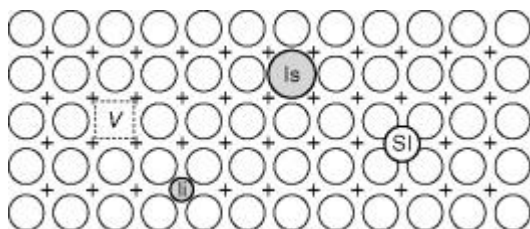


# INDIAN SCHOOL MUSCAT

## CLASS XII CHEMISTRY

### CASE BASED QUESTIONS

- 1 Interstitial sites are defined from the crystal structure. The simplest case corresponds to the close-packed stacking of hard spheres leading to the face-centered cubic (fcc) lattice or to the hexagonal close-packed (hcp) lattice. Two kinds of interstitial site, octahedral and tetrahedral, are usually distinguished in such close-packed structure. For an fcc lattice, there is one octahedral site and two tetrahedral sites per lattice site. For fcc pure metals such as Ni or  $\gamma$ -Fe, small impurity atoms such as C, H, or O, for example, would occupy the octahedral sites that are the larger ones. Point defects are the simplest defects that can be found in any crystal phase. They are localized on single sites of the crystal structure; these sites can be regularly occupied by some chemical species or else regularly unoccupied sites of the vacant interstitial sublattice. Figure defines the simplest and common point defects that can be present in pure solid chemical elements.

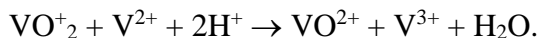


- a) In Frenkel defect
- Cations are present in the interstitial sites
  - Anions are present in the interstitial sites
  - Electrons are present in the interstitial sites
  - Cations and anions are missing from the lattice
- b) The most efficient packing is shown in
- simple cubic cell
  - hcp and ccp
  - bcc and ccp
  - bcc and hcp
- c) In an ionic oxide of metal M, oxide ions are arranged in hcp array and positive ion M occupy two thirds of octahedral void. What is the formula of the compound?
- d) Assertion : When strontium chloride is present along with sodium chloride, some of the sites of sodium ions are occupied by strontium ions .  
Reason : Cationic vacancies generated are equal in number to that of strontium ions.
- e) Why does white ZnO (s) become yellow upon heating?
- f) Calculate the efficiency of packing in a ccp structure.
- 2 Azeotropic mixtures reach a point at which liquid and vapor compositions become the same at a certain temperature and pressure. Azeotropic mixtures cannot be separated into their pure

species by a single column. Distillation is the oldest, easiest, and cheapest procedure for purification of solvents and is based on the application of Raoult's law. The physical foundations of this separation technique depend on the distribution of the constituents between the liquid and vapor phases being at the equilibrium. In general, the composition of the vapor is different from the composition of the distilled mixture, but azeotropic mixtures distil without changing its composition.

- a) Which of the following mixtures will not show a deviation from Raoult's law?
  - (i) Carbon disulphide and acetone
  - (ii) Chloroform and acetone
  - (iii) Benzene and toluene
  - (iv) Phenol and aniline
  
- b) Maximum boiling azeotrope will have
  - (i) A–B interactions are stronger than those between A–A or B–B.
  - (ii) Vapour pressure of solution increases because more number of molecules of liquids A and B can escape from the solution.
  - (iii) Vapour pressure of solution decreases because less number of molecules of only one of the liquids escapes from the solution.
  - (iv) A–B interactions are similar to those between A–A or B–B
  
- c) Why is it not possible to obtain pure ethanol by fractional distillation? What general name is given to binary mixtures which show deviation from Raoult's law and whose components cannot be separated by fractional distillation?
  
- d) Pure water has a vapor pressure of 31.1 mmHg at 29.6 °C. A solution is prepared by adding 86.8 g of "Y", a non-volatile non-electrolyte to 350 g of water. The vapor pressure of the resulting solution is 28.6 mmHg. Calculate the molar mass of Y.

