Solved Question Paper-Dec ~~2018~~ 2019

CHEMISTRY-I

Subject Code : BTCH-101-18
M.Code : 75343

Time : 3 Hrs.   **Max. Marks : 60**

SECTION-A

Answer briefly :

1. **What do you understand by effective nuclear charge?**

Ans. The effective nuclear charge (often symbolized as Z_{eff} or Z^*) is the net positive charge experienced by an electron in a polyelectronic atom. The term "effective" is used because the shielding effect of negatively charged electrons prevents higher orbital electrons from experiencing the full nuclear charge of the nucleus due to the repelling effect of inner-layer electrons.

It is the next charge experienced by an election in a poly electronic atom or in an atom having multiple electrons.

$Z_{eff} = Z - S$
$Z =$ Atomic no.
$S =$ No. of shielding elections

2. **Why d and f orbital show poor shielding effect?**

Ans. Poor shielding means poor screening of nuclear charge. In other words, the nuclear charge is not effectively screened by electrons in question. The shielding effect of different orbitals is as follows: s orbital's > p orbital's > d orbital's > f orbital's.

Electrons which are closer to the nucleus experience greater nuclear attraction and effectively shield other electrons from nuclear attraction. The electrons in the s-orbital have maximum probability of being found near the nucleus and this probability goes on decreasing in case of p,d and f orbitals. Or in other words we can say that distance of electrons from nucleus increases its shielding effect decreases.

3. **What is the essential condition for a molecule to be IR active?**

Ans. It should be polar or it shoud have chanding dipole moment. The molecule should not be symmetrical for IR active. HCl, NH_3 are IR active but H_2, N_2 and CCl_4 are not IR active.

4. **What is isomerism?**

Ans. Isomerism is the phenomenon in which more than one compounds have the same chemical formula but different chemical structures. Chemical compounds that have identical chemical formulae but differ in properties and the arrangement of atoms in the molecule are

called isomers.

5. How do Vander Waals interactions occur?

Ans. Van der Waals forces include attraction and repulsions between atoms, molecules, and surfaces, as well as other intermolecular forces. They differ from <u>covalent</u> and <u>ionic</u> bonding in that they are caused by correlations in the fluctuating polarizations of nearby particles (a consequence of quantum dynamics. Being the weakest of the weak chemical forces, with a strength between 0.4 and 4kJ/mol, they may still support an integral structural load when multitudes of such interactions are present. The force results from a transient shift in electron density. Specifically, the electron density may temporarily shift more greatly to one side of the nucleus.

6. Can oxidation state be negative? Discuss.

Ans. Conceptually, the oxidation state, which may be positive, negative or zero, is the hypothetical charge that an atom would have if all bonds to atoms of different elements were 100% ionic, with no covalent component. The oxidation state of an atom does not represent the "real" charge on that atom, or any other actual atomic property. This is particularly true of high oxidation states, where the ionization energy required to produce a multiply positive ion is far greater than the energies available in chemical reactions.
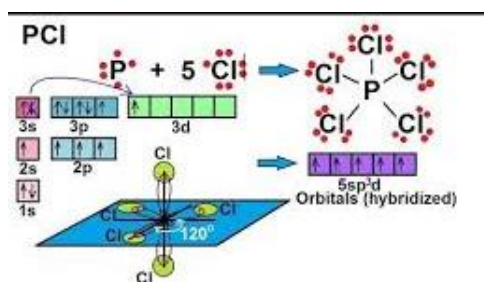
7. How many signals would you expect to see in the ^{1}H NMR spectrum of the following:

$$CH_3CH_2CH_2CH_3$$
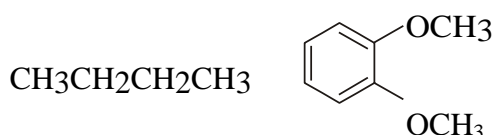
Ans. For Ist molecule no of signals = 2 and for second molecule no of signals = 2

8. What are the shapes PCl$_5$ and H$_2$O?

Ans. PCl$_5$ have trigonal bipyramidal and H$_2$O have bent shape.

