INTERMOLECULAR FORCES AND POTENTIAL ENERGY SURFACES

1 MARK

EASY:

1. Van der Waal's forces are directly proportional to which factor?
   Boiling point of the substances.
2. What type (s) of intermolecular forces exist between Br_2 and CCl_4?
   Dispersion forces
3. The strength of Vander waals forces depends upon which factor?
   It depends upon three factors, size of the molecule, molecular structure, number of electrons present in the molecule.
4. Write down the formula of critical volume for Van der Waal's gas.
   $V_c = 3nb$
5. Write down the relation of critical pressure for Van der Waal's gas
   $P_c = a / 27b^2$
6. Give one example of dipole – dipole interaction.
   Me_2O
7. Which interaction is the strongest interaction?
   Ionic interaction
8. Write down the relation of critical temperature for Van der Waal's gas.
   $T_c = 8a / 27bR$.

5 mark

Easy

1. Define Van der Waal's forces. Discuss their nature. 2 + 3
   The intermolecular attractive forces existing between all molecules when they are close to one another called van der Waal's forces. These forces are very weak in nature and operate only when molecules are very close to one another. The attractive force is opposed by two factors:
   (i) The repulsive force between the electron clouds of the adjacent molecules.
   (ii) The repulsive force between the nuclei of nearby atoms.
   However, the attractive forces overpower the repulsive forces.

Moderate

1. Compare the strength of intermolecular forces in H_2 and Halogens and arrange them in increasing order w.r.t. strength. When a real gas behave as ideal gas?
   H_2 being the smallest molecule, the strength of intermolecular forces among its molecules would be the least. Among the halogens it would go on increasing with increase in their respective size which is directly related with their molecular masses. So trend in the variation of strength would follow the order: $H_2 < F_2 < Cl_2 < Br_2 < I_2$.
   The molecular mass of I_2 being maximum, its molecule will have maximum number of electrons in it and so it will have the maximum strength of intermolecular among its molecules.
   Real gas behaves as ideal gas at its Boyle's temperature.

15 MARKS

Hard

1. (a) What would have happened to the gas if the molecular collisions were not elastic?

2. (b) CO_2 is heavier than O_2 and N_2 gases present in the air but it does not form the lower layer of the atmosphere. Why?
(c) Why in case of hydrogen and helium, the compressibility factor is always greater than 1 and increases with increase in pressure?
(d) Why gases can be liquefied by cooling?
(e) Which type of liquids will have higher boiling points? 'Polar or Non – polar liquids" – Give reason for your answer. 3 + 3 + + 3 + 3 + 3

(a) On every collision, there would have been loss of energy. As a result, the molecules would have slowed down and ultimately settle down in the vessel. Moreover, the pressure would have gradually reduced to zero.
(b) Gasses possess the property of diffusion which is independent of the force of gravitation. Due to diffusion, the gases mix into each other and remain almost uniformly distributed in the atmosphere.
(c) The molecules of hydrogen and helium are of very small mass and consequently the force of attraction between the molecules is always negligible, Thus neglecting the term a/V, the equation $PV - Pb + a/V = RT = P'V'$ is reduced to $PV - Pb = RT = P'V'$
Or, $PV = P'V' + Pb$
i.e., the product PV is greater than $P'V'$ even at low pressure.
(d) All gases are composed of molecules, which are in a state of constant rapid motion. If the temperature is lowered, the kinetic energy of the gas molecules decreases and as a result, molecules move close to each other. Consequently, the volume occupied by the gas also decreases. If this lowering of temperature is continued, at some stage, the molecules will come so close together that they change into the liquid state.
(e) The polar liquids will have comparatively higher boiling points than that of non – polar liquids. It is because the Non – polar liquids will have only weak intermolecular forces existing among their molecules. But greater energy would be required for the vapourisation of polar molecules which possess permanent dipole moment in addition to the intermolecular forces among their molecules.

EASY

1. (a) Discuss types and conditions of hydrogen bonding. 5
(b) Write the equation of state for the real gas with proper notations. Mention the significance of constants a and b. 5
(c) Discuss the critical phenomenon of real gas. 2
(d) Calculate the Boyle temperature for a gas whose van der Waals constant $a = 7.18\ L^2\ atmMol^{-2}$, $b = 0.854\ L\ Mol^{-1}$ and $R = 0.082 L\ atm\ K^{-1}\ mol^{-1}$.

(a) Conditions for the formation of Hydrogen – bonding
Hydrogen bond formation depends on few factors------
(i) Hydrogen bonding takes place with an atom having high electronegativity. Higher the electronegativity of the atom, stronger is the hydrogen bonding.
(ii) The atom which is involved in Hydrogen bonding should be small in size because smaller atoms can attract the electron density of the covalent bond more efficiently, thus can produce the polarity in the molecule and consequently the strength of the hydrogen bonding increases.
Types of hydrogen - bonding:
Hydrogen bonding is classified into two groups:
(i) Inter – molecular Hydrogen – bonding: If the hydrogen bonding takes place between two separate molecules of same type or different type then that kind of hydrogen bonding is called intermolecular hydrogen bonding. Example: H_2O, HF, ROH etc.

(ii) Intra – molecular Hydrogen – bonding: If the hydrogen bonding takes place within the molecule itself, then that is called intra – molecular Hydrogen bonding. Example: Ortho – nitro phenol, Salicyldehyde.

(b) Equation of state for real gas (van der Waals equation) is given by

$(P + n^2a/V^2)(V – nb) = nRT$

P = pressure of gas, V = volume of gas, n = number of moles of gas, R = molar gas constant, T = absolute temperature, a and b = van der Waals constant.

For one mole of gas equation of state is $(P + a/V^2)(V – b) = RT$

'a' and 'b' are van der Waals constants in the equation of state for real gas.

'a' is a measure of intermolecular force of attraction among the molecules. Higher is the value of 'a' higher is the intermolecular forces of attraction and easier is to liquefy the gas. The effect of intermolecular attraction is to reduce the pressure of gas from the ideal value that appears in absence of 'a'.

'b' is related to size (radius) of a molecule, higher is the value of 'b' higher is the size of the molecule. The molecules in a real gas has non – zero volume and molecules behave as small but impenetrate sphere, as a result n moles of gas molecules vove not in a volume V but less than V equal to V – nb where 'b' is roughly the volume taken up by Avogadro number (N_A) molecules themselves. Effect of 'b' (size) is to increase the pressure from that expected for ideal gas behaviour where 'b' is zero. It can be shown that $b = 4N_A(4/3\pi r^3)$, Where N_A is Avogadro number and r is the radius of the molecule.

(c) Critical phenomenon is observed by real gas which has both 'a' and 'b' values. To understand it we consider a gas taken in a bulb which is connected to a mercury manometer. The bulb is gradually cooled, at temperatures liquid and vapour phases of the gas becomes clearly visible. The bulb is surrounded by a jacket which is used to function as a thermostat. The temperature of the thermostat is slowly increased until the meniscus just vanishes. The temperature and the pressure at which the meniscus disappears are noted. The bulb is then very slowly cooled and the temperature and pressure are again noted at which the surface of separation just reappears. This average of the two temperature (T_C) and critical pressure (P_C). The mercury manometer is used to measure P_C. The molar volume of the gas at T_C and P_C is called critical volume V_C. A beautiful colour appears when the system is at T_C, P_C. This phenomenon of real gas is called critical phenomenon.

Boyle temperature is given by $T_B = a / Rb$ where a and b are van der Waals constant.

$a = 7.18\ L^2\ atm\ mol^{-2}$ $b = 0.854\ L\ mol^{-1}$ $R = 0.082\ L\ atm\ K^{-1}\ mol^{-1}$

So $T_B = 7.18\ L^2\ atm\ mol^{-2} / (0.854\ L\ mol^{-1})(0.082\ L\ atm\ K^{-1}\ mol^{-1}) = 102.53\ K$.

Moderate

1. (a) Out of N_2 and NH_3, which one will have greater value for van der Waal's constant 'a' and which one will have greater value for van der Waal's constant 'b'? 5

(b) What is the application of Potential Energy Surface (PES)? 5

(c) Using van der Waals equation, calculate the pressure exerted by one mole of carbon dioxide. When it occupies a volume of 0.05 litre at 100°C, given that a = 3.592, b = 0.0426 and R = 0.0821 litre atmosphere/degree mole. Write down the different types of interaction forces. 5

(a) (i) As NH_3 is more liquefiable (due to hydrogen bonding), intermolecular forces of attraction are stronger than in N_2. Hence, NH_3 will have greater value for 'a'.

(ii) As NH_3 molecule is larger in size than N_2, hence , NH_3 will have greater value for 'b'(For NH_3 $a = 4.17\ L^2\ atm\ mol^{-2}$ $b = 0.0371\ L\ mol^{-1}$.For N_2 $a = 1.39\ L^2\ atm\ mol^{-2}$ $b = 0.0319\ L\ mol^{-1}$.)

(b) A potential energy surface is a tool for finding the analysis of molecular shapes and chemical kinetics of a reaction. Once the necessary points are evaluated on a PES, the point can be classified according to the first and second derivatives of the energy with respect to position. These correspond to the gradient and the curvature of the curve respectively. Stationary points have physical meaning i.e. energy minima correspond to physically stable chemical species and saddle points correspond to transition states, the highest energy point on the reaction coordinate.

(c) It is given that , n = 1 mole V = 0.05 litre; a = 3.592 atms. Litre^2 mole^{-2} b= 0.0426 litre /mole; R = 0.0821 litre atmosphere/degree/mol; T = 100ºC + 273 = 373K
Van der Waal's equation, for one mole
$(P + a/V^2) (V – b) = RT$
$P + a /V^2 = RT / (V – b)$
$P = RT/ (V – b) – a/V^2$
Substituting the value of a, b, V and T in the equation
P = (0.0821 x 373)/ (0.05 – 0.0426) - 3.592/0.0025 = 2701.5 atm.

The following types of intermolecular force exists between the molecules of different substances:
1. Dipole – dipole interaction
2. Induced dipole – induced dipole
3. Ion – dipole
4. Ion – induced dipole
5. Instantaneous dipole - Instantaneous induced dipole forces.

ORGANIC REACTIONS AND SYNTHESIS OF DRUG MOLECULE

1 Mark

Easy

1. Write the name of one reagent which is used to oxidise alcohols to acids.

Potassium permanganate ($KMnO_4$)

2. What is the reactivity order of alkyl halide in SN2 mechanism?

MeX > 1º > 2º > 3º.

3. In SN1 type reaction which type of solvent is used?

In SN1 reaction polar aprotic solvent is uned.

Moderate

1. Hydrolysis of Isopropyl chloride follows which type of mechanism?

It follows both SN1 and SN2 mechanism.

2. What is the hybridization of carbon atom in carrying the negative charge?

Sp^3 hybridization.

Hard

1. What is the important characteristics having a nucleophile?

Nucleophile must have lone pair of electrons.