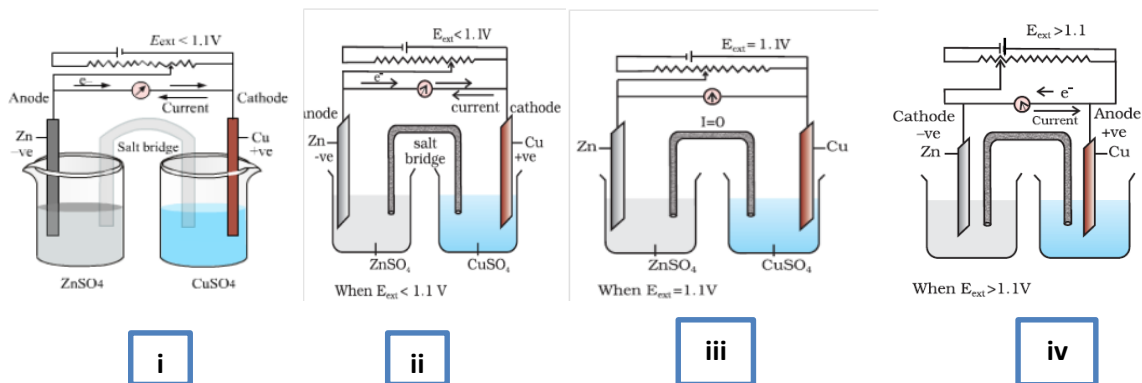
- 3 The vanadium redox battery (VRB) employs two “electrolyte tanks” that store energy in the form of the two vanadium redox couples and a cell “stack” where the charge/discharge reactions occur. To date, 2 M vanadium electrolyte have been successfully used in large demonstration projects for stationary applications. For mobile applications however, higher vanadium concentrations are required to reduce the size and weight of the battery. The main limitation for the vanadium electrolyte concentration and subsequently its energy density in the VRB is the thermal precipitation of the V(V) ion at elevated temperatures.



Given :  $E^0_{\text{V}^{3+}/\text{V}^{2+}} = -0.255\text{V}, E^0_{\text{VO}^{2+}/\text{VO}^{+2}} = +1.004\text{V}$

- a) Write the oxidation and reduction half reactions of the above cell.
- b) Calculate the standard emf and Gibbs energy for the above cell.
- c) The difference in potentials of electrode and electrolyte is
  - (i) Cell potential

- (ii) Electrode potential
  - (iii) Potential difference
  - (iv) Cell voltage
- d) Which figure depicts an electrolytic cell?



4 A reaction mechanism is the detailed picture of how a reaction occurs at molecular level. It consists of a set of proposed elementary steps involving molecular species – reactants as well as reaction intermediates. A reaction mechanism explains how a given reaction might occur at molecular level and from which a rate law can be derived, which must agree with the one determined experimentally. If the mechanism consists of more than one elementary step, the sum of these steps must be equal to the overall balanced equation for the reaction. For example, the reaction:

$2A + B \rightarrow C + D$  may involve the following elementary steps:

Step-1:  $A + B \rightarrow X$ ;

Step-2:  $X + A \rightarrow Y$ ;

Step-3:  $Y \rightarrow C + D$

Overall reaction:  $2A + B \rightarrow C + D$

- a) What do you understand by the term elementary reaction?
- b) Which of the above steps will be the rate determining step, if the rate law is given as  $\text{rate} = k[A]$ .
- c) Write the rate equation for the reaction  $2A + B \rightarrow C + D$ , if the order of the reaction is zero.
- d) For the reaction:
 
$$2 \text{N}_2\text{O}_5(\text{g}) \rightarrow 4 \text{NO}_2(\text{g}) + \text{O}_2(\text{g})$$
 Given rate =  $k[\text{N}_2\text{O}_5]$ .  
 Predict a mechanism for the same.
- e) The decomposition of  $\text{N}_2\text{O}_5$  is first order with a rate constant of  $4.80 \times 10^{-4}$  /sec at  $45^\circ\text{C}$ .
  - i) If the initial molarity of  $\text{N}_2\text{O}_5$  is  $1.65 \times 10^{-2}$  mol/L, what is the concentration at 825 s?
  - ii) At what time would the  $\text{N}_2\text{O}_5$  concentration be  $1.00 \times 10^{-2}$  mol/L?
  - iii) At what time would 25% of  $\text{N}_2\text{O}_5$  remain?

5 Activated carbon (AC) is an extremely porous carbonaceous adsorptive substance which has a rigid carbon matrix with high surface area and broad functional groups. The structure is connected by chemical bonds; arranged irregularly, generating a highly porous arrangement of corners between the carbon layers. Activated carbons are produced high-temperature and chemical activation of waste biomass. The pores in the lattice network of activated carbon permit the removal of impurities from gaseous and liquid medium through adsorption. With COVID 19 around, using a face mask is one of the best methods to stay safe. The mask combined with activated carbon can be beneficial for adsorbing and disinfecting the virus as it is the versatile adsorbent for the elimination of the organic, inorganic, and pathogenic contaminants.

a) For the process of adsorption

- (i)  $\Delta H = 0$
- (ii)  $\Delta H = T\Delta S$
- (iii)  $\Delta G = +ve$
- (iv)  $\Delta H < 0$

b) On the basis of data given below predict which of the following gases shows least adsorption on a definite amount of charcoal?