9. Define entropy and gibbs free energy.

Ans. Entropy is defined as the randomness in the system and is represented by symbol S. The second law of thermodynamics says that the entropy of the universe always increases for a spontaneous process:

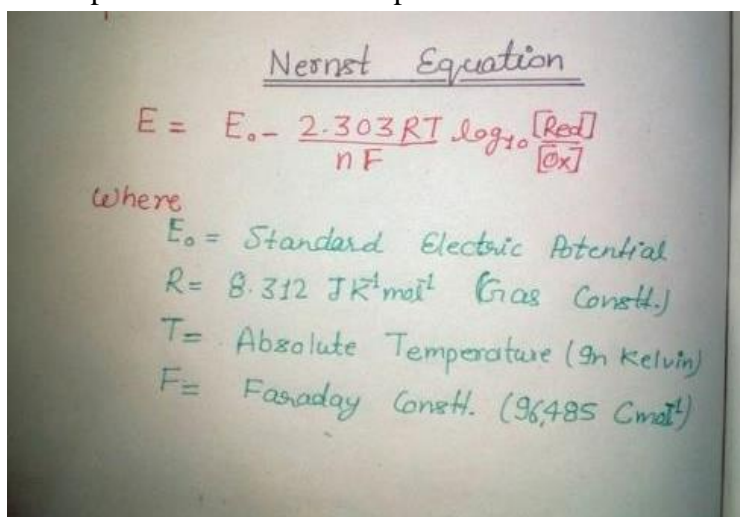$$\Delta S_{universe} = \Delta S_{system} + \Delta S_{surroundings} > 0$$

Gibbs free Energy is defined as the free energy that can be convertible into usefull work. At constant temperature and pressure, the change in Gibbs free energy is defined as :
$$\Delta G = \Delta H - T\Delta S$$
When G, is negative, a process will proceed spontaneously and is referred to as exergonic.

10. Write down the Nernst equation and define electric potential.

Ans. Electric potenial is the potential of an electrode to get oxidized or to get reduced generally represented as oxidation potential and reduction potential.

Nernst Equation

$$E = E_0 - \frac{2.303RT}{nF} \log_{10} \frac{[Red]}{[Ox]}$$

Where

E_0 = Standard Electric Potential

R = 8.312 $JK^{-1}mol^{-1}$ (Gas Const.)

T = Absolute Temperature (In Kelvin)

F = Faraday Const. (96,485 $Cmol^{-1}$)

SECTION-B

11. a) Obtain the time-dependent Schrödinger wave equation for a particle.

Ans.

b) Give the physical meaning of wave function.

Ans. The wave function ψ does not have any physical significance but the ψ^2 describes the intensity of electron cloud and in quantum mechanics the intensity is described as the probability of electron cloud in three dimensional space. In other words it describes the orbital of electron.

12. Write short notes on :

a) Shielding and deshielding of protons (4)

Ans. The basic principle of NMR is to apply an external magnetic field called B0 and measure the frequency at which the nucleus achieves resonance.

Electrons orbiting around the nucleus generate a small magnetic field that opposes B0. In this case we say that electrons are shielding the nucleus from B0.

Shielding:

The higher the electron density around the nucleus, the higher the opposing magnetic field to B0 from the electrons, the greater the shielding. Because the proton experiences lower external magnetic field, it needs a lower frequency to achieve resonance, and therefore, the chemical shift shifts upfield (lower ppms) .
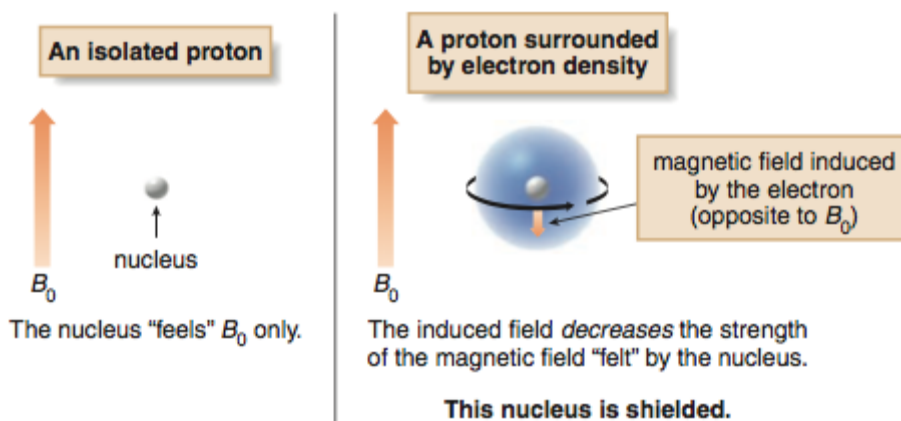
Deshielding:

If the electron density around a nucleus decreases, the opposing magnetic field becomes small and therefore, the nucleus feels more the external magnetic field B0, and therefore it is said to be deshielded. Because the proton experiences higher external magnetic field, it needs a higher frequency to achieve resonance, and therefore, the chemical shift shifts downfield (higher ppms).
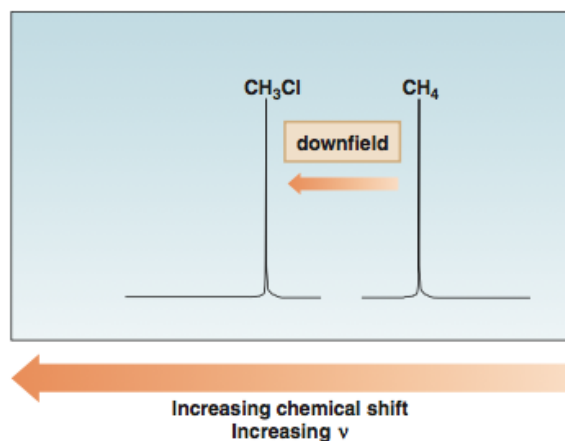
b) Factors affecting vibrational frequency (4)

Ans. The value of vibrational frequency of a bond calculated by Hooke's Law is not always equal to their observed value. The force constant is changed with the electronic and steric effects. Factors affecting vibrational frequencies and IR Spectroscopy of Hydrocarbons caused by other groups present in the surroundings. Following are some important factors affecting

the vibrational frequency of a bond.

1. **Effect of Bond Order**

Bond order affects the position of absorption bands. Higher the bond order larger is the band frequency. A C-C triple bond is stronger than a C=C bond, so a C-C triple bond has higher stretching frequency than does a C=C bond.

2. **Resonance and Inductive Electronic Effects**

A range of frequency for each stretch is usually assigned as the exact position of the absorption band depends on other structural features of the molecule, such as electron delocalization, the electronic effect of neighbouring substituents, and hydrogen bonding.
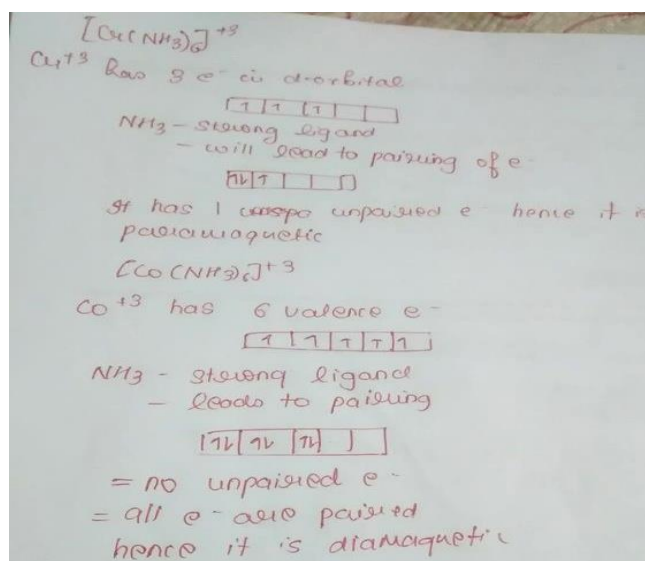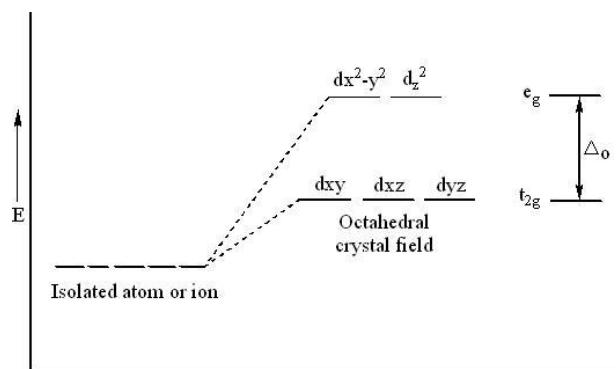
3. **Hydrogen Bonding**

The presence of hydrogen bonding changes the position and shape of an infrared absorption band. Frequencies of both stretching as well as bending vibrations are changed because of hydrogen bonding. The X-H stretching bands move to lower frequency usually with increased intensity and band widening.