5 Mark

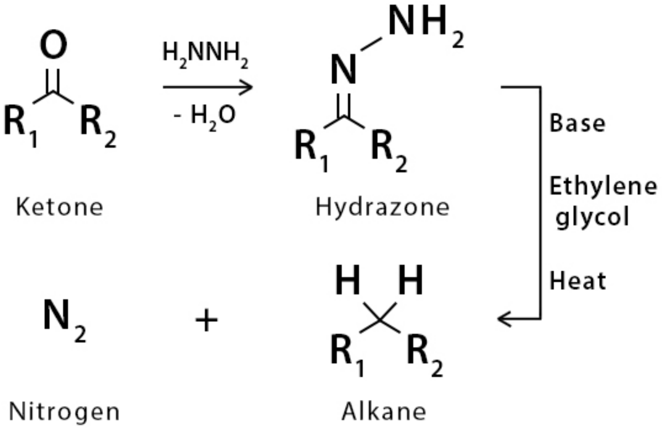
Easy

1. Explain the following reactions with a suitable example:

(a) Wolff – Kishner Reaction 3

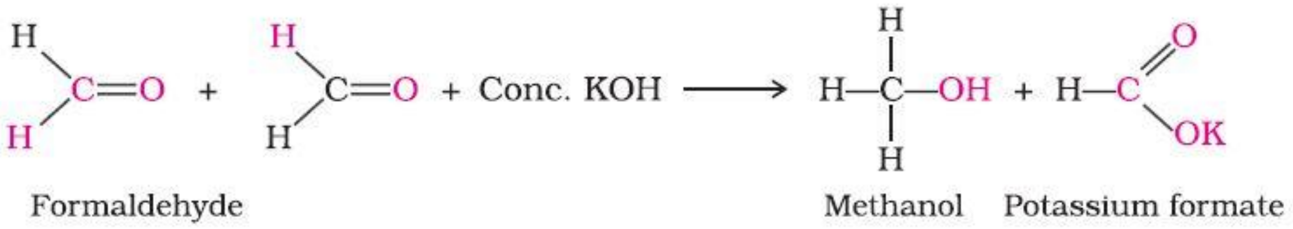
(b) Cannizzaro Reaction 2

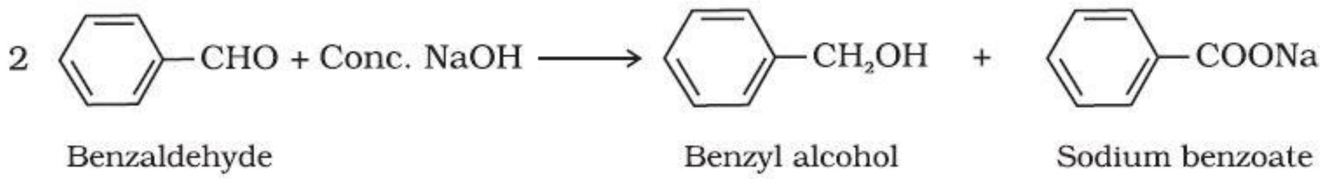
(a) Wolff – Kishner Reduction: In this reaction, ketone initially reacts with hydrazine to produce hydrazine which on heating in presence of KOH or C_2H_5OH in ethylene glycol solvent yields propane.



(b) Cannizzaro Reaction: Aldehydes having no α- hydrogen undergo self-oxidation reduction reaction in presence of strong base like ethanoic KOH to produce corresponding acid and alcohol. This is called Cannizzaro reaction.

Example: Reaction between two formaldehyde molecules (having no α – hydrogen) produce sodium or potassium formate and methyl alcohol in presence of 50% ethanoic NaOH or KOH solution.





Moderate

1. What are the differences in between SN1 and SN2 reactions? Between $CH_3CH_2CH_2Cl$ and CH_3OCH_2Cl which would react faster in SN1 solvolysis?

Differences between SN1 and SN2 reactions:

SN1 Reaction	SN2 Reaction
It is a first order process and follows first order rate law.	It is a bimolecular process and follows second order rate law
Nucleophilic attack can take place from either side of the positively charged carbon atom.	Nucleophilic attack takes place from back side of the carbon atom bearing the leaving group.
Recimic mixture of the product is obtained but no inversion occurs.	Inversion of configuration takes place but no racemic mixture is obtained in the product.
It is favoured by the polar solvent.	It is favoured by the non polar solvent.
Low concentration of nucleophile favours the SN1 process.	High concentration of nucleophile favours the SN2 process.

Between $CH_3CH_2CH_2Cl$ and CH_3OCH_2Cl, the first compound would react faster in SN1 solvolysis. The reaction is, $CH_3CH_2CH_2Cl$ will produce stabler carbocation in step I compared to CH_3OCH_2Cl

$CH_3CH_2CH_2Cl \longrightarrow CH_3CH_2CH_2^+ + Cl^-$ (slow, rate determining step)

$CH_3CH_2CH_2^+ \longrightarrow CH_3CH\,^+CH_3$

The above compound can get internal rearrangement via 1 – 2 proton shift to produce stabler 2° carbocation.

$CH_3OCH_2Cl \longrightarrow CH_3OCH_2^+ + Cl$ (unstable 1° carbocation)

The second compound producing unstable 1° Carbocation and unable to rearrange itself to produce stabler carbocation.

15 Mark

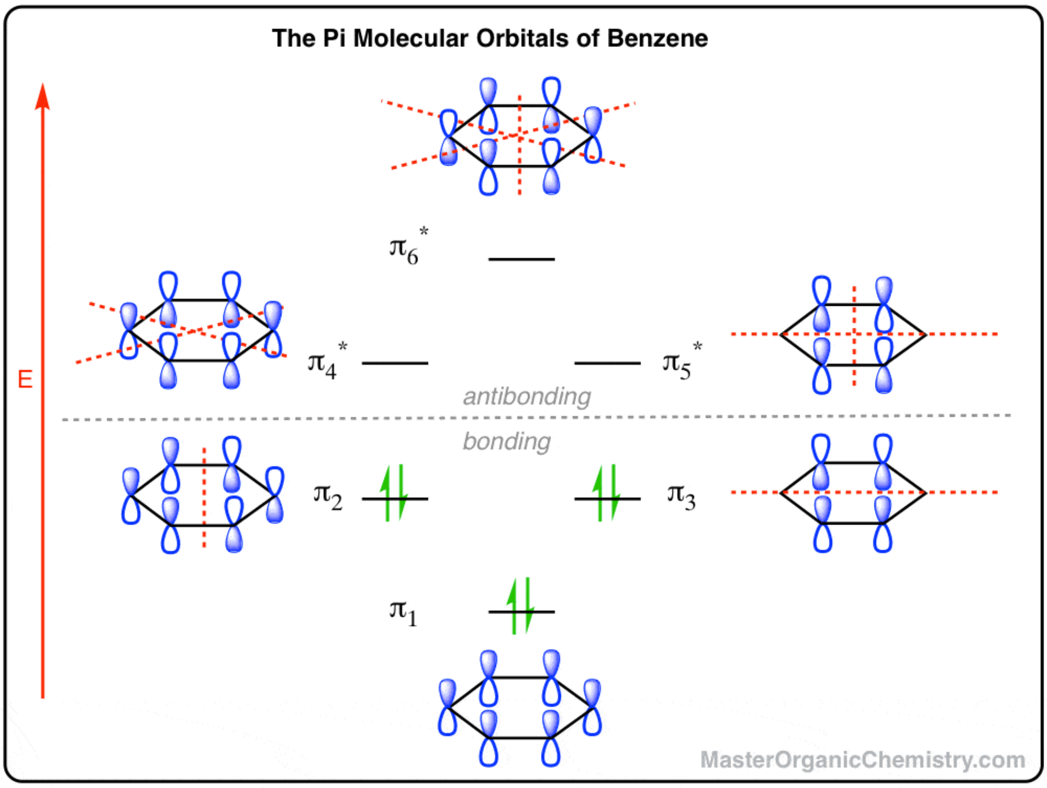
Easy

1. (a) Draw the π – molecular orbital diagram of Benzene. Predict whether the following compounds are aromatic, anti – aromatic or anti – aromatic: (i) Furan, (ii) Cyclopentadienyl cation. 5

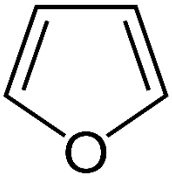
(b) Write notes on Synthesis of paracetamol. 5

(c) Nitration is also in absence of H_2SO_4 yet H_2SO_4 has no effect on benzene under the conditions employed. Show the mechanism of nitration of benzene. 5

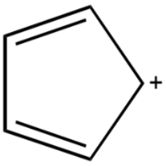
(a) π – molecular orbital diagram of Benzene



Furan: Furan is an aromatic heterocyclic compound with 6π electrons. It is a planar cyclic system.



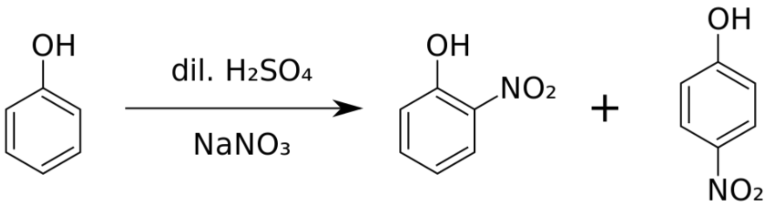
Cyclopentadienyl cation: Cyclopentadienyl cation is an aromatic heterocyclic system with positive charge. It is a 2π – electron system. [(4n + 2)π electrons, where n = 0]

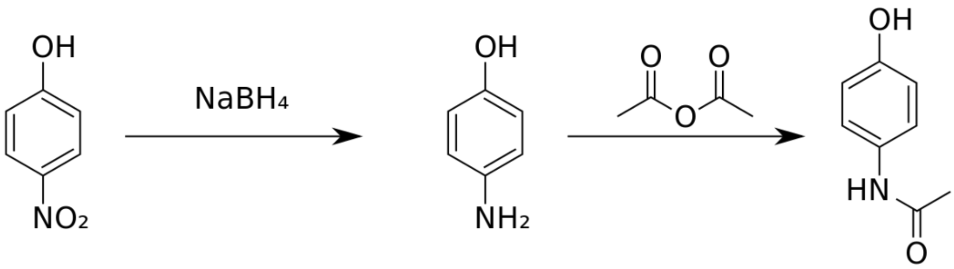


(b) Synthesis of paracetamol: Paracetamol is synthesized by nitration of phenol using sodium nitrate which yields a mixture of ortho and para nitro phenol, from which para nitrophenol (b. p. 279ºC) is separated out by steam distillation. Nitration in phenol is an electrophilic substitution and requires mild conditions as compared to nitration in benzene as phenol’s oxygen is highly activating. The nitro group of para nitro phenol is then reduced to para amino phenol. At the final stage, the amino group is acetylated using acetic anhydride. For the reduction of the nitro group, sodium borohydride is used in the laboratory, but for industrial production, direct hydrogenation is used.

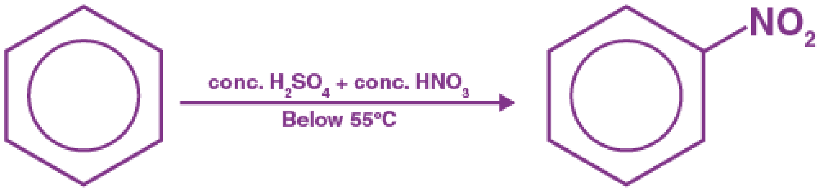
Medical Utility:

Paracetamol is used to give relief from fever caused by common cold, influenza, viral infection. It also helps to get relief from muscle pain, sinus pain etc.



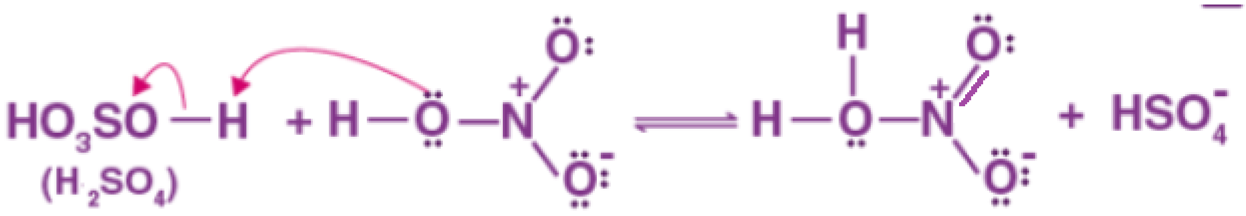


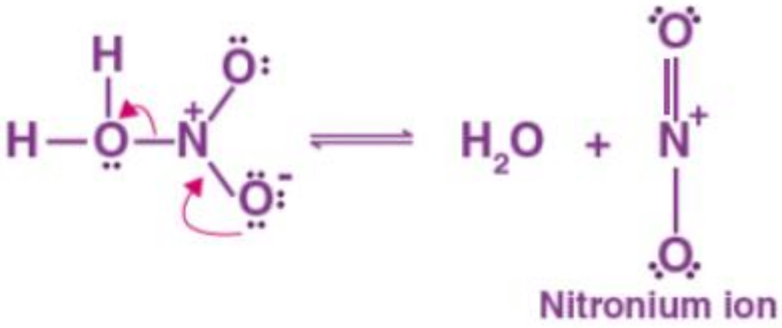
(c) Benzene reacts with concentrated nitric acid at 323-333K in the presence of concentrated sulphuric acid to form nitrobenzene. This reaction is known as nitration of benzene.