Gas	CO <sub>2</sub>	SO <sub>2</sub>	CH <sub>4</sub>	H <sub>2</sub>
Critical temp./K	304	630	190	33

- (i) CO<sub>2</sub>
- (ii) SO<sub>2</sub>
- (iii) CH<sub>4</sub>
- (iv) H<sub>2</sub>

c) What is the role of activated charcoal in gas mask used in coal mines?

d) Why do physisorption and chemisorption behave differently with rise in temperature?

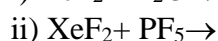
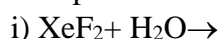
6 In the year 1962, the first noble gas compound XePtF<sub>6</sub> was synthesized and the era of the noble gas chemistry began. Xenon (II) fluoride is one of the most easily handled noble gas compounds - therefore its chemistry is the most extensive. Its synthesis is relatively simple and there is no danger of the formation of explosive xenon oxides or oxide fluorides in higher oxidation states. Very pure XeF<sub>2</sub> in a greater quantity can be best prepared by UV irradiation of xenon – fluorine gaseous mixture. XeF<sub>2</sub> has considerable potential in oxidative fluorination because of its low average bond energy (133.9 kJ/mol) and because of the inertness of its reduction product xenon. XeF<sub>2</sub> can be used as fluorinating agent for fullerenes, as etching reagent of silicon with an advantage that the final products of etching process are gases SiF<sub>4</sub> and Xe which can be pumped off. XeF<sub>2</sub> is an excellent ligand because of its semi ionic character and its small size (65Å).

a) Explain the geometry of XeF<sub>2</sub>.

b) What inspired N. Bartlett for carrying out reaction between Xe and PtF<sub>6</sub>?

c) Give the formula of a xenon compound which is isostructural with i) ICl<sub>4</sub><sup>-</sup> and ii) IBr<sub>2</sub><sup>-</sup>

d) Complete the reaction



- e) What is the product obtained when xenon is treated with excess fluorine at 573K and 60-70 bar pressure? Does the hydrolysis of this product lead to a redox reaction? Explain.

7 Transition elements are those with partially filled *d* or *f* shells. The *3d* transition metals have been extensively studied and their periodic properties analyzed. The elements scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, and zinc have the atomic configuration  $[\text{Ar}]4s^23d^x$ . These *3d* metals have a propensity for five or ten electrons in the *3d* shell and this manifests itself as an anomaly in the electron occupation of the *4s* shells for the elements chromium and copper. The first row, atomic numbers 21–30, is called *3d* transition metals, shown below. Much less general information is available on the *4d* and *5d* transition metals. However, the *4d* elements niobium, molybdenum, palladium, and silver, and the *5d* elements tantalum, tungsten, platinum, and gold are technologically important.

Element	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
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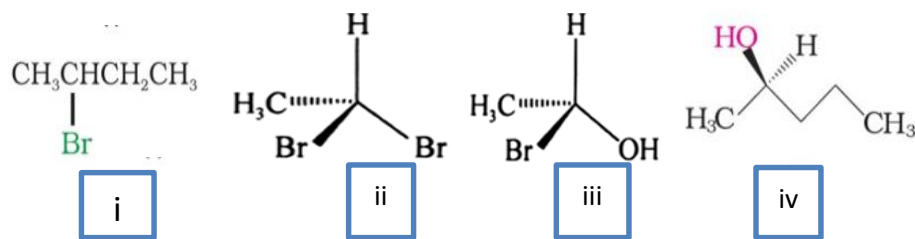
- Write the formula of a compound where transition metal, from the above series, is in the +7 oxidation state.
- Which among the above is not regarded as a transition metal and why?
- Copper(I) is diamagnetic whereas copper(II) is paramagnetic. Explain
- What is the reason for a metal exhibiting its highest oxidation state in its oxide form?
- In the above, which metal in the +3 oxidation state will be colorless in aqueous solution?