13.   a) What is crystal field theory? How does this theory account for the fact that $[CoF_6]^{3-}$ is paramagnetic but $[Co(NH_3)_6]^{3+}$ is diamagnetic though both are octahedral. (6)

Ans. Crystal field theory (CFT) describes the breaking of degeneracies of electron orbital states, usually d or f orbitals, due to a static electric field produced by a surrounding charge distribution (anion neighbors).

In an octahedral complex, the metal ion is at the centre and the ligands are at the six corners. In the figure, the directions x, y and z point to the three adjacent corners of the octahedran. The lobes of the e_g orbitals (dx^2-y^2 and dz^2) point along the x, y and z axis while the lobes of the t_{2g} orbitals (dxy, dzx and dyz)point in between the axes. As a result, the approach of six ligands along the x, y z, -x,-y and –z directions will increase the energy of dx^2-y^2 and dz^2 orbitals (which point towards the ligands) much more than that it increases the energy of dxy, dzx and dyz orbitals (which point in between the metal-legand bond axis).

Thus, under the influence of an octahedral field, the d orbitals split into triply degenerate orbitals with less energy and another as doubly degenerate orbitals with higher energy. The main energy level between these two sets of orbitals is taken as zero, which is called *bari centre*. The splitting between these two orbitals is called crystal field splitting. The magnitude of stabilization will be $0.4\ \Delta_o$ and the magnitude of destabilization will be $0.6\ \Delta_o$.

Octahedral crystal field diagram

[Cu(NH₃)₆]⁺³

Cu⁺³ has 9 e⁻ in d-orbital

NH₃ - strong ligand
 - will lead to pairing of e⁻

It has 1 unpaired e⁻ hence it is paramagnetic

[Co(NH₃)₆]⁺³

Co⁺³ has 6 valence e⁻

NH₃ - strong ligand
 - leads to pairing

= no unpaired e⁻
= all e⁻ are paired
hence it is diamagnetic

(b) Discuss the role of doping on the band structure of solids. (2)

Ans. In semiconductor production, doping is the intentional introduction of impurities into an intrinsic semiconductor for the purpose of modulating its electrical, optical and structural properties. The doped material is referred to as an extrinsic semiconductor. A semiconductor doped to such high levels that it acts more like a conductor than a semiconductor is referred to as a degenerate semiconductor. In the context of phosphors and scintillators, doping is better known as activation. Doping is also used to control the color in some pigments.

14. a) Derive the van der Waals equation for describing P-V-T relationship in real gases. (5)

b) Explain the different type of molecular forces. (3)

Intermolecular forces are electrostatic in nature; that is, they arise from the interaction between positively and negatively charged species. Like covalent and ionic bonds, intermolecular interactions are the sum of both attractive and repulsive components.

Types:

1. Dipole–Dipole Interactions

Polar covalent bonds behave as if the bonded atoms have localized fractional charges that are equal but opposite (i.e., the two bonded atoms generate a *dipole*). If the structure of a molecule is such that the individual bond dipoles do not cancel one another, then the molecule has a net dipole moment. Molecules with net dipole moments tend to align themselves so that the positive end of one dipole is near the negative end of another and vice versa.

2. London Dispersion Forces/ Instantaneous dipole–induced dipole interactions

Fritz London (1900–1954), a German physicist who later worked in the United States. In 1930, London proposed that temporary fluctuations in the electron distributions within atoms and nonpolar molecules could result in the formation of short-lived instantaneous dipole moments, which produce attractive forces called London dispersion forces between otherwise nonpolar substances.