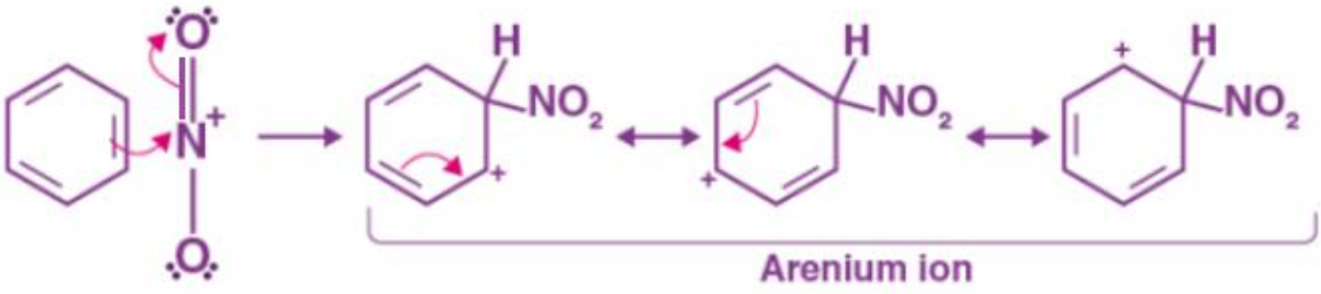
Mechanism of nitration of benzene:

Step 1: Nitric acid accepts a proton from sulphuric acid and then dissociates to form nitronium ion.

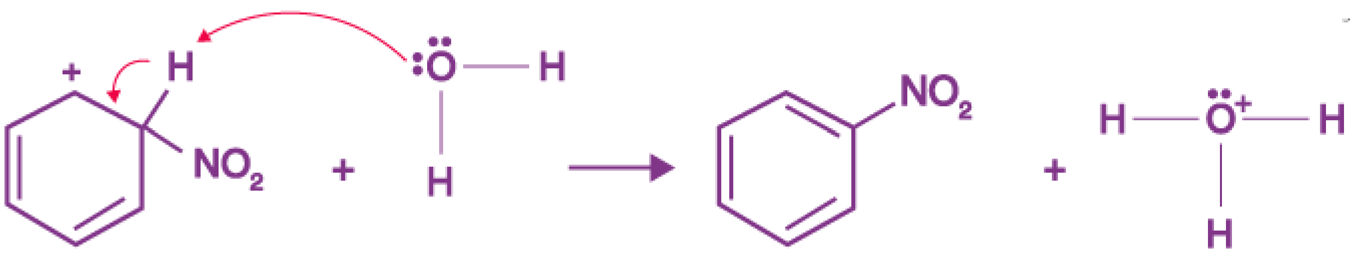




Step 2: The nitronium ion acts as an electrophile in the process which further reacts with benzene to form an arenium ion.



Step 3: The arenium ion then loses its proton to Lewis base forming nitrobenzene.



Moderate:

1. (a) Write notes on synthesis of aspirin. What is its medical utility? 5

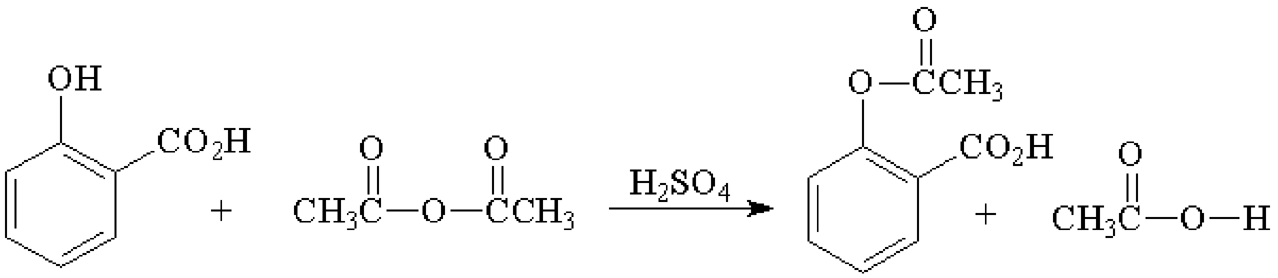
(b) Explain why – (i) p- nitrophenol has higher boiling point than o – nitrophenol.

(ii) The amino group in aniline is o – and p – directing but the amine group is meta directing. 6

(c) What products are obtained when (i) Toluene is treated with alkaline $KMnO_4$ (ii) Benzoic acid treated with lithium aluminium hydride. 4

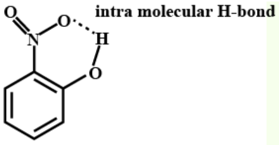
(a) Synthesis of Aspirin: The chemical name of Aspirin is 2 – acetoxybenzoic acid or acetylsalicylic acid. Asperin is an analgesic and used to get relief from pain without causing any significant disturbance in our nervous system.

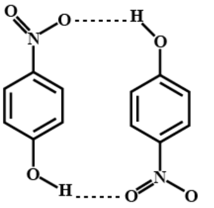
Synthesis: Aspirin is synthesised by treating salicylic acid with acetic anhydride in presence of a strong acid like H_3PO_4 which acts as catalyst. The result of this reaction is acetylsalicylic acid or aspirin and acetic acid is released as by product of the reaction. Aspirin is sparingly soluble in water and therefore gets precipitated on addition of water. Under this process the hydroxyl group (- OH) of the salicylic acid turns into ester group (- $OCOCH_3$).



Medical Utility: Aspirin is generally used to treat fever, headache and inflammatory diseases like rheumatoid arthritis. It is also as an analgesic for acute pain.

(b) (i)





Intermolecular H-bond

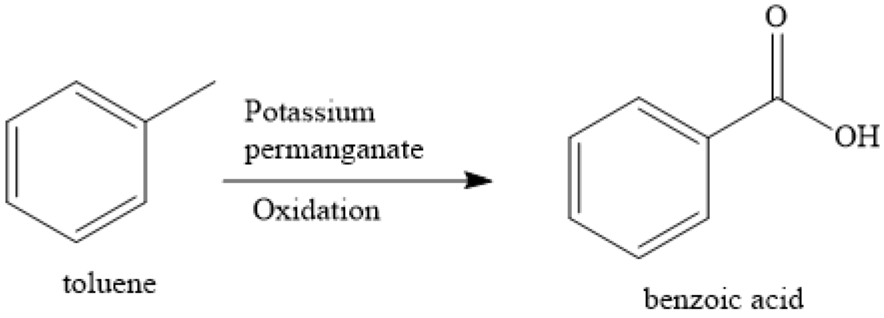
O-nitrophenol has intramolecular hydrogen bonding. P-nitrophenol has intermolecular hydrogen bonding. Intermolecular hydrogen bonding leads to a molecular association. This increases boiling point. Hene, O-nitrophenol has a lower boiling point than P-nitrophenol.

(ii) In aniline NH_2 increases e density at o- and p- positions due to +R effect. But when it is nitrated by nitrating mixture, a substantial amount of m-nitro aniline is formed.

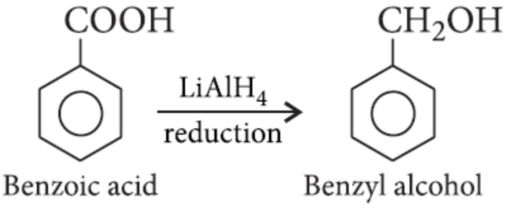
But in acidic medium (Nitrating mixture - HNO_3(c) + H_2SO_4(c)).

$NH_2 + H^+ \rightleftharpoons NH_3^+$ is e– withdrawing group and so is m - directing. So gives larger amount of m- nitroaniline.

(c) (i) When toluene (methyl benzene) is oxidized with alkaline potassium permanganate solution, benzoic acid product is obtained. The aliphatic methyl group is oxidized to the aromatic carboxylic functional group.



(ii) Benzoic acid can be reduced to benzyl alcohol by lithium aluminium hydride.



Hard:

1. (a) Arrange C_6H_5CHO, $C_6H_5COCH_3$, $C_6H_5CO\ C_6H_5$ in decreasing order of reactivity towards nucleophile addition reactions. Which of the species NO^+, CCl_4, CH_3, CN^- is an nucleophile? 4 + 1

(b) Free radicals are paramagnetic, but carbonium ions and carbanions are diamagnetic. What is the main product of reaction of alkyl halide and potassium nitrite? 2 + 3

(c) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohols, whereas in the presence of alc. KOH, alkenes are formed as the major products. Explain. Name two acylating agents and their structure. 3 + 2

(a) $C_6H_5CHO > C_6H_5COCH_3 > C_6H_5CO\ C_6H_5$

Reasons: (i) Benzene ring causes the electron – donating resonance effect (+ M effect); while the alkyl group causes the electron – donating inductive effect (+I). So both these group increases the electron density on the carbonyl carbon and, therefore, reduces the positive charge on the carbonyl carbon, thereby tendency of nucleophilic attack is reduced. Hence C_6H_5CHO is more reactive towards nucleophiles than $C_6H_5COCH_3$ and $C_6H_5CO\ C_6H_5$.

(ii) The +I effect of alkyl group is weaker than +M effect of benzene ring. In other words, - CH_3 group reduces the positive charge on the carbonyl caused by – C_6H_5 group. Hence $C_6H_5COCH_3$ is more reactive towards nucleophiles than $C_6H_5CO\ C_6H_5$.

CN^- is an nucleophile, since it has lone – pairs of electrons on both N atom and C atom.

(b) Free radicals possess odd electrons in them and are, therefore, paramagnetic in nature. While carbonium ion and carbanions have no unpaired electron in them and are diamagnetic.

Alkyl nitrite, since $O^- - N = O$ is an important ambident nucleophile.

$R - X + KNO_2 \longrightarrow RONO$ (major) + RNO_2 (Minor) +KX

(c) Aqueous KOH contains only OH^- ions, which act as nucleophile and these brings about hydrolysis of alkyl chloride to the corresponding alcohol.

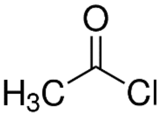
$RCl + OH^- (aq) \longrightarrow ROH + Cl^- (aq)$ [Hydrolysis reaction]

On the other hand, alcoholic KOH, contains ethoxy ions ($C_2H_5O^-$), which are more than OH^- ions. Consequently, ethoxy ion preferentially bring about dehydrohalogination to form alkenes.

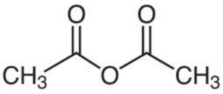
$H_2C(H) - CH_2 (Cl) + KOH (alc.) \longrightarrow H_2C = CH_2 + H_2O + KBr$

On the other hand, in haloarenes (Ar – X), the halogen atom releases electron to the benzene nucleus through resonance, thereby making ortho and para positions of benzene nucleus relatively electron – rich w.r.t. halogen atom. As a result, the electrophile attacks at ortho or para position. Hence, haloarenes undergo electrophilic substitution reaction.

Acylating agent : Acetyl Chloride



Acetic anhydride.



