefore, aryl halides are less reactive than alkyl halides.

(iii) Polarity of the C–X bond : In aryl halide C–X bond is less polar than in alkyl halides. Because sp^2-hybrid carbon of C–X bond has less tendency to release electrons to the halogen than a sp^3-hybrid carbon in alkyl halides. Thus, halogen atom in aryl halides cannot be easily displaced by nucleophile.

(33) Reactions involving Grignard reagent must be carried out under anhydrous condition.

Ans. (1) Grignard reagent (RMgX) is an organometallic compound. The carbon–magnesium bond is highly polar and magnesium–halogen bond is in ionic in nature. Grignard reagent is highly reactive.

(2) The reactions of Grignard reagent are carried out in dry conditions because traces of moisture may spoil the reaction and Grignard reagent reacts with water to produce alkane. Hence, reactions involving Grignard reagent must be carried out under anhydrous condition.

(34) Alkyl halides are generally not prepared by free radical halogenation of alkane.

Ans. (1) Free radical halogenation of alkane gives a mixture of all different possible monohaloalkanes as well as polyhalogen alkanes.

(2) In this method, by changing the quantity of halogen the desired product can be made to predominate over the other products. Hence, alkyl halides are generally not prepared by free radical halogenation of alkane.

Chapter 11. Alcohols, Phenols and Ethers

(35) Methanol is more soluble in water than propan-1-ol.

Ans. (1) Methanol being lower members of alcohols is more soluble in water, but as the size of an alkyl group or molecular weight of alcohol increases the solubility decreases.

(2) The solubility of methanol in water is due to polar characters of alcohols ($\mathrm{R}-\overset{-\delta}{\mathrm{O}}-\overset{+\delta}{\mathrm{H}}$) and water ($\overset{+\delta}{\mathrm{H}}-\overset{-\delta}{\mathrm{O}}-\overset{+\delta}{\mathrm{H}}$).

(3) The solubility of methanol is due to the formation of intermolecular hydrogen bonding between polar molecules of methyl alcohol and water. Hence, methyl alcohol is an associated liquid.

(4) In methyl alcohol, size of methyl group being very small, –OH group constitutes major part of the molecule giving more solubility. As size of alkyl group increases, the non-polar character increases the solubility decreases. Hence, methanol is more soluble in water than propan-1-ol.

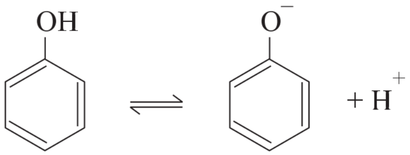
(36) Phenol is more acidic than ethyl alcohol.

Ans. (1) In ethyl alcohol, the –OH group is attached to sp^3-hybridized carbon while in phenols, it is attached to sp^2-hybridized carbon.

(2) Due to higher electronegativity of sp^2-hybridized carbon, electron density on oxygen decreases. This increases the polarity of O–H bond and results in more ionization of phenol than that of alcohols.

$$C_2H_5-\underset{\cdot\cdot}{\ddot{O}}-H \rightleftharpoons C_2H_5 \rightarrow \overset{-}{\underset{\cdot\cdot}{\ddot{O}}}: \;+ \overset{+}{H}$$

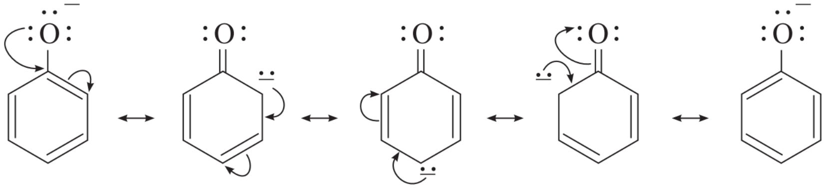
alkoxide ion



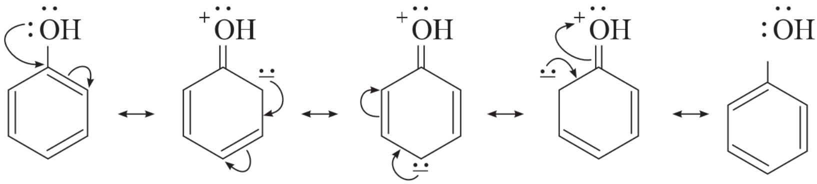
phenoxide ion

(3) Electron donating inductive effect (+ I effect) of the alkyl group destabilizes alkoxide ion. As a result alcohol does not ionize much in water, therefore, alcohol is neutral compound in aqueous medium.

(4) In alkoxide ion, the negative charge is localized on oxygen, while in phenoxide ion the negative charge is delocalized. The delocalization of the negative charge (structures I to V) makes phenoxide ion more stable than that of phenol.