3. Hydrogen Bonds

Molecules with hydrogen atoms bonded to electronegative atoms such as O, N, and F (and to a much lesser extent Cl and S) tend to exhibit unusually strong intermolecular interactions.
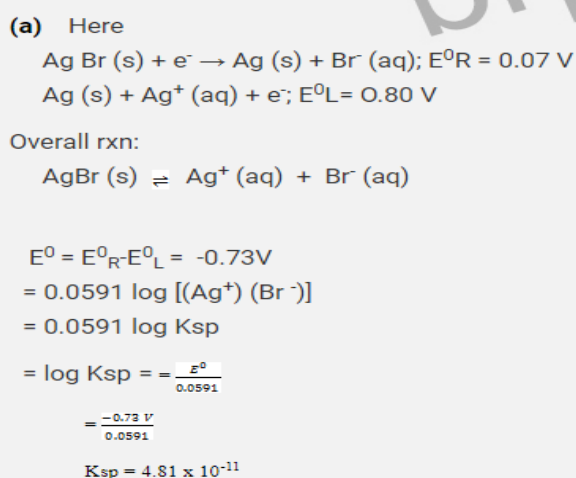
SECTION-C

15. a) **Calculate the solubility product of AgBr in water at 25°C from the cell :** (4)

   a. $Ag, Ag^{\square} Br_{(sat,sol)} | AgBr_{(s)}, Ag$

   The standard potentials are $E^{\square}_{AgBr,Ag} \square \ 0.07V \ ; E^{\square}_{Ag \square, Ag} \square \ 0.80V$

Ans.

(a) Here

Ag Br (s) + e⁻ → Ag (s) + Br⁻ (aq); E⁰R = 0.07 V

Ag (s) + Ag⁺ (aq) + e⁻; E⁰L= 0.80 V

Overall rxn:

AgBr (s) ⇌ Ag⁺ (aq) + Br⁻ (aq)

$E^0 = E^0_R - E^0_L = -0.73V$

$= 0.0591 \log [(Ag^+)(Br^-)]$

$= 0.0591 \log Ksp$

$= \log Ksp = = \dfrac{E^0}{0.0591}$

$= \dfrac{-0.73 \, V}{0.0591}$

$Ksp = 4.81 \times 10^{-11}$

b) Calculate the standard free energy change ($\Delta G°$) of the reaction : (4)

$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow C(g) \quad \Delta H = -282.84 kJ$$
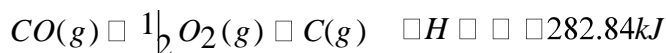
The standard entropy of $CO_2(g)$, $CO(g)$ and $O_2(g)$ are 213.80, 197.90 and 205.01 J K^{-1} mol^{-1}, respectively. Is this reaction feasible at standard state?

Ans.

1. $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393$ kJ
2. $2CO(g) + O_2 \rightarrow 2CO_2(g)$; $\Delta H = -588$ kJ

To solve this problem, we use Hess's Law.

Our target equation has C(s) on the left hand side, so we re-write equation 1:

1. $C(s) + O_2(g) \rightarrow CO_2(g)$; $\Delta H = -393$ kJ

Our target equation has CO(g) on the right hand side, so we reverse equation 2 and divide by 2.

3. $CO_2(g) \rightarrow CO(g) + \tfrac{1}{2}O_2$; $\Delta H = +294$ kJ

That means that we also change the sign of ΔH and divide by 2.

Then we add equations 1 and 3 and their ΔH values.

This gives

$C(s) + \tfrac{1}{2}O_2(g) \rightarrow CO(g)$; $\Delta H = -99$ kJ

Using your numbers, the standard enthalpy of formation of carbon monoxide is -99 kJ/mol.

I think that your value for the heat of combustion of CO is incorrect. It should be -566 kJ.

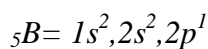This would give the correct value of -110 kJ for the heat of formation of CO.

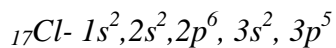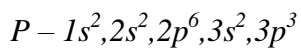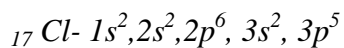16. **a) Discuss the molecular geometries of the following :**

   i) **BCl_3**

   ii) **PCl_5**

   (Atomic number: B = 5, P = 15) (4)

Ans. **BCl_3:** The central atom has no lone pair and there are three bond pairs. Hence, it is of the type AB3. Hence, it is trigonal planar.