PERIODIC PROPERTIES

1 Mark

Easy

1. What is the shape of XeF_4 molecule?

Square planar

2. Give an example of compound having zero dipole moment.

CCl_4

3. Give an example of soft acid.

Hg^{2+}

Moderate

1. What is the shielding constant value for I s orbital electron?

0.30

2. What is the order of second ionisation potentials of carbon, nitrogen, oxygen and fluorine?

O > F > N > C

3. What is the hybridization of XeF_4?

Sp^3d^2.

Hard

1. What is the increasing order of electron affinity values of O, S and Se?

O < S > Se.

2. Write the increasing order of effective nuclear charge in Na, Al, Mg and Si?

Na < Mg < Al < Si.

5 Mark

Moderate

1. (a) State the reason for the presence of only one electron in the 4s subshell of chromium? 2

(b) Which of the following has larger size and why? (i) Mg^{2+} (ii) N^{3-}

The ground state electronic configuration of Chromium (24) is : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$. It has only one electron in 4s subshell as the second electron is shifted to 3d subshell to make it half filled to achieve additional stability.

(b) Mg^{2+} and N^{-3} ions have same number of valence electrons. Both are having total 10 electrons but Mg is a 3rd period element with one more orbital than N (2nd period) element. But in +2 state Mg is having only two orbitals, as N. As atomic number of Mg is 12 and that of N is 7, number of proton present in Mg is more than N and therefore exerting greater pull on outermost electrons resulting smaller size.

Hence we can conclude that N^{-3} has larger size than $Mg^{+2.}$

Hard

Arrange the halogens in ascending order as per their boiling point and mention the periodic trends of atomic radii. 5

In group 17, i.e., for halogens, the boiling points increase with increase in atomic number. Therefore, the ascending order of boiling point of halogens is --- F > Cl > Br > I

On moving from left to right in a period, the number of shells remain the same but due to increase in atomic number (no. of protons), the nuclear charge increases progressively and as a result atomic radii decreases. This trend continues upto group 17 (halogens) but for group 18 (inert gases), the size increases abruptly.

Easy

1. Differentiate between electronegativity and electron affinity of an element. Explain the acidity order of silicon halides as given by $SiF_4 > SiCl_4 > SiBr_4 > SiI_4$.

Electronegativity	Electron affinity
Electronegativity is the ability of an atom to attract electrons from outside.	Electron affinity is the amount of energy released when a neutral atom or molecule gains an electron from outside.
Qualitative property	Quantitative property
Measured from Pauling units	Measured from either eV or kj/mol
Applied for a single atom.	Can be applied for either an atom or a molecule.

Silicon halides can behave like Lewis acids although octet is fulfilled for Si atom in all silicon halides. This is due to the reason that the strongly electronegative halogens can pull electron density from silicon end (Si – X covalent bonds) towards themselves making silicon electron deficient. However, the acidic strength of silicon halides will depend on the electronegativity of halogens connected with Si atom.

Fluorine being most electronegative among halogens, SiF_4 has highest acidic character and reverse is true for SiI_4. Moreover, Br and I can donate their extra electron density to vacant 3d orbital of 'Si' via back bonding resulting lowering of electron deficiency of silicon.

Therefore, the acidic strength order is $SiF_4 > SiCl_4 > SiBr_4 > SiI_4$

15 Mark:

Easy:

1. (a) State Hund's rule of spin multiplicity and Pauli Exclusion principle. Write down the electronic configuration of Fe (Z = 26)

(b) Calculate the effective nuclear charge of 4s electrons of Fe (Z = 26) with the help of Slater's rule.

(c) Define Pauling Scale of electronegativity.

(d) Electron affinity of Cl is greater than F, explain the phenomenon.

(e) Between $BeCl_2$ and $BaCl_2$ which one has more melting point and why?

(f) Write short note on " Fajan's rule.

(a) Hund's rule of maximum multiplicity: Pairing of electrons in the degenerate molecular orbitals does not occur, until each of them has one electron.

Pauli's exclusion principle: Two electrons in the same orbital cannot have set of all the four quantum numbers identical. It means maximum number of electrons in a orbital is two and they must have opposite spins.

Electronic configuration of Fe (26) is ---- $1s^2$, $2s^2$, $2p^6$ $3s^2$, $3p^6$, $3d^6$, $4s^2$.

(b)The ground state electronic configuration of Fe (26) is ---- $1s^2$, $2s^2$, $2p^6$ $3s^2$, $3p^6$, $3d^6$, $4s^2$.

The shielding constant contribution calculation -----

For 4s electrons:

No. of electrons in the same group (4s) = 0

14 electron in (n – 1) groups, (3s, 3p) and 3d: 0.85 each : 0.85 x 14 = 11.90

10 electrons in groups further left, i.e., ≤ (n – 2): 1.0 each : 1.0 x 10 =10.0

Total (σ) = (11.90 + 10.0) = 21.90

Thus $Z_{eff} = 26 - 21.90 = 4.10$.

(c) Pauling scale: Let us consider a chemical reaction: $A_2 + B_2 \rightarrow 2\,A - B$

The reaction can also be represented as --- $A – A + B – B \rightarrow 2 (A – B)$

According to Pauling, the bond dissociation energy of the A – B bond is $E_A – E_B$ which will be equal to the bond dissociation energies E_{A-A} and E_{B-B} for A – A and B – B molecules respectively.

Thus, $E_{A-B} = \sqrt{} E_{A-A} . E_{B-B}$

If we consider the electronegativity of atom 'A' and 'B' as χ_A and χ_B respectively, then according to Pauling, the difference in electronegativity between these two atoms will be ---

$\chi_A - \chi_B = \sqrt{} \Delta/23.06 + \alpha = 0.208 \sqrt{} \Delta + \alpha$

Where α is a constant.

Therefore, if electronegativity value of any one of these two (χ_A or χ_B) is known, the other can be calculated.

(d) Down the group we expect the electron affinity to decrease, but in this case the lesser electron affinity of fluorine with respect to chlorine is due smaller size of fluorine. The smaller size results very strong repulsion between the incoming electron and the relatively compact 2p sub shell of fluorine. As a result the electron affinity decreases. On the contrary, the relatively large 3p subshell of chlorine can accommodate the incoming electrons more easily resulting greater electron affinity than fluorine.

(e) According to Fajan's rule, polarization power of cations increases with decrease in size, i.e., smaller the size of the cation greater is the polarization power.

Therefore, polarization power of $Be^{2+} > Ba^{2+}$

Therefore, $BeCl_2$ is more covalent than $BaCl_2$. Hence , $BaCl_2$ will be less covalent and has higher melting point.

(f) Fajan's Rule: The electrovalent compounds are never 100% ionic in nature. There is always some percentage of covalent character in it. The concept of development of partial covalent character in the ionic compounds was first introduced by Fajon.

When a cation approaches an anion, the positively charged cation attracts the electron cloud of the anion.

The ability of a cation to deform the electron cloud around the anion is said to be polarization power of the cation and the tendency of an ion to get polarized or deformed is called polarizability.

The extent of polarizability of an anion and polarizing power of a cation is governed by a number of rules, commonly known as Fajon's rule. As per these rules, the polarization in ionic compounds is favoured by

(i) High positive charge on cation

(ii) Small size of cation

(iii) High negative charge on anion

(iv) Large size of anion.

(i) The polarization power of the cation increases with increasing the charge, i.e., higher the charge on the cation greater is the polarization power. Hence, the polarization power varies, $B^{+3} > Be^{+2} > Li^+$

(ii) The polarization power of cations increases with the decrease in size, i.e., smaller the size of the cation greater is its polarization power. Hence, the polarization power in this series is as follows, $Li^+ > Na^+ > K^+$.

(iii) Greater the negative charge of an anion, higher is its polarizability because it is difficult for a highly charged anion to control its outer orbital electrons and hence it can be deformed very easily. For example, the polarizability of halides follows the order, $I^- > Br^- > Cl^- > F^-$.

(iv) Larger the size of an anion greater is its polarizability. This is because, with increasing size, the distance between the electrons of the outermost orbit and the nuclei increases and hence the nuclei cannot control the electrons of the outer most shell.

Thus the order of polarizability in the halide series is as follows: $I^- > Br^- > Cl^- > F^-$.

Therefore, the Fajan's rule can be the summarized as smaller cations with low positive charge and smaller anions carrying low negative charge will favour the formation of ionic compounds whereas smaller cations carrying high positive charge will lead to the formation of covalent compounds.

2. (a) What is screening constant? Calculate the effective nuclear charge (Z_{eff}) of one 4s electron of the following: Cu (Z = 29) and K (Z = 19) 5

(b) p – block elements form acidic, basic and amphoteric oxides. Explain each property by giving two examples and also write the reactions of these oxides with water. 6

(c) What is the merits and demerits of long periodic table? 4

(a) Screening constant: In multi – electron atoms, the nuclear charge realized by the outer orbital electrons become less due to the shielding or screening of the inner orbital electrons. This is called shielding or screening effect. The actual amount of nuclear charge felt by an electron is termed as effective nuclear charge. The effective nuclear charge (Z_{eff} or Z^*) is --- $Z^* = Z - \sigma$

Where Z is the actual nuclear charge and σ is the screening or shielding constant.

The magnitude of screening depends on the number of inner orbital electrons. Greater the number of inner electrons, higher would be the screening effectand consequently the effective nuclear charge felt by the outer orbital electrons will decrease. Hence, we can conclude that with decreasing effective nuclear charge, ionization energy decreases.

Cu (29) has ground state electronic configuration: $1s^2$, $2s^2$, $2p^6$ $3s^2$, $3p^6$, $3d^{10}$, $4s^1$.

Effective nuclear charge for one (4s) electron is calculated as follows----

No other electron in the same group (4s) = 0

18 electrons in (n – 1) groups, (3s, 3p) and 3d : 0.85 each : 0.85 x 18 = 15.3

10 electrons in groups further left, i.e., ≤ (n – 2) : 1.0 each : 1.0 x 10 = 10.00

Total (σ) = 25.30

Thus Z_{eff} = 29.00 -25.30 = 03.70

K (19) has ground state electronic configuration $1s^2$, $2s^2$, $2p^6$ $3s^2$, $3p^6$, $4s^1$.

No of electron in the same group (4s) = 0

8 electrons in (n – 1) groups, (3s, 3p): 0.85 each : 0.85 x 8 = 6.80

10 electrons in groups further left, i.e., ≤ (n – 2) : 1.0 each : 1.0 x 10 = 10.00

Total (σ) = 16.80

Thus, Z_{eff} = 19.00 – 16.80 = 02.00

(b) In p – block elements last electron (valence electron) enters the p-orbitals. In p – block elements some are metals, some are non – metals and some are metalloids.

Metals --- Al, Ga, Tl, Bi

Nonmetals --- B, C, N, S

Metalloids: As, Sb, Si, Ge

Types of oxides of p-block elements are described below and two examples each of different types are also given.

<u>Basic oxides</u> --- Bi_2O_3, Tl_2O_3

The basic oxides react with acids to form salts

$Bi_2O_3 + 6\ HCl \rightarrow 2BiCl_3 + 3H_2O$

$Ti_2O_3 + 3H_2SO_4 \rightarrow Ti_2(SO_4)_3 + 3H_2O$

Acidic oxides----- CO_2, SO_2

These oxides are said to be acidic oxides because they react with water to form acid

$CO_2 + H_2O \rightarrow H_2CO_3$ (Carbonic acid)

$SO_2 + H_2O \rightarrow H_2SO_3$ (sulphurous acid)

Amphoteric Oxides --- Al_2O_3, PbO

These oxides have both basic and acidic properties. These oxides react with both strong acids and strong bases.