(I) (II) (III) (IV) (V)



(VI) (VII) (VIII) (IX) (X)

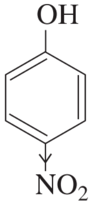
The delocalization of charge in phenol (structures VI to X), the resonating structures have charge separation (where oxygen atom of OH group to be positive and delocalization of negative charge over the ortho and para positions of aromatic ring) due to which phenol molecule is less stable than phenoxide ion. This favours ionization of phenol. Thus, phenols are more acidic than ethyl alcohol.

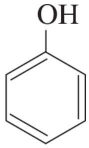
(37) *p*-Nitrophenol is a stronger acid than phenol.

Ans.(1) In ρ-nitrophenol, nitro group (NO_2) is an electron withdrawing group present at para position which enhances the acidic strength (–I effect).

The O–H bond is under strain and release of proton (H^+) becomes easy. Further ρ-nitrophenoxide ion is more stabilised due to resonance.

(2) Since the absence of electron withdrawing group (like $-NO_2$) in phenol at ortho and para position, the acidic strength of phenol is less than that of ρ-nitrophenol.

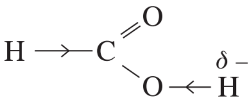




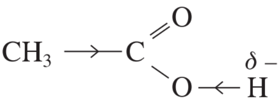
Chapter 12. Aldehydes, Ketones and Carboxylic Acids

(38) Formic acid is stronger than acetic acid.

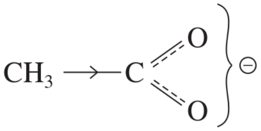
Ans.



Formic acid



Acetic acid



Destabilization of anion

In acetic acid, methyl group is an electron donating group. The acetate ion formed gets destabilized due to electron releasing effect of methyl group (+ I effect) which is higher than that of H-atom in the corresponding formic acid. As a result, acetic acid dissociates to a lesser extent. Thus, decreasing the acidity of acetic acid.

$$CH_3-COOH+H_2O \rightleftharpoons CH_3-COO^- + H_3O^+$$

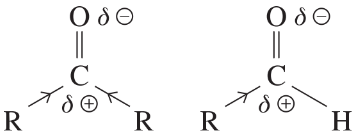
Formic acid having lower pK_a value than acetic acid. Hence, formic acid is a stronger acid than acetic acid.

(39) Aldehydes are more reactive toward nucleophilic addition reaction than ketones.

Ans. The reactivity of aldehydes and ketones is due to the polarity of carbonyl group which results in electrophilicity of carbon. The reactivity is further explained on the basis of electronic effect and steric effects.

(1) **Influence of electronic effects :** A ketone has two electron donating alkyl groups (+ I effect) bonded to carbonyl carbon which are responsible for decreasing its positive polarity and electrophilicity. In contrast, aldehydes have only electron donating group bonded to carbonyl carbon. This shows aldehydes are more electrophilic than ketones.

(2) **Steric effects :** Two bulky alkyl groups in ketone come in the way of incoming nucleophile. This is called steric hindrance to nucleophilic attack.



(Ketone) (Aldehyde)

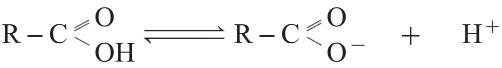
On the other hand, nucleophile can easily attack the carbonyl carbon in aldehyde because it has one alkyl group and is less crowded or sterically less hindered. Hence, aldehyde are more reactive and can easily attacked by nucleophiles.

(40) Aldehydes give positive test for Fehling's solution while ketones give negative test.

Ans. Aldehydes can be oxidised to their corresponding carboxylic acids by Fehling's solution but ketones cannot be oxidised hence ketones give negative test for Fehling's solution.

(41) Carboxylic acid gives acidic test.

Ans. Carboxylic acid contains carboxyl $\left(-C \genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH} \right)$ group. This group is capable of dissociating giving stable carboxylate ion (due to resonance) and H^+.



$$R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow OH} \rightleftharpoons R-C\genfrac{}{}{0pt}{}{\nearrow O}{\searrow O^-} + H^+$$

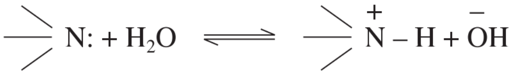
carboxylic acid carboxylate ion

Therefore, carboxylic acid gives acidic test.

Chapter 13. Amines

(42) Amines are weak bases.

Ans. The basic strength of amines is expressed in terms of K_b or $_pK_b$ value. According Lowry-Bronsted theory the basic nature of amines is explained by the following equilibrium equation.



Amine Conjugate acid

In this equilibrium amine accepts H^+, hence an amine is a Lowry-Bronsted base.