8 Among the most important classic reagents containing many industrial applications which can be used to remove toxic metal ions from contaminated water and soil stand out ethylenediaminetetraacetic acid (EDTA). The EDTA ligand is hexadentate and the atoms responsible for coordinating with the chrome are four oxygen atoms of the carboxylic groups and two nitrogen atoms of the amine groups. EDTA as the best ligand used for the complexation reaction with chromium at oxidation states,  $\text{Cr}^{+3}$  and  $\text{Cr}^{+6}$  contained in solid waste from the leather industry. Because of the potential toxic effects of chromium solid waste containing this metal there are grounds for serious concern for the tanning and leather processing industry. The application of tannery waste as organic fertilizer has led to extensive contamination by chromium in agricultural areas and may cause the accumulation of this metal in soils and plants.

- Define the term denticity.
- Write the IUPAC name and explain the hybridisation of  $[\text{Cr}(\text{CN})_6]^{3-}$ .
- What is the oxidation state of chromium in  $[\text{Cr}(\text{EDTA})]^-$
- Give the electronic configuration of the following complex on the basis of Crystal Field Splitting theory  $[\text{Cr}(\text{CN})_6]^{3-}$
- How many ions are produced  $[\text{Cr}(\text{CN})_6]\text{Cl}_3$  by in solution?

9 Enantiomers are two chemically identical molecular species which differ from each other as non-superposable mirror images. The most simple and vivid model for enantiomeric structures is the two hands, left and right. The chirality of enantiomeric molecules is caused by the presence of one or more chiral elements in their structure. The chirality and optical activity of the enantiomers are determined by their absolute configuration, i.e. the spatial arrangement of the atoms in the molecule. Designation of the configuration of enantiomers should be made in accordance with the Cahn-Ingold-Prelog *R*, *S*-system. The Delta-Lambda designations for enantiomers of octahedral complexes and the d,l Fischer-Rosanoff designations. Conventional chemical synthesis, in contrast to asymmetric synthesis, deals mostly with the transformations of achiral compounds. If these reactions result in the formation of a chiral element in the molecule, the reaction product appears to be an equivalent mixture of a pair of enantiomers, a racemate, which is optically inactive.

- Define the term racemization
- Which of the following compounds will give racemic mixture on nucleophilic substitution by  $\text{OH}^-$  ion? Explain your answer.
  - 2-Bromobutane
  - 1-Bromobutane
  - 2-Bromopropane
  - 2-Bromopropan-2-ol
- Why are aryl halides less reactive towards nucleophilic substitution reactions than alkyl halides? How can we enhance the reactivity of aryl halides?
- Identify chiral and achiral molecules in the following:



10 Phenolic compounds are classified as primary antioxidants which are mainly free radical scavengers (FRS) that delay or inhibit the initiation step or interrupt the propagation step of lipid oxidation, thus decreasing the formation of volatile decomposition products (e.g., aldehydes and ketones) that cause rancidity. The antioxidant potential of phenolic compounds depends on the number and arrangement of the hydroxyl groups in the molecules of interest (Cao et al, 1997, Sang et al, 2002). Phenolic antioxidants (AH) can donate hydrogen atoms to lipid radicals and produce lipid derivatives and antioxidant radicals, which are more stable and less readily available to promote autoxidation. The phenoxyl radical is stabilized by delocalization of its unpaired electron around the aromatic ring, which participates in the termination reaction. The potential mechanism of the protective effects of phenolic compounds, including flavonoids, is thought to be due to their direct scavenging of free radicals hydroxytyrosol, one of the major phenolic constituents in olive oil, was reported to reduce the risk of coronary heart disease and atherosclerosis by itself. Resveratrol is a polyphenolic compound with potent antioxidant activity. It is found in a number of plants, notably grapes, pistachio, peanuts and berry fruit, and is attracting increased attention due to its health benefits, especially in common age-related diseases such as cancer, type 2 diabetes, cardiovascular disease, and neurological conditions.

- a) Phenol has a pK<sub>a</sub> value greater than
  - (i) ethanol
  - (ii) o-nitrophenol
  - (iii) o-methylphenol
  - (iv) o-methoxyphenol
- b) Out of o-nitrophenol and p-nitrophenol, which is more volatile? Explain.
- c) What happens when benzene diazonium chloride is heated with water?
- d) Explain why nucleophilic substitution reactions are not very common in phenols.
- e) Write steps to carry out the conversion of phenol to aspirin.

11 Aldehydes were converted to carboxylic acids using sodium hypochlorite as oxidant in a single step, involving microwave assistance and without a metal catalyst in basic media. The use of microwave irradiation increased both conversion and yield due to an easier work-up and the reaction time was reduced. Two advantages of this oxidation are the relatively low cost and low pollution. This oxidative method has been applied to alcohols successfully. In addition, the carboxylic acid was obtained in sufficiently purity using only thermal heating not to require additional chromatographic purification. The benzylic alcohols give the corresponding benzoic acids, electron donors decrease the yield, while electron withdrawing groups facilitate the oxidation. Alkanols are also oxidized, in the case of ethanol the problem was the isolation of acetic acid formed in the aqueous media.

