2015

Question 1

Which would undergo SN_2 reaction faster in the following pair and why? [1]

$CH_3 - CH_2 - Br$ and $CH_3 - CH_2 - I$

Answer:

Number of octahedral voids formed = Number of atoms of element Y

Number of atoms of element Y in the ccp unit cell = 4

∴ Number of octahedral voids formed = 4

Now, Number of octahedral voids occupied by atoms of X = 23×4=83

Ratio of the numbers of atoms of X and Y = 83 : 4

Hence, the formula of the compound is X_2Y_3

Question 2

Which allotrope of sulphur is thermally stable at room temperature? [1]

Answer:

The rhombic allotrope of sulphur (α-suphur) is thermally stable at room temperature.

Question 3

Write the IUPAC name of the given compound: [1]

$$HO - CH_2 - CH = \underset{\displaystyle CH_3}{\overset{\displaystyle |}{C}} - CH_3$$

Answer:

2, 5-Dimethyl hexane-1, 3-diol.

Question 4

What is the formula of a compound in which the element Y forms ccp lattice and atoms of X occupy $\frac{2}{3}$rd of octahedral voids? [1]

Answer:

The number of tetrahedral voids formed is equal to twice the number of atoms of element Y. But only $\frac{2}{3}$ of these tetrahedral voids are occupied by atoms of element X.

Therefore the ratio of number of atoms of X and Y is

$2x\frac{2}{3} : 1 = 4:3$

The formula of compound is X_4Y_3

Question 5

Physisorption is reversible while chemisorption is irreversible. Why? [1]

Answer:

Physisorption takes place by the help of non covalent attraction between adsorbate and adsorbent making the process reversible while Chemisorption takes place by the help of covalent bonding resulting it irreversible.

Question 6

a. Write down the IUPAC name of the following complex: [2]

$[Cr(en)_3]Cl_3$

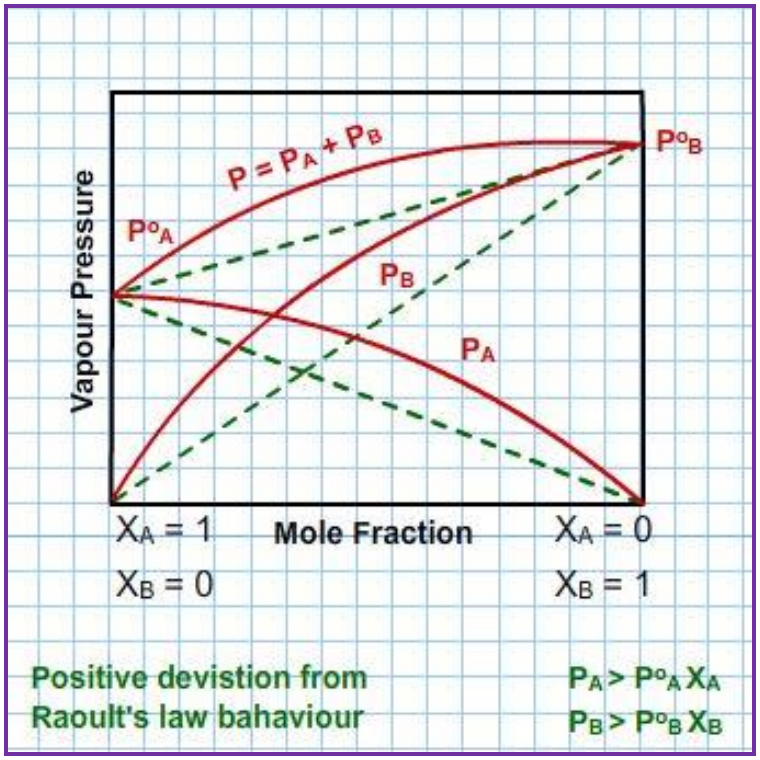
Answer:
Tris(ethane−1,2−diamine) chromium(III) chloride

b. Write the formula for the following complex:
Potassium tri oxalato chromate (III)