$Al_2O_3 + 6HCl \rightarrow 2Al^{3+} + 6Cl^- + 3H_2O$

$Al_2O_3 + 2NaOH + 3H_2O \rightarrow 2Na^+ + 2[Al(OH)_4]^-$

$PbO + 2HNO_3 \rightarrow Pb^{2+} + 2NO_3^- + H_2O$

$PbO + NaOH \rightarrow Na^+ + [PbO.OH]^-$

(c)Merits of long periodic table:

1. It is based on atomic number, which is an even better fundamental property compared to atomic mass

2. Position of an element in the tables related to its electronic configuration

3. It shows regular changes in properties of elements on moving across a period or down a group.

Defects of long periodic table:

1. Position of hydrogen is still not satisfactory, as the properties relate to both Group I and Group 17.
2. It fails to accommodate the inner transition elements, i.e., the lanthanides and the actinides, into the main body of the periodic table.

Moderate

1. (a) What is the difference between ionization energy and electron affinity? The first ionization energy of carbon is greater than that of boron whereas the reverse is true for the second ionization energy. 5

(b) Why does Mn (II) is $3d^5$? Would you classify Zn as a transition element? Give reasons for your answer. 5

(c) Explain that ionisation energy of neon is more than any other element of the second period? Why do the transition elements form complexes readily? 5

(a) Ionization energy is the amount of energy required to remove the most loosely bound electron from an isolated atom in the gaseous state while electron affinity is the amount of energy released when an electron is added to an isolated atom in the gaseous state.

The first ionization energy of carbon is greater than boron as nuclear charge on carbon (Z = 6) is greater than the nuclear charge on boron (Z = 5).

The second ionization energy of boron is greater than carbon as the second electron has to be removed from 2s orbital of B^+ in ($1s^2\ 2s^2$) which requires more energy than the removal of electron from 2p orbital of C^+ ion ($1s^2\ 2s^2\ 2p^1$).

(b) The electronic configuration of Mn is $3d^5\ 4s^2$ and that of Mn (II) is $3d^5$. All the 5 electrons in d orbital are unpaired. It is this maximum possible number of unpaired electrons the d- orbitals which makes it most paramagnetic amongst bivalent ions of the first transition series. Also it is half field state, which is very stable configuration.

Zinc (Z = 30) has electronic configuration [Ar] $3d^{10}4s^2$. It has fully filled d – subshell in its elemental from as well as its common oxidation state i.e., Zn^{2+} in having $3d^{10}$ configuration. According to definition of transition element, it cannot be included in the transition elements. It does not show the characteristic properties of transition element, excepting its tendency to form complexes. But it is classified with transition elements because the last electron enters in the d – orbitals of its penultimate shell.

(c) Noble gases have the highest ionization energy in their respective periods. For example, ionization energy of Ne is more than any other element of the second period. So is the case with Ar. This is due to the fact that $ns^2\ np^6$

arrangement which occurs in noble gases is highly stable and hence larger amount of energy is needed to remove an electron from this stable arrangement.

The transition elements form complexes due to

(i) Their small cation size

(ii) High effective nuclear charge

(iii) Availability of vacant (n – 1)d orbitals of appropriate energy for accepting lone pairs of electrons donated by ligand.

Hard

1. (a) "The complexes of first transition series are mainly high-spin while those of second and third transition series are of low – spin type" ---- Explain. First ionisation energies of 5d elements are higher than 3d and 4d elements. Give reason. 5

(b) Explain why the second ionization energies for copper and chromium are enormously high? Iron is a transition element but sodium is not. Explain. 5

(c) First ionisation energies of copper is higher than those of alkali metals while second and third energies are lower. Explain. Why are lanthanides and actinides placed in separate rows at the bottom of the periodic table? 5

(a) The element of the first transition series, i.e., from Sc to Zn involve filling of 3d – orbitals. As compared to 4d and 5d orbitals, the 3d orbitals are relatively smaller in volume. Therefore, Inter electronic repulsion, which may come into play due to occupation by two electrons in an orbital (low spin) would be very large. Therefore, crystal field splitting for 3d block of elements is small. First raw transition metals prefer to form high spin complexes.

On the other hand, in the second and third transition series, 4d and 5d orbitals have bigger sizes than 3d orbitals. Therefore, in the second and third transition series, inter electronic repulsion are quite small. Hence, crystal field splitting energy is quite high which result in low spin complexes.

First ionisation energies of 5d elements are higher than 3d and 4d elements. This is due to the fact that outer valance electrons of 5d elements experience greater effective nuclear charge than 3d and 4d elements due to poor shielding of the nucleus by 4f electrons.

(b) Cu =[Ar] $3d^{10}$ $4s^1$; and Cr = [Ar] $3d^5$ $4s^1$ Their first ionization energies are low because removal of one electron gives a stable $3d^{10}$ or $3d^5$ configuration. The second ionization energies are expected to be high because of removal of an electron from stable completely filled orbital $3d^{10}$ for Cu^+ and half filled orbital $3d^5$ for Cr^+.

Iron has electronic configuration =[Ar] $3d^6$ $4s^2$ while sodium has electronic configuration [Ne}$3s^1$.Thus in iron last electron enters a d- orbital, so it is a transition element while in sodium last electron enter s – block element.

(c) Cu has =[Ar] $3d^{10}$ $4s^{1\text{configuration.}}$ As filled 3d sub shell is much less effective in shielding the outer s- electron than a noble gas shell present in alkali metal, so the 4s electron of copper is more tightly bound than in alkali metal. However, 2nd and 3rd ionization energy values of copper are lower as compared to those of alkali metals due to the loss of electron from diffused d- orbital, while 2nd ionization energy in alkali metal would be very high as this electron is being removed from a noble gas core.

This arrangement has been made due to the following reasons:

(i) to keep the elements having similar properties in a single row.

(ii) to avoid sidewise expansion of the periodic table.

SPECTROSCOPIC TECHNIQUES AND APPLICATION

Easy

1. Which type of charge is carried by electromagnetic waves?

No charge.

2. Which spectroscopic technique is most useful to identify the presence of known impurity in a drug substance?

NMR

3. What is the full form of MRI

Magnetic Resonance Imaging.

4. Write one name of a molecule which have infrared active vibrations.

NO

Moderate

1. What is fingerprint region range in IR spectra?

1600 – 400 cm^{-1}

2. Which is detected by IR spectra?

Functional group.

Hard

1. What will be the absorbance if % Transmittance = 80?

Absorbance A = log (1/Transmittance) = log (100/80) = 0.097

2. The wavelength of an absorption is 495 nm. In what part of the electromagnetic spectrum does this lie?

UV – Visible range.

5 marks

Easy

1. Intensity of spectral line depends on which factor? What is Lambert – Beer Law?

Intensity of spectral lines depends on

i) It depends on the wave functions of the two states between which the transition occurs i.e. on the transition probability.

ii) It depends on the population in the initial energy level from which transition into other levels occur. Greater is the population in the initial energy level more intense is the spectral lines.

iii) The intensity of spectral lines depends also on the amount of absorbing species giving rise to the spectrum.

Lambert – Beer Law:

Extent of absorption by an absorbing solute in a solution is given by Lambert – Beer Law. If I_0 is the intensity of incident monochromatic radiation of a particular frequency and I_t is the intensity of transmitted radiation then by this law, $I_t = I_0e^{-kCl}$.

where k is a constant characteristic of the absorbing solute. C is molar concentration of the solute and l is the total length of absorption cell.

Hard

1. Distinguish between diffraction and scattering. What do you understand by an isobestic point? 3 + 2

i) Diffraction is a process observed only in waves, whereas scattering takes place in waves as well as particles.

ii) Diffraction is a coherent process i.e., it requires that the surface must be regular so far as distances are concerned in comparison to the wavelength of the diffracted wave. But scattering is an uncoherent process i.e., it will take place when the surface is rough in terms of distances as compared to wavelength of light.

An isobestic point for different absorption spectra is that point where the wavelength corresponding to those spectra is equal and the corresponding wavelength at this point is called isobestic wavelength.

Moderate

1. What kind of molecules shows IR spectra? "IR spectra is often characterized as molecular finger prints". Justify statement. 2 + 3

Molecules must possess permanent dipole moment e.g., CO, NO, CN etc. For a diatomic molecule if they don't have a permanent dipole moment then these molecules during vibration must show a change in the dipole moment. For example, O_2, N_2, H_2, are IR inactive because they are not satisfying either of the above conditions.

Different functional groups produce recognizable peaks at nearly definite positions in IR spectra. Most of the peaks can be assigned due to presence of specific groups in the molecule. So IR spectra can be used in establishing the identity of the compounds e.g., it can be characterized as finger print of the molecule.

15 marks

Moderate

(a)What do you mean by shielding and deshielding effects involved in NMR spectroscopy? 3

(b)Given that the spacing of the lines in the microwave spectrum of $^{27}Al\ ^{1}H$ is constant at 12.604 cm^{-1}. Calculate the moment of inertia and bond length of the molecule. (Mass of ^{27}Al = 26.981 amu). 5

(c) ^{13}C is NMR active while ^{12}C is not. Explain. 2

(d) Predict the kind of electronic transition in (a) Cl_2 and (b) carbonyl group. Also give their intensity. 5

(a) Shielding and deshielding is related to NMR spectra. A hydrogen nuclei is said to be shielded from an external magnetic field if it is in electron rich environment. Proton adjacent to electron withdrawing group are said to be deshielded.

If a nucleus is surrounded by many electrons the magnetic field of the electrons usually opposes the applied magnetic field B_0. So the magnetic field at the nucleus is less than the applied field. The nucleus of interest is said to be shielded by the electrons, this is khown as shielding effect.

(b) Spacing of the lines in microwave spectra for $^{27}Al\ ^{1}H$ = 2B

2B = 12.604 cm^{-1}. So B = 6.302 cm^{-1}

I (moment of inertia) = $h/8\pi^2BC$ = 6.6626×10^{-34} Js /8 x $(3.14)^2$ x (6.302 cm^{-1}) (3×10^{10} cms^{-1})

= 4.443×10^{47} Js^2 = 4.443×10^{-47} kgm^2 (since 1J = 1 kg m^2 s^{-2})

Reduced mass $\mu = m_{Al}m_H/(m_{Al} + m_H)$

= (26.98g /mol / N_A) x (1.01g /mol / N_A) / (26.98g /mol / N_A + 1.01g /mol / N_A)

=(26.98 x 1.01)$(g/mol)^2$/ N_A^2 / 1/N_A (26.98 + 1.01) g/mol

$= 1/N_A[(26.98 \text{ x } 1.01)/ 27.99] \text{ g/mol} = (1/6.02 \text{ x } 10^{23}/\text{mol}) \text{ x } 0.9735 \text{ g/mol}$

$= 1.617 \text{ x } 10^{-24} \text{ g} = 1.617 \text{ x } 10^{-27} \text{ kg}.$

$I = \mu r^2$ where r is bond length.

$R = \sqrt{}(I/\mu) = \sqrt{} (4.443 \text{ x } 10^{-47} \text{ kgm}^2)/ (1.617 \text{ x } 10^{-27}\text{kg}) = \sqrt{}(2.748 \text{ x } 10^{-20}\text{m}^2) = 1.658\text{x } 10^{-10}$ m.

So, Moment of inertia (I) = $4.443 \text{ x } 10^{-47} \text{ kg m}^2$; Bond length (r) = $1.658 \text{ x } 10^{-10}$ m.

(c) ^{12}C does not have a nuclear spin and cannot be used in an NMR experiment. In contrast; its isotope ^{13}C, whose natural abundance is only 1.1%, has a nuclear spin ½.

(d) The transition in Cl_2 are: (i) $\sigma \rightarrow \sigma^*$(allowed transition), which is strong in intensity, (ii) $n \rightarrow \sigma^*$ (forbidden transition) which is weak in intensity.