According to Lewis theory, the species which donates a pair of electrons is called a base.

The nitrogen atom in amines has a lone pair of electrons, which can be donated to suitable acceptor like proton H^+ .

The aqueous solutions of amines are basic in nature due to release of free OH^- ions in solutions. Hence amines are Lewis bases. There exists an equilibrium in their aqueous solutions as follows :

$$R - \ddot{N}H_2 + H_2O \rightleftharpoons R\overset{+}{N}H_3 + OH^-$$

Since OH^- is a stronger base, equilibrium shifts towards left hand side giving less concentration of OH^-.

Here, K_b value is smaller and ${}_pK_b$ value is larger.

Hence, amines are weak bases.

(43) Primary or aliphatic amine is a stronger base than ammonia.

Ans. (1) The alkyl group in primary amines has $+I$ effect, i.e. (electron releasing).

$R - \ddot{N}H_2 \quad \ddot{N}H_3$

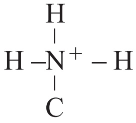
The alkyl group tends to increase the electron density on the nitrogen atom. As a result, amines can donate the lone pair of electrons on nitrogen more easily than ammonia.

(2) The amine being a base, can donate a pair of electrons to an acid. The alkyl group with $+I$ effect will disperse the positive charge on the cation more than ammonia.

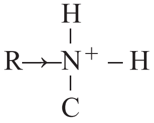
$$R\ddot{N}H_2 \xrightarrow{H^+} [RNH_3]^+$$

Alkyl amine Alkyl ammonium ion

$\ddot{N}H_3 + H^+ \longrightarrow NH_4^+$



$$H-\overset{\overset{H}{|}}{\underset{\underset{C}{|}}{N^+}}-H$$



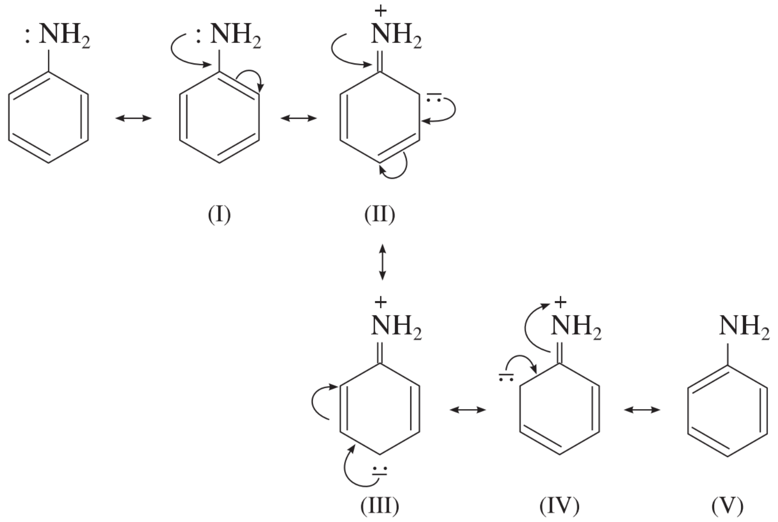
$$R\rightarrow\overset{\overset{H}{|}}{\underset{\underset{C}{|}}{N^+}}-H$$

Ammonia Ammonium ion $+I$ effect

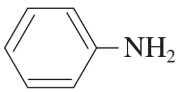
Due to $+I$ effect of alkyl group cation formed by primary amine is more stable compared to cation formed from ammonia. Also it is seen that observed increasing basic strength from ammonia to primary amine is explained on the basis of increased stabilization of conjugate acids by $+I$ effect for the presence of alkyl (R) groups. Hence, primary or aliphatic amine is a stronger base than ammonia.

(44) Aniline is less basic than ammonia.

Ans. Less basic character of aniline can be explained on the basis of resonance shown by aniline.

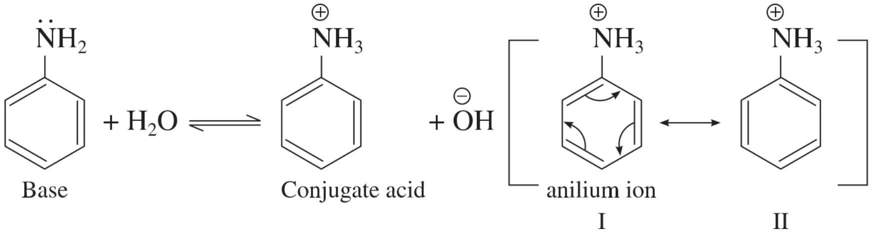


NH_3



$K_b = 1.8 \times 10^{-5}$ $\quad$ $K_b = 4.2 \times 10^{-10}$

Due to resonance, the nitrogen atom of amino group in aniline acquires a positive charge, hence, lone pair of electrons is less available for protonation as compared to that of ammonia. Aniline is resonance stabilized by five resonance structures. On the other hand, aniline in aqueous medium, accepts a proton does not have lone pair of electrons on nitrogen to produce a very low concentration of anilium ion and anilium ion shows only two resonance structures and therefore less stabilized than aniline.