$_5B = 1s^2, 2s^2, 2p^1$

$_{17}Cl- 1s^2,2s^2,2p^6, 3s^2, 3p^5$

(b)PCl_5

$P – 1s^2,2s^2,2p^6,3s^2,3p^3$

$_{17}Cl- 1s^2,2s^2,2p^6, 3s^2, 3p^5$
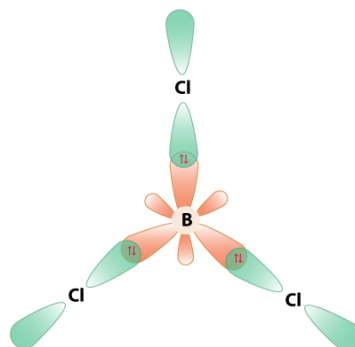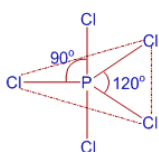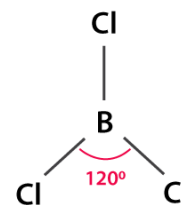
One 's', three 'p' and one 'd' orbitals of same shell participates to give sp³d hybd. with trigonal bipyramidal shape with bond angles 90° & 120°. **Example:** PF_5 & PCl_5,

$P(G.S.) = 1s^2 2s^2 2p^6 3s^2 3p^3$

$P(E.S.) = 1s^2 2s^2 2p^6 3s^1 \quad 3p^3 \qquad 3d^1$
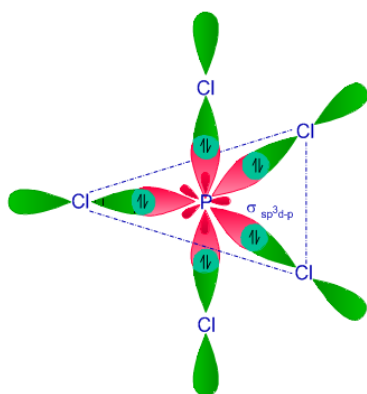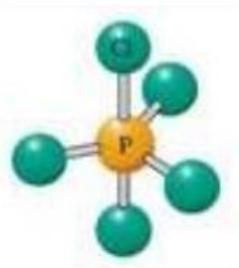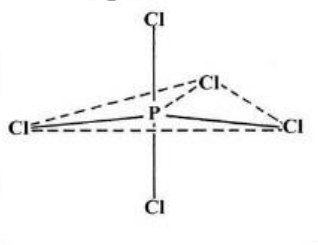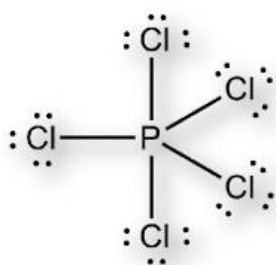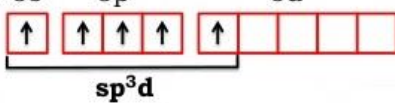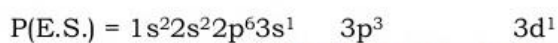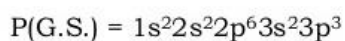
Trigonal bipyramidal structure of PCl_5

Trigonal planar structure of BCl_3

b) **What is effective nuclear charge? Which element has the highest effective nuclear charge?** (2)

Ans. The effective nuclear charge (often symbolized as Z_{eff} or Z^*) is the net positive charge experienced by an electron in a polyelectronic atom. The term "effective" is used because the shielding effect of negatively charged electrons prevents higher orbital electrons from experiencing the full nuclear charge of the nucleus due to the repelling effect of inner-layer electrons.

Chlorine, because chlorine is in the same period as phosphorus and sodium, but has the most protons in its shell (the most right within the same period) it has the greatest effective nuclear charge.

c) **What is ionization energy? Which elements have the highest ionization energy?** (2)

Ans. Ionization energy or ionisation energy, denoted E_i, is the minimum amount of energy required to remove the most loosely bound electron, the valence electron, of an isolated neutral gaseous atom or molecule. It is quantitatively expressed as

$$X(g) + energy \rightarrow X^+(g) + e^-$$
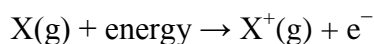
where X is any atom or molecule capable of ionization, X^+ is that atom or molecule with an electron removed, and e^- is the removed electron. This is generally an endothermic process. Generally, the closer the outermost electrons to the nucleus of the atom, the higher the atom's or element's ionization energy.

Fluorine is said to have the highest ionization energy (with the exception of Helium and Neon)

17. **Explain the following terms :** (4 × 2)

a) **Chirality**

Ans. Chirality is a property of asymmetry important in several branches of science. The word *chirality* is derived from the Greek χειρ (*kheir*), "hand," a familiar chiral object.