In C=O group, $\sigma \rightarrow \sigma^*$ and $\pi \rightarrow \pi^*$, both are allowed transitions and strong in intensities, whereas $n \rightarrow \pi^*$, and $n \rightarrow \sigma^*$, both are forbidden and of weak intensity.

Hard

1. (a) Calculate the force constant for the bond in HCl from the fact that the fundamental vibration frequency is $8.667 \text{ x } 10^{13} \text{ s}^{-1}$. 4
   (b) Calculate the energy of one photon of light of wavelength 2450Å. Will it be able to dissociate a bond in diatomic molecule which absorbs this photon and has a bond energy equal to 95 kcal per mole. 6
   (c) Write the principal and application of NMR and MRI. 5

   (a) Fundamental vibration frequency (υ) of HCl is related to force constant (k) by equation
   $\upsilon = 1/2\pi \sqrt{}k/\mu$ where μ is reduced mass of HCl. (Frequency is in Hz $=s^{-1}$)
   Reduced mass of HCl is given by $\mu = m_H m_{Cl}/(m_H + m_{Cl})$
   Where m_H and m_{Cl} are mass of one atom of H and Cl respectively.
   Mass of one atom of H = 1 gm/ N_A = 1gm/ $6.023 \text{ x } 10^{23} = 1.66 \text{ x } 10^{-24}$ gm
   Mass of one atom of Cl = 35.5 gm/ N_A = 35.5gm/ $6.023 \text{ x } 10^{23} = 58.94 \text{ x } 10^{-24}$ gm
   So, reduced mass of HCl = $(1.66 \text{ x } 10^{-24} \text{ gm}) (58.94 \text{ x } 10^{-24} \text{ gm})/ (1.66 + 58.94) \text{ x } 10^{-24}$ gm
   $= 97.84 \text{ x } 10^{-48} \text{ gm}^2/ 60.6 \text{ x } 10^{-24}\text{gm} = 1.614 \text{ x } 10^{-24}$ gm.

   $\upsilon= 1/2\pi \sqrt{}k/1.614 \text{ x } 10^{-24}$ gm.
   $\upsilon^2 = 1 / 4\pi^2 \text{ x } k/ 1.614 \text{ x } 10^{-24}$ gm.
   $k = (4\pi^2\upsilon^2) \text{ x } (1.614 \text{ x } 10^{-24} \text{ gm.}) =4 \text{ x } (3.14)^2 \text{ x } (8.667 \text{ x } 10^{13} \text{ s}^{-1})^2 \text{ x } (1.614 \text{ x } 10^{-24} \text{ gm.})$
   $= 4 \text{ x } (3.14)^2 \text{ x } (75.12 \text{ x } 10^{26} \text{ s}^{-2}) \text{ x } (1.614 \text{ x } 10^{-24} \text{ gm.}) = 4781.6 \text{ x } 10^2 \text{ g s}^{-2} = 4.7816 \text{ x } 10^5 \text{ g s}^{-2}$
   $= 4.78 \text{ x } 10^5 \text{ gs}^{-2} = 4.78 \text{ x } 10^5 \text{ dyn cm}^{-1}$ (since 1 dyn = 1 g cm s^{-2}
   We can express force constant (k) in SI unit, that is in Nm^{-1}
   $k = (4.78 \text{ x}10^5) \text{ x } (10^{-5N}) \text{ x } (10^2\text{m}^{-1})$ since 10^5 dyn = 1N and 10^2 cm = 1m
   $= 478 \text{ N m}^{-1}$

   (b) Energy of one photon, $\varepsilon = h\upsilon= h\, c/\lambda$ since $c = \upsilon\lambda$
   If h, c and λ all are taken in SI unit then energy ϵ will be obtained in joule (J) which is SI unit of energy.
   $h = 6.626 \text{ x } 10^{-34} \text{ Js}$, $c = 2.998 \text{ x } 10^8 \text{ ms}^{-1}$
   $\lambda = 2450\text{Å} = 2450 \text{ x } 10^{-8} \text{ cm} = (2450 \text{ x } 10^{-8} \text{ x } 10^{-2}) \text{ m} = 2450 \text{ x } 10^{-10}$
   $\epsilon =(6.626 \text{ x } 10^{-34} \text{ Js}) \text{ x } (2.998 \text{ x } 10^8 \text{ ms}^{-1}) / (2450 \text{ x } 10^{-10} \text{ m}) = 8.108 \text{ x } 10^{-19}$ J.

   Energy of one mole photon, $E = N_A \epsilon$ where N_A is Avogadro number
   $=(6.023 \text{ x } 10^{23}) \text{ x } (8.108 \text{ x } 10^{-19} \text{ J})$

$= 48.83 \times 10^4$ J = 488.3 kJ

Bond energy of diatomic molecule = 95 kcal / mol = (95 x 4.184) kJ / mol

=397.48 kJ / mol

To break one mole of diatomic molecule 397 kJ energy is required whereas one mole of photon can supply 488 kJ energy. So the radiation of wavelength 2450Å will not be able to dissociate the diamagnetic molecule.

(c) Application of NMR: Nowadays proton NMR spectroscopy is used widely to diagnose disease. Living tissue is rich in proton nucleus ^1H and ^{31}P is also present in the cells. Both the nuclei ^1H and ^{31}P have magnetic moments and can show NMR absorption signals. NMR studies of both these nuclei have found application in medicine. ^{31}P shows wide range of chemical shiefts and its coupling patterns to nearby hydrogens can give structural information in the cell. Disorders in the soft tissue in a body can occur due to alteration in the type or concentration of phosphorous – containing chemicals in the cells and NMR studies can be useful in the diagnosis of damage of tissues.

Application of MRI: Proton NMR spectra has now developed in medical science in a different way. The technique is known as Magnetic Resonance Imaging (MRI). In this technique proton NMR spectra of the cells in living tissue is not produced, rather a density map (or image) of the proton in the tissue is produced. From image it become possible to know whether there has been a damage of the soft tissue in the part of the body studied. The most important fact about MRI photograph is that it can distinguish between normal cell and cancerous cell.

In the MRI technique part of the body such as, eyes nose, spinal cord, brain can be studied. The part of the body to be studied is placed in a magnetic field with a known varying gradient and the size of the proton NMR signals is measured as a function of distance along field.

Easy:

(a) Most of absorption bands in the UV – Visible spectra are very broad. Give reasons. 3

(b) Why does 1, 3 butadiene possess higher λ_{max} value than that of ethane? 3

(c) Why the colour of sky is blue? 2

(d) Predict the proton NMR spectra of CH_4. 3

(e) Name any four surface characterization techniques. 4

(a) UV visible spectra involve transitions between electronic energy level which are associated with vibrational and rotational energy levels. The electronic transition may occur from any of the several vibrational and rotational states of one electronic level to any of the various corresponding states of higher level. Since a large number of transitions are possible, so a large number of absorptions will take place corresponding to different wavelengths. Hence, spectra are very board.

(b) In 1, 3 butadiene $\pi_2 \rightarrow \pi_3^*$ excitation takes place, which requires lesser energy (of higher wavelength) than $\pi \rightarrow \pi^*$ excitation in ethane.

(c) The Rayleigh scattering causes the blue light from the sun to be scattered more than other wavelength light.

(d) In CH_4 contain equivalent protons which do not show spin – spin interaction. Hence, their proton NMR spectra will consist of one signal only, i.e. a singlet.

(e) The important surface characterization techniques are:

(i) Macromolecular crystallography (MX)

(ii) X – Ray Reflectively (XRR)

(iii) Scattering – SAXS and WAXS

(iv) X – Ray Photoelectron Spectroscopy (XPS) in Surface Chemical Analysis

(v) Dynamic Secondary Ion Mass Spectrometry.

STEREOCHEMISTRY

1 Mark

Easy

1. For n – butane which type of conformation is the least stable?
   Fully eclipsed.
2. How many stereo isomer are possible for 2, 3 – pentanediol?
   Four.
3. Give one example of ionization isomerism.
   $[Co(NH_3)_5(SO_4)]Br$ and $[Co(NH_3)_5 Br] (SO_4)$
4. Which isomerism is shown by alkenes but not by alkanes?
   Geometrical isomerism.

Moderate

1. Give one example of Coordination isomerism.
   $[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$
2. How many number of ions generated when potassium ferrocyanide dissolved in water?
   5
3. How many Chiral centres are present in meso – tartaric acid?
   Two.

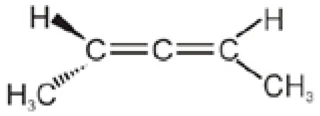
Hard

1. Give one example of ambidentate ligand.
   NO_2^-

5Mark

Easy

1. (a) Define specific rotation for an optically active molecule.
   (b) What is the necessary and sufficient condition for a molecule to be optically active?
   (c) The following compound not have a chiral center still it shows optical activity---- comment



(a) Specific rotation is the degree of a rotation of plane polarized light by an optically active compound when the light is passed through one decimeter (10 cm) of a solution having a concentration one gram per cm^3.
The specific rotation of a compound is representated as $[\alpha]_D^t$ where t stands for temperature and D for D- lines of sodium light.
$[\alpha]_D^t = \alpha_{obs}/l \times C$, where l represents the length of the solution column in decimeters and C represents the concentration of the substance.

(b) The necessary and sufficient condition for a molecule to be optically active is that its should be chiral i.e., the molecule and its mirror imag should be non super imposable.

(c) There exist same molecules which possess no asymetric carbon or chiral centre, yet they exibit optical activity. This is because they have chirality in them as a whole.
2,3 pentadiene exibits optical activity due to the reason that two – CH_3 groups that are singly bonded to the terminal carbon atoms of the allene system are lying perpendicularly to one another in two separate planes. As a consequence this compound exist in two non superimposable mirror images.

Modarate

1. (a) Distinguish between constitutional isomers and stereo isomers.
   (b) What is chirality?
   (c) Does presence of two chiral carbon atoms always make the molecule optically active? Explain.

(a)

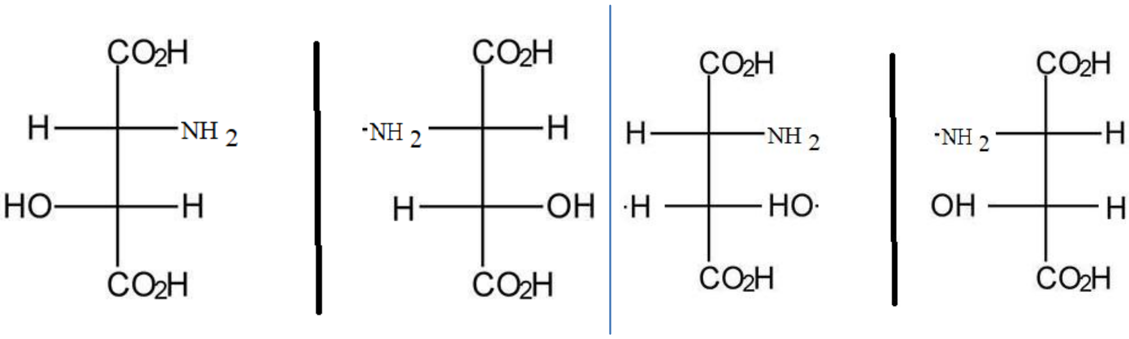
Constitutional Isomers	Stereo Isomers
They have same molecular formula but different chemical structure	They have same molecular formula and same chemical structure
They may possess different functional group	They may possess same functional group
They have different connectivity of atoms in different structure.	They have same connectivity of atoms but different orientation of groups in space
They have different physical as well as chemical properties.	They have same physical and chemical properties but different optical properties.

(b) Chiral objects are those which possess no element of symmetry and is not superimposable to its mirror image. This phenomenon is called chirality.