Thus, aniline is more stable than anilium ion. Hence, aniline accepts proton less readily or less basic in nature than ammonia.

(45) The disaccharide sucrose gives negative Tollens test while the disaccharide maltose gives positive Tollen's test.

Ans. (1) In disaccharide sucrose, the reducing groups of glucose and fructose are involved in glycosidic bond formation, sucrose is a non-reducing sugar. As there is no free aldehyde group, it does not reduce Tollen's reagent to metallic silver. Hence, sucrose gives negative Tollen's test.

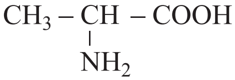
(2) While the disaccharide maltose is a reducing sugar because a free aldehyde group can be produced at C_1 of second sugar molecule. It is a reducing sugar. It reduces Tollen's reagent to shining silver mirror. Hence, maltose gives positive Tollen's test.

(46) On complete hydrolysis DNA gives equimolar quantities of adenine and thymine.

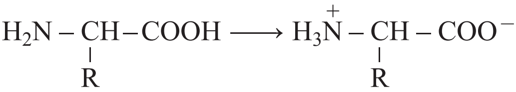
Ans. On complete hydrolysis DNA yields 2-deoxy-D-ribose, adenine, thymine, guanine, cystosine and phosphoric acid. Since adenine always forms two hydrogen bonds with thymine, the hydrolysis of DNA gives equimolar quantities of adenine and thymine.

(47) α-Amino acids have high melting points compared to the corresponding amines or carboxylic acids of comparable molecular mass.

Ans.

Formula	Molecular mass	Melting point
 $CH_3-\underset{\displaystyle NH_2}{\underset{\vert}{CH}}-COOH$ Amino acid	89	293.5 °C
CH_3-NH_2	87	– 55 °C
CH_3-COOH	88	– 7.9 °C

α-Amino acids have high melting points compared to the corresponding amines or carboxylic acids of comparable molecular mass due to the presence of both acidic (carboxylic group) and basic (amino group) groups in the same molecule. In aqueous solution, proton transfer from acidic group to amino (basic) group of amino acid forms a salt, which is a dipolar ion called zwitter ion.



$$\underset{\text{Amino acid}}{H_2N-\underset{\displaystyle R}{\underset{|}{CH}}-COOH} \longrightarrow \underset{\text{Zwitter ion (dipolar ion)}}{H_3\overset{+}{N}-\underset{\displaystyle R}{\underset{|}{CH}}-COO^-}$$

Amino acid

Zwitter ion
(dipolar ion)

(48) Hydrolysis of sucrose is called inversion.

Ans. $\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow[\text{invertase}]{H^+} \underset{\text{D-(+) glucose}}{C_6H_{12}O_6} + \underset{\text{D-(–) fructose}}{C_6H_{12}O_6}$

Sucrose is dextrorotatory. On hydrolysis it gives equimolar mixture of D-(+) glucose and D-(–) fructose. Since the laevorotation of fructose (– 92.4°) is more than dextrorotation of glucose (+ 52.7°), the hydrolysis product has net laevorotation. Thus, hydrolysis of sucrose brings about a change in the sign of rotation, from dextro (+) to laevo (–) and the product is called as invert sugar and so the hydrolysis of sucrose is called inversion.

(49) On boiling egg albumin becomes opaque white.

Ans. Upon boiling the egg, denaturation occurs. During denaturation, secondary and tertiary structures are destroyed, but primary structure remains intact. Egg contains soluble globular proteins, which forms insoluble fibrous proteins (opaque) on boiling egg.

Chapter 16. Green Chemistry and Nanochemistry

(50) Green chemistry plays an important role in sustainable development.

Ans. Sustainable development is a development that protects the environment and the world's resources. We can achieve sustainable development by adapting the twelve principles of green chemistry.

Green chemistry designs safer chemicals which are less toxic. It normally leads to low cost, use of less energy, environmentally friendly solvents and less production of waste. Green chemistry works on the principle of atom economy and minimum or no waste production. It encourages the use of renewable feed stocks and reduces the use of toxic and hazardous chemicals. It eliminates majorly stoichiometry reactions and prefers to use catalysis. It preserves the environment and safety requirements with added benefit of cost reduction.