- a) Addition of water to alkynes occurs in acidic medium and in the presence of Hg<sup>2+</sup> ions as a catalyst. Name the product will be formed on addition of water to but-1-yne under these conditions.
- b) An organic compound (A), C<sub>4</sub>H<sub>9</sub>Cl on reacting with aqueous KOH gives (B) and on reaction with alcoholic KOH gives (C) which is also formed on the vapours of (B) over heated copper. The compound (C) readily decolorises bromine water. Ozonolysis of (C) gives two compounds (D) and (E). Compound (D) reacts with NH<sub>2</sub>OH to give (F) and the compound (E) reacts with NaOH to give an alcohol (G) and sodium salt (H) of an acid. (D) can also be prepared from propyne on treatment with water in presence of Hg<sup>2+</sup> and H<sub>2</sub>SO<sub>4</sub>. Identify (A) to (H).
- c) What happens when benzaldehyde is treated with
  - i) Alkaline potassium permanganate
  - ii) Concentrated sodium hydroxide

12 The basicity of amines of different classes do not follow a simple pattern because the number of groups bonded to nitrogen affects the electron density at the nitrogen atom. And, the stability of the conjugate acid in the solvent has a major effect on basicity. Thus, the basicity of amines can be explained only for amines with similar structures at the nitrogen atoms.

The basicity of an amine is increased by electron-donating groups and decreased by electron-withdrawing groups. Aryl amines are less basic than alkyl-substituted amines because some electron density provided by the nitrogen atom is distributed throughout the aromatic ring. Basicity is expressed using  $K_b$  values measured from the reaction of the amine with water. An alternate indicator of basicity is pK<sub>b</sub>, which is  $-\log K_b$ . A strong base has a large  $K_b$  and a small pK<sub>b</sub>. The basicity of amines is also expressed by the acidity of their conjugate acids. A strong base has a weak conjugate acid, as given by a small value of  $K_a$  and a large pK<sub>a</sub>.

The basicity of heterocyclic amines depends on the location of the electron pair of the nitrogen atom, its hybridization, and whether or not resonance stabilization is possible. In pyrrole, the electron pair is part of the aromatic system. As a result, pyrrole is a very weak base. Pyridine is a weaker base than saturated amines of similar structure because its electron pair is in an  $sp^2$ -hybridized orbital, and the electron pair is more tightly held by the atom.

- a) Amongst the following, the strongest base in aqueous medium is \_\_\_\_\_.
- $CH_3NH_2$
  - $(CH_3)_3N$
  - $(CH_3)_2NH$
  - $C_6H_5NHCH_3$
- b)  $CH_3NH_2 \xrightarrow{HNO_3}$
- $CH_3-O-N=O$
  - $CH_3-O-CH_3$
  - $CH_3OH$
  - $CH_3CHO$
- c) Why is aniline soluble in aqueous HCl?
- d) An organic compound X with molecular formula  $C_8H_9ON$  on hydrolysis gives Y,  $C_6H_7N$  which on treatment with chloroform and alcoholic potash gives foul smelling compound Z. X reacts with nitrating mixture followed by hydrolysis to form p-nitro aniline. Identify X, Y and Z. Also write the reactions involved.

13 The nucleic acids, deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) are the molecules responsible for carrying the genetic information of a cell. As proteins are polymers of amino acids, nucleic acids are long chain "polymers" of nucleotide building blocks. Each nucleotide is made up of a nucleoside along with phosphoric acid. Each nucleoside is made up of a simple aldopentose sugar and a heterocyclic amine base. Base refers to the ability of the nitrogen lone pair to accept a proton.

- a) Dinucleotide is obtained by joining two nucleotides together by phosphodiester linkage. Between which carbon atoms of pentose sugars of nucleotides are these linkages present?
- 5' and 3'
  - 1' and 5'
  - 5' and 5'
  - 3' and 3'
- b) DNA and RNA contain four bases each. Which of the following bases is not present in RNA?
- Adenine
  - Uracil
  - Thymine
  - Cytosine
- c) Explain the  $\alpha$ -helix and  $\beta$ -pleated sheet structure of proteins.
- d) Give one structural and one functional difference between DNA and RNA.
- e) "The two strands of DNA are not identical but are complementary." Explain.