(c) Not necessarily. The presence of two similar chiral carbon atoms may or may not make the molecule optically active. If the molecule as a whole is achiral, it is optically inactive. For example, (+) tartaric acid and (-) tartaric acid are optically active because their molecules are chiral. On the other hand meso – tartaric acid is optically inactive because its molecule is achiral. i.e., the molecule and its mirror image are superimposable due to the presence of a plane of symmetry in it.

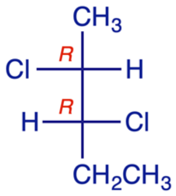
Hard

1. (a) What will happen if one of the OH group of tartaric acid is replaced by NH_2 Group?
   (b) How many pairs of enantiomers are possible for the compound, 2, 3 dichloropentane?

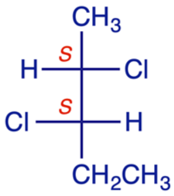


If one of the OH groups of tartaric acid is replaced by NH_2 group, possible configuration will be above. Thus , number of optically active forms will increase. Beside the above four forms there are diasteriods.

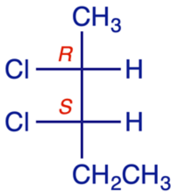
(b)Two pairs of enantiomers, i.e., four optically active forms of 2, 3 – dichloropentane are possible.



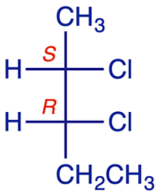
1
2R,3R



2
2S,3S



3
2R,3S



4
2S,3R

15 Mark

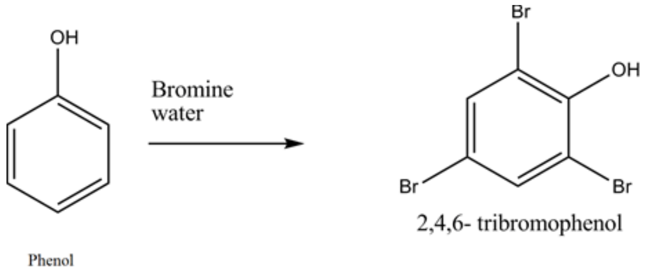
Easy

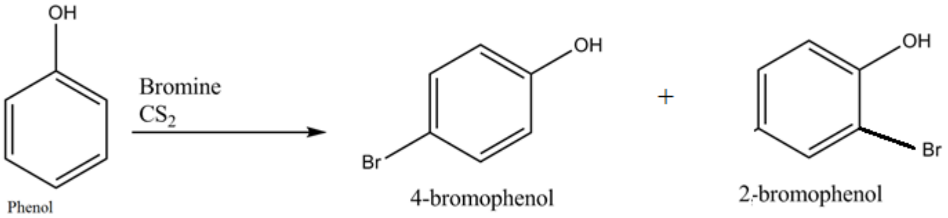
1. (a) Phenol on treatment with Br_2 in CS_2 at low temperature gives two isomeric monobromophenols X and Y. But phenol on treatment with bromine water gives a white precipitate Z. Identify the products X, Y and Z with chemical reactions. 6

(b) What do you mean by enantiomer and diastereomer? Differentiate them with examples. 4

(c) Explain the difference between a meso – isomer and a recimic mixture. What characteristics do they have in compound? 5

(a)





(b) Enantiomers: The stereoisomers which are non – superimposable mirror images of each other are known as enantiomers. Chirality is the most fundamental condition of enantiomerism.

Characteristics:

1. Enantiomers have similarities in their physical properties such as melting and boiling points, solubilities, refractive index etc. although they have difference in their optical properties like direction of rotation of plane polarized light.
2. They have identical chemical properties except the rate of reaction.
3. Enantiomers differ in their biological properties.

Diastereomerism: Stereoisomers of a compound which are neither mirror images of each other non superimposable are known as diastereomers.

Characteristics:

1. Diastereomers have different physical as well as chemical properties.
2. Diastereomers possess similar chemical properties although the rate at which they react with other optically active substance may vary.
3. Stereoscopic characterization , specially the NMR and mass spectra od diastereomers may have difference.

Comparison of Enantiomers and Diastereomers:

Enantiomers	Diastereomers
Enantiomers have mirror image relationship.	Diastereomers do not have any mirror image relationship.
They have similarities in physical properties.	They possess difference in physical properties
Enantiomers can show optical rotation to the same	Diastereomers may show optical rotation in the same

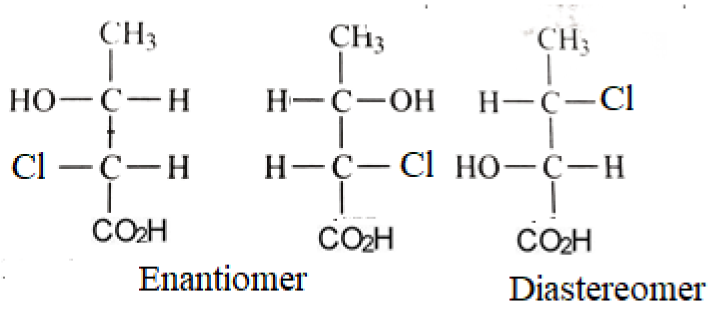
extent but in opposite direction	or opposite directions but to the same extent.
These cannot be separated by the methods like fractional distillation, absorption chromatography etc.	These can be separated by these methods

(c) A meso isomer is a single compound, a recimic mixture contains an equimolar mixture of two compounds. The meso isomer is inherently inactive because of internal compensation; the racimic mixture does not rotate the plane of polarized light because the effect of one of the isomers cancels the effect of the other. The recimic mixture can be separated into two optically active compounds by physical means. The meso isomer and the racimic mixture have in common their inability to rotate the plane of polarized light. Both have two centres of (opposite) chirality.

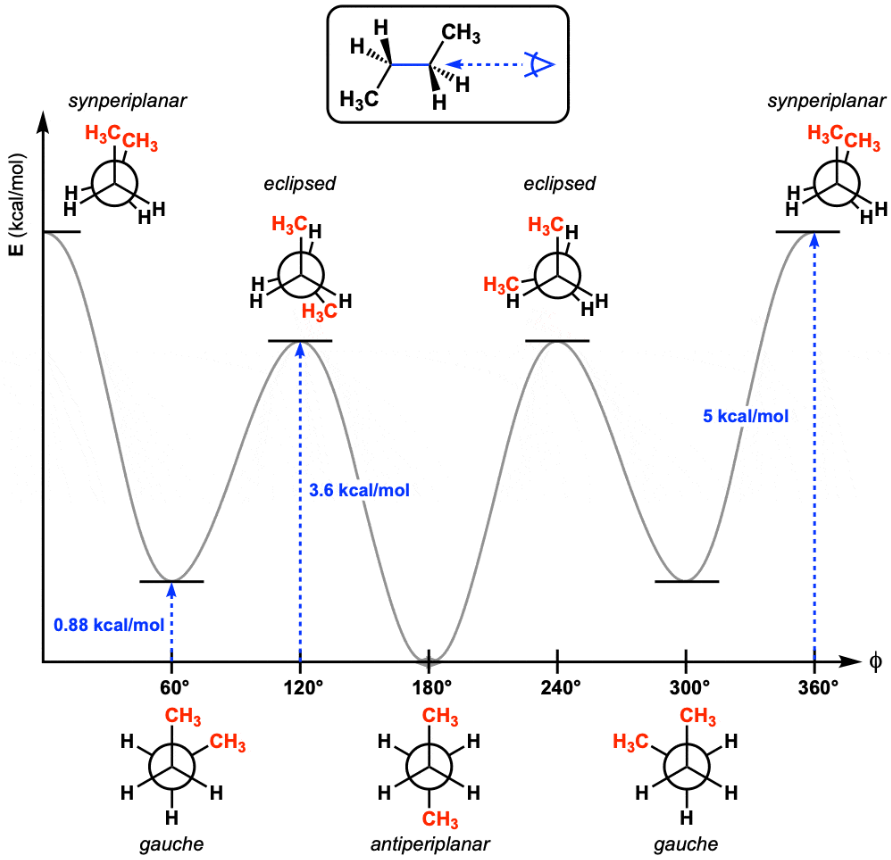
Moderate

1. (a) Draw all the stereo isomers for the following: 4
   $CH_3CH(OH) – CH (Cl) COOH$
   (b) Arrange the different conformations of n – butane in terms of their stability. 5
   (c) The following compounds are optically active or not: 6
   (i) n- propanol (ii) n – butanol (iii) 2 – chlorobutane.

(a)



(b)



(c) (i) n – propanol is optically inactive because it has no chiral carbon. $CH_3 - CH_2 - CH_2\ OH$

(ii) n – butanol is optically inactive because it has no chiral carbon. $CH_3 - CH_2 - CH_2 - CH_2\ OH$

(iii) 2 – chlorobutane is optically active because it has one chiral carbon. $CH_3 - CH\ (Cl) - CH_2CH_3$

Hard

1. (a) Define the following elements of symmetry with a suitable example in each case: 8

(i) Rotational axis of symmetry

(ii) Plane of symmetry

(iii) Centre of symmetry

(iv) Alternating axis of symmetry

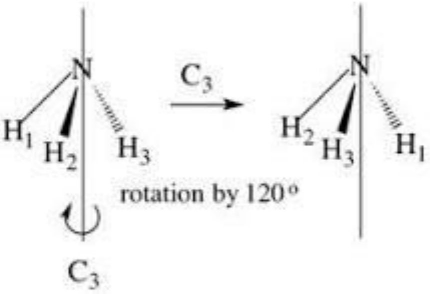
(b) Draw all possible stereo isomers for butane – 2, 3 – diol. Are all of them optically active? 3

(c) Draw all Fischer projection formula of following stereoisomers:

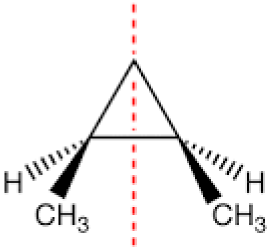
(i) (2R, 3R) – 2, 3 – dibromobutanedioic acid.

(ii) S – 2 – Hydroxy – 2 – phenylpropanoic acid.

(a) (i) Proper Rotations - Rotation by $360^o/n$. This is simply rotation about an axis, which passes through the molecule by an angle of $360^o/n$ (or $2\pi/n$). When repeated n times, the molecule returns to the original orientation. The appearance of the molecule must be exactly the same after the operation.



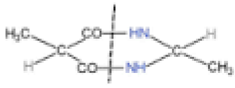
(ii) Plane of symmetry: A plane of symmetry is an imaginary plane that bisects a molecule into halves that are mirror images of each other.



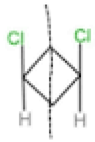
3

(iii) Centre of symmetry: Center of symmetry of a molecule is the center point from which the identical atoms exist on the opposite side from this center at equal distance.

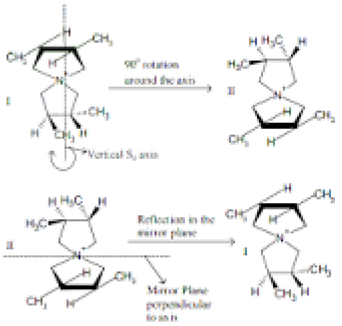
(i)



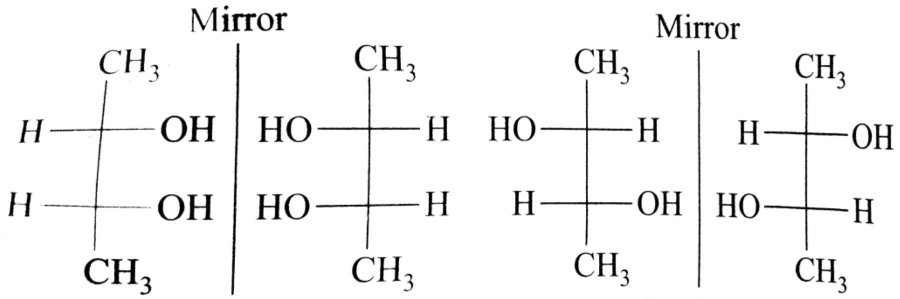
(iii)



Alternating axis of symmetry: A molecule possess an n-fold alternating axis of symmetry if when rotated through an angle of $360^o/n$ about this axis and then followed by reflection in plane perpendicular to the axis; the molecule is indistinguishable from the original molecule.