An object or a system is *chiral* if it is distinguishable from its mirror image; that is, it cannot be superposed onto it. Conversely, a mirror image of an *achiral* object, such as a sphere, cannot be distinguished from the object. A chiral object and its mirror image are called *enantiomorphs* (Greek, "opposite forms") or, when referring to molecules, *enantiomers*. A non-chiral object is called *achiral* (sometimes also *amphichiral*) and can be superposed on its mirror image.

b) **Enatiomers**

Ans. an enantiomer is one of two stereoisomers that are mirror images of each other that are non-superimposable (not identical), much as one's left and right hands are mirror images of each other that cannot appear identical simply by reorientation. A single chiral atom or similar

structural feature in a compound causes that compound to have two possible structures which are non-superposable, each a mirror image of the other. Each member of the pair is termed an <u>enantiomorph</u> (*enantio* = opposite; *morph* = form) the structural property is termed enantiomerism. The presence of multiple chiral features in a given compound increases the number of geometric forms possible, though there may still be some perfect-mirror-image pairs.
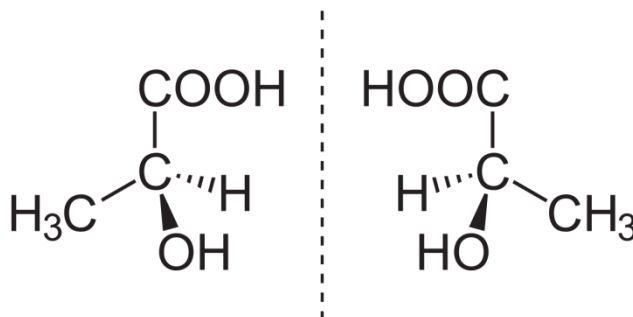
c) Diastereomers

Ans. Diastereomers (sometimes called diastereoisomers) are a type of a stereoisomer. Diasteoreomers are defined as non-mirror image non-identical stereoisomers. Hence, they occur when two or more stereoisomers of a compound have different configurations at one or more (but not all) of the equivalent (related) stereocenters and are not mirror images of each other. When two diastereoisomers differ from each other at only one stereocenter they are epimers. Each stereocenter gives rise to two different configurations and thus typically increases the number of stereoisomers by a factor of two.

Diastereomers differ from enantiomers in that the latter are pairs of stereoisomers that differ in all stereocenters and are therefore mirror images of one another.

d) Optical activity

Ans. Optical rotation or optical activity (sometimes referred to as rotary polarization) is the rotation of the orientation of the plane of polarization about the optical axis of linearly polarized light as it travels through certain materials. Optical activity occurs only in chiral materials, those lacking microscopic mirror symmetry. Optical activity is measured using a polarized source and polarimeter.

18. a) Discuss the synthesis of a commonly used drug molecule by taking suitable example. (4)

Ans. Aspirin (acetylsalicylic acid) is a synthetic organic derived from salicylic acid. Salicylic acid is a natural product found in the bark of the willow tree and was used by the ancient Greeks and Native Americans, among others, to counter fever and pain. However, salicylic acid is bitter and irritates the stomach. A German chemist named Felix Hoffman is credited with being the first to synthesize aspirin in 1897.

Chemical Equation:

Salicylic acid $(C_7H_6O_3)$ + Acetic anhydride $(C_4H_6O_3)$ → Acetylsalicylic acid $(C_9H_8O_4)$ + Acetic Acid $(C_2H_4O_2)$
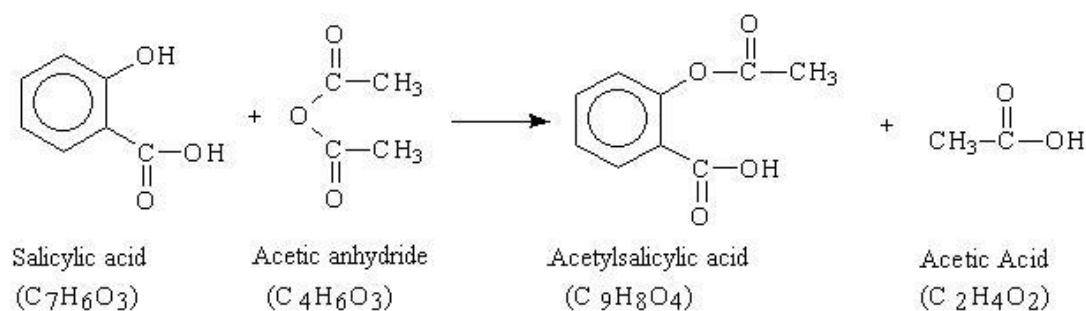
Procedure:

1. Using a weigh boat, weigh out 5.00 g of salicylic acid $(C_7H_6O_3)$. Transfer this to a 125 mL Erlenmeyer flask using a powder funnel.

2. Using the graduated cylinder, measure out 7.00 mL of acetic anhydride and add this to the flask.

3. Carefully add 8 drops of concentrated sulfuric acid (18 M H_2SO_4), a catalyst, to the flask.

4. At your lab bench, assemble a hot water bath using a 600 or 800 mL beaker and place the flask in the water bath.

5. Place the flask in the water bath and heat. After the water begins to boil, heat for an additional 15 minutes.

6. After heating, turn the bunsen burner off and CAREFULLY remove the flask from the water bath (remember it is hot!) and allow the flask and contents to cool on the lab bench for about 3 minutes.

7. After the flask has cooled for about 3 minutes, CAUTIOUSLY add 15 mL of room temperature water to the flask to facilitate the decomposition of the excess acetic anhydride. Swirl the flask to mix the contents.

8. Label your flask containing the reaction mixture and place it in an ice bath and cool until the crystallization of the aspirin appears complete (approx. 15 min.). If crystals do not appear, you can scratch the walls of the flask with a stirring rod to induce crystallization.
 9. Collect the solid aspirin using a Buchner funnel and filter paper as shown in Figure 2. Be sure to seat the filter paper in the filter with a small amount of water.

10. Rinse the flask twice with 3 mL of ice cold water to remove any residual crystals.

11. Discard the filtrate left in the filter flask into the waste container under the hood. Transfer as much of the solid as possible from the Buchner funnel to a clean, dry 250 mL beaker.

12. Add 10 mL of 95% ethanol to the beaker and if necessary, warm (do not boil) the mixture in the water bath to dissolve the crystals. If the crystals do not all dissolve, add 2 mL more of the ethanol and continue to warm the mixture to dissolve the crystals.

13. When the crystals are all dissolved, add 10 mL of deionized water, cover the beaker with a watch glass, and allow the solution to cool slowly on the lab bench undisturbed for about 10 minutes.

14. After the 10 minutes cooling on the lab bench, complete the crystallization by placing the beaker and contents in the ice bath.

15. Using a clean circle of filter paper, collect the purified aspirin by suction filtration as before.

16. Dry the crystals by pulling air through them for about 15 minutes

17. Place the aspirin onto a doubled piece of paper towel and set aside to dry while performing the qualitative analysis of the aspirin.

18. Note the weight of the dry aspirin.

b) **Discuss the S_N2 mechanism of alkvl halides in terms of kinetics, stereochemistry and reactivity of alkyl halides.** (4)

Ans.

(b) SN2 Mechanism of alkyl halides:

Substitution Nucleophilic Biomolecularddz (SN2) Reaction follows second order kinetics. The rate determining step depends on both the concentrate of alkyl halides (R-X) and nucleophile present in the reaction. It is a one step process and there is no formation of intermediates. The basic mechanism of reaction is:

$$Nu^- + \overset{\delta+}{C} - \overset{\delta-}{X} \longrightarrow \overset{}{C} - Nu + X^-$$
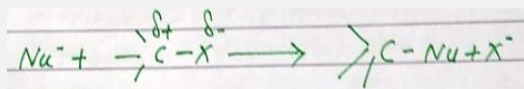
Order of reactivity of alkyl halide towards this type of reaction is:
$$1^0 > 2^0 > 3^0.$$
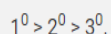
Order of reactivity of halide are:
R-1 > R-Br > R-Cl > R-F.
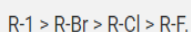
Sn^2 creates a product with an inverted stereo structure to that of the substrate. Essentially the nucleophile attaches to the opposite side form the leaving group results in the inversion of molecules original stereochemistry.