(b) Stereoisomers of butane 2, 3 – diol

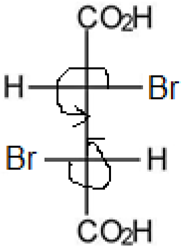


Meso compound
(Superposable mirror images)

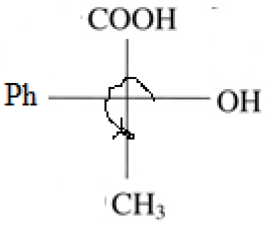
Enantiomers
(Nonsuperposable mirror images)

Meso compounds are optically inactive as they possess plane of symmetry. But the two enantiomers are optically active.

(c) (i) (2R, 3R) – 2, 3 – dibromobutanedioic acid.



(ii) S – 2 – Hydroxy – 2 – phenylpropanoic acid



USE OF FREE ENERGY IN CHEMICAL EQUILIBRIA

1 MARK

HARD

1. In a certain process 678 J of heat is absorbed by a system while 290 J of work is done on the system. What is the change in internal energy for the process?

968 J

MODERATE

1. State one application of first law of thermodynamics.

Hess's law is an application of first law of thermodynamics.

2. For the reaction $2Al_2O_3 = 4Al (s) + 3O_2(g)$, $\Delta H = 334kJ$, what is the enthalpy of formation of Al_2O_3 ?

-1670 kJ

3. What is the amount of free energy change for a reversible process?

Free energy change for a reversible process is equal to zero.

Easy

1. Give one example of State Function

Enthalpy.

2. Write one process where entropy decreases.

The conversion of CO_2 into dry ice, here entropy decreases.

3. At inversion temperature what is the Value of Joule – Thomson coefficient?

At inversion temperature Joule Thomson Coefficient value is Zero.

4. Give one example of intensive property.

Density.

5 marks

Easy:

1.(a) Explain the term chemical potential. 1

(b) Derive the relation of EMF of cell with ΔG and ΔH. 4

For a pure substance chemical potential is equal to molar Gibbs free energy. In a system of variable composition chemical potential of a substance is equal to the rate of change of the Gibbs free energy G of the system with respect to the moles of i added at constant T, P and other mole numbers. Thus for a two component mixture chemical potential of the component 1 is μ_1 and is given by,

$$\mu = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n2}$$

(b) Relation between ΔG and EMF of a cell (E).

The relation between ΔG and E is $\Delta G_{T,P} = -nFE$. Electrical work is produced at the cost of decreade in Gibbs free energy.

Relation between ΔH and E

We know at constant T, P, $\Delta G = \Delta H - T\Delta S$

From Gibbs – Helmholtz equation for a reaction

$$\Delta S = \left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\left[\frac{\partial(-nFE)}{\partial T}\right]_P = nF\left(\frac{\partial E}{\partial T}\right)_P$$

We have, $\Delta H = \Delta G + T\Delta S$

Therefore, $\Delta H = -nFE + TnF\left(\frac{\partial E}{\partial T}\right)_P = -nF\,[\,E - T\left(\frac{\partial E}{\partial T}\right)_P]$

2. How many types of hardness is possible? Why hard water is not suitable for boiler use? 3 + 2

Hardness of water is of two types.

(i) Temporary Hardness : It is caused due to presence of bicarbonates of calcium and magnesium. It can be removed easily by boiling.

(ii) Permanent Hardness: It is caused due to presence of chlorides and sulphates of calcium and magnesium salts. It cannot be removed by boiling.

Huge quantity of water is used in boilers for generation of steam. If hard water is used in the boiler, a number of difficulties arise which are as follows:

Scale and sludge formation

Boiler Corrosion

Priming and foaming

Caustic embrittlement.

Moderate:

1. Show that, entropy of mixing of ideal gases $\Delta S_{mix} > 0$. 5

Mixing of two or more gases are spontaneous process, hence it should be accompanied by increase in entropy.

Let n_1 moles of ideal gas A_1 and n_2 moles of gas A_2 having volume V_1 and V_2 at constant pressure P and temperature T be separated by a partition. After removing the partition, these two gas mixed spontaneously when the total pressure P and the final temperature T remain constant and both gas occupying the entire volume, $V = V_1 + V_2$ of the cylinder.

Hence the entropy change $\Delta S_1 = n_1R \ln (V_1 + V_2) / V_1$

Similarly for gas A_2 $\Delta S_2 = n_2R \ln (V_1 + V_2) / V_2$

Since gases are ideal, each gas acts independently of the other. Hence entropy change of mixing ΔS_{mix} is equal to the sum of the entropy change due to their individual isothermal volume expansion.

$\Delta S_{mix} = \Delta S_1 + \Delta S_2 = n_1R\ln\frac{(V_1+V_2)}{V_1} + n_2R\ln\frac{(V_1+V_2)}{V_2} = -n_1Rln\frac{V_1}{V_1+V_2} - n_2Rln\frac{V_2}{V_1+V_2}$

If X_1 and X_2 are the mole fraction of gas A_1 and A_2 respectively in the mixture, then,

$X_1 = n_1/ (n_1 + n_2) = n_1 / n = V_1 / (V_1 + V_2)$

$X_2 = n_2/ (n_1 + n_2) = n_2 / n = V_2 / (V_1 + V_2)$

Entropy of mixing:

$\Delta S_{mix} = - n_1R \ln X_1 – n_2R \ln X_2 = -nR(n_1/n \ln X_1 + n_2/n \ln X_2) = -nR(X_1 \ln X_1 + X_2 \ln X_2)$

The equation may be generalise to the mixing of N ideal gases,

$\Delta S_{mix} = -nR\sum_{i=1}^{N} X_i lnX_i$

Molar entropy of mixing

$(\Delta S_{mix})_{mix} = -R\sum_{i=1}^{N} X_i lnX_i$

Since mole fraction X_i of gas always less than 1, hence $\ln X_i$ always less than zero. So ΔS_{mix} is always > 0.

Hard

1. 'All adiabatic reversible expansions lead to a fall of temperature.' – Comment or Justify. 5

   From 1st law of thermodynamics $\Delta U = Q + W$ where W is negative for expansion process. In adiabatic process Q = 0. So, for adiabatic process $\Delta U = W$. In reversible expansion appreciable work is produced and ΔU is negative for a adiabatic reversible expansion since W is negative in expansion process. For ideal gas internal energy (U) depends only on temperature and $\Delta U = C_v\Delta T$. Since in adiabatic reversible expansion ΔU is negative it is seen that for this process ΔT is negative (because C_V is always positive) $\Delta T = T_{final} - T_{initial}$. For adiabatic reversible expansion of ideal gas $T_f < T_i$.. For adiabatic reversible expansion there occurs a fall of temperature. (For real gases volume increase has negligible effect on ΔU and there is cooling effect in adiabatic reversible expansion in all cases).

   15 Marks

   Easy

   1. (a) What is the condition of spontaneity in terms of entropy? The condition of spontaneity : $\Delta G_{x,\,y} < 0$; $\Delta A_{p,r} < 0$, where G is the Gibbs Free Energy and A is the Helmholtz free energy. Identify x, y, p and r. 2 + 4
      (b) State whether the following properties are extensive or intensive properties:
      Pressure, Concentration, Entropy, Viscosity, Temperature. 5
      (c) For a reaction both ΔH and ΔS are positive. Under what conditions will the reaction be spontaneous? What is state function? Give example. 2 + 2

      (a) Condition of spontaneity in terms of entropy for isolated system $\Delta S > 0$.
      Condition of spontaneity in terms of entropy for non-isolated system $\Delta S_{total} > 0$
      $\Delta S_{total} = \Delta S_{universe} = \Delta S_{system} + \Delta S_{surrounding} > 0$
      Condition of spontaneity in constant T, P process is $\Delta G_{T,\,P} < 0$.
      Condition of spontaneity in constant T, V process is $\Delta A_{T,\,V} < 0$.
      (b) Pressure : intensive property
      Concentration : intensive property
      Entropy: extensive property
      Viscosity : intensive property
      Temperature: intensive property.
      (c) If $T\Delta S > \Delta H$ the reaction will be spontaneous. If ΔS and ΔH both are positive, then T must be high for the spontaneity of the reaction.
      A state function is a property that depends only on the state of the system and not on how the system has been achieved. Example: Enthalpy, Entropy etc.

Moderate

1. (a) Write the Nernst equation for the cell reaction in the Daniel cell. How will the E_{cell} effected when the concentration of Zn^{2+} is increased?

(b) What do you mean by hardness of water? Explain how hard water fails to form lather with soap? What is alkalinity of water? 5

(c) Define corrosion. What are different types of corrosion? 5

(a) Daniel Cell is represented as $Zn\,|\,(s)\ \ Zn^{2+}\,||\,(aq)\ \ Cu^{2+}\,|\,(aq)\ \ Cu\ (s)$

The cell reaction for 2F electricity drawn is $Zn\ (s) + Cu^{2+}\ (aq) = Zn^{2+}\ (aq) + Cu\ (s)$

Nernst equation for the cell reaction is

$$E = E^0 - \frac{RT}{2F}\ln(a_{Zn^{+2}} \times a_{Cu})/\,(a_{Zn^{+2}} \times a_{Cu})$$

$$= E^0 - \frac{RT}{2F}\ln C_{Zn^{+2}}/C_{Cu^{+2}}$$

Assuming activity if ion equal to concentration of the ion and activity of solid = 1.

The Nernst equation shows that if concentration of Zn^{2+} is increased cell potential E decreases. [$\Delta G_{T, P}$ = -nFE. For spontaneous reaction E is positive and ΔG is negative. Decrease of E with increase of concentration of Zn^{2+} makes ΔG less negative. The tendency of forward reaction is diminished and this is an accord with Le – Chatelir principle that if a product species is added the reaction is shifted to the left side.]

(b) Hardness is the characteristic of water which prevents formation of lather with soap. This is due to the presence of certain salts of calcium, magnesium and other heavy metals dissolved in it. The salts are calcium chloride, calcium carbonate, calcium bicarbonate, magnesium chloride, magnesium carbonate, magnesium bicarbonate etc.

Hard water, when treated with soap (sodium or potassium salt of higher fatty acid like oleic, palmitic or stearic) does not produce lather, but forms scum or precipitate. The reactions of soap (sodium stearate) with calcium and magnesium salts are depicted below.

$2\ C_{17}H_{35}COONa + CaSO_4 \longrightarrow (C_{17}H_{35}COO)_2\ Ca \downarrow + 2Na_2SO_4$

$2\ C_{17}H_{35}COONa + MgCl_2 \longrightarrow (C_{17}H_{35}COO)_2\ Mg \downarrow + 2NaCl$

When all the Ca & Mg removed then hard water getting soft and it produces lather.

The alkalinity of natural water is ordinarily due to presence of carbonates, bicarbonates of calcium and magnesium. The alkalinity of water can be considered mainly due to Hydroxide, Carbonates and Bicarbonates.

The alkalinity of water can be estimated separately by titration against standard acid solution.

Corrosion may be defined as the process of slow deterioration of surface of metal due to direct attack by atmospheric gases, moisture present in the atmosphere or by any other chemical or electrochemical environment.

Different type of corrosion:

Dry Corrosion

Liquid – metal corrosion

Wet Corrosion (Electrochemical corrosion)

(i) Wet corrosion of metal with evolution of H_2gas

(ii) Wet corrosion of metal by absorption of O_2.