Answer:
$K_3[Cr(C_2O_4)_3]$

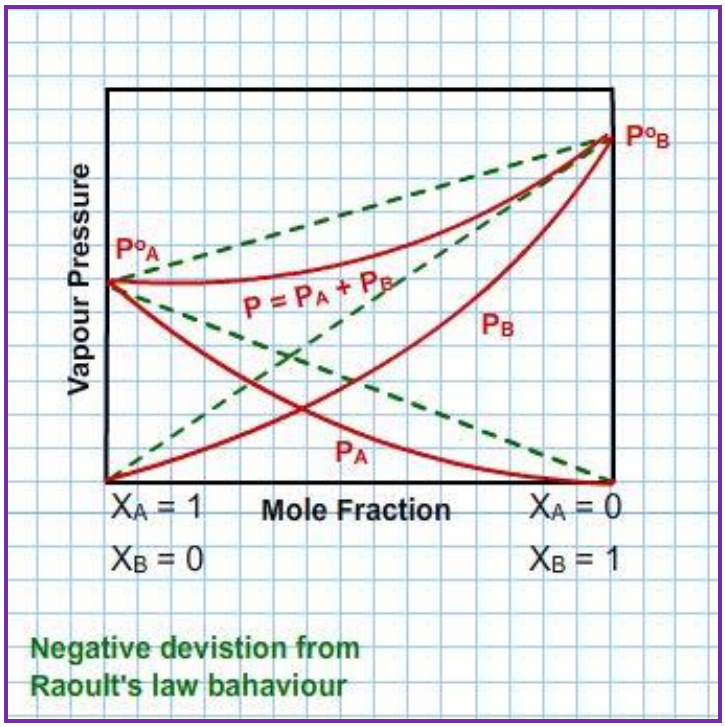
Question 7
What is meant by negative deviation from Raoult's law? Give an example. What is the sign of ΔmixH for negative deviation? [2]

Answer:
Solutions showing positive deviations from Raoult's law: Let Take a binary solution with have components A and B. If the force of attraction between molecular of and A and B in the solution are weaker than that of between A — A and B — B, then the tendency of escaping of molecules A—B from the solution becomes more than that of pure liquids. The total pressure of the solution will be greater than the corresponding vapour pressure of ideal solution of the same component A and B. This type of solution shows positive deviation from Raoult's law. The positive deviation of solution have been shown in figure. Some en
ergy loose when we mix both solutions. This reaction is endothermic reaction. For Endothermic reaction delta H is always positive.



Solutions showing negative deviations from Raoult's law: Let Take a binary solution with have components A and B. If the force of attraction between molecular of and A and B in the solution are stronger than that of between A — A and B — B, then the tendency of escaping of molecules A—B from the solution becomes less than that of pure liquids. The total pressure of the solution

will be lower than the corresponding vapour pressure of ideal solution of the same component A and B. This type of solution shows negative deviation from Raoult's law. The negative deviation of solution have been shown in figure. Some energy released when we mix both solutions. This reaction is exothermic reaction. For Exothermic reaction delta H is always negative.



OR

Define azeotropes. What type of azeotrope is formed by negative deviation from Raoult's law? Give an example. [2]

Answer:

The non-ideal solutions that do not obey Raoult's law over the entire range of concentration and have vapour pressures lower than those predicted by Raoult's law show a negative deviation from Raoult's law.

Example: A mixture of chloroform and acetone. In case of solutions showing negative deviations Δ_{mix} H has a negative sign.

Question 8

Name the reagents used in the following reactions: [2]

i. $CH_3 - CHO \xrightarrow{?} CH_3 - \underset{\displaystyle OH}{\underset{|}{CH}} - CH_3$

Answer:

Following are the names of the reagents used in the given reactions:

i. Grignard's reagent(methyl magnesium bromide)
ii. Thionyl chloride

Question 9

a. Following reactions occur at cathode during the electrolysis of aqueous copper (II) chloride solution: [2]

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $\quad E^0 = +0{\cdot}34$ V

$H^{+}(aq) + e^{-} \rightarrow \frac{1}{2}H_2(g)$ $\quad E^0 = 0.00$ V

On the basis of their standard reduction electrode potential (E^0) values, which reaction is feasible at the cathode and why?

Answer:

Given:

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$ $\quad E° = +0.34$ V

$H^{+}(aq) + e^{-} \rightarrow \frac{1}{2}\ 12H_2(g)$ $\quad E° = 0.00$ V

The relationship between the standard free energy change and the standard emf of a cell reaction is given by

$\Delta G° = -nFE°$

Thus, the more positive the standard reduction potential of a reaction, the more negative is the standard free energy change associated with the process and, consequently, the higher is the feasibility of the reaction.

Since $E^{o}_{Cu^{2+}/Cu}$ has a greater positive value than $E^{o}_{H^{+}/H}$, the reaction that is feasible at the cathode is

$Cu^{2+}(aq) + 2e^{-} \rightarrow Cu(s)$

b. State Kohlrausch law of independent migration of ions. Write its one application.

Answer:

According to Kohlrausch's law of independent migration of ions, "The limiting molar conductivity of an electrolyte can be represented as the sum of the limiting molar conductivities of the anion and cation of the electrolyte."

The law is used to determine the limiting molar conductivity of weak electrolytes whose molar conductivity increases steeply on dilution.

Question 10

Why do transition elements show variable oxidation states? In 3d series (Sc to Zn), which element shows the maximum number of oxidation states and why? [2]

Answer:

Transition elements have an incomplete set of d-orbitals in their penultimate shell. They have their valence electrons in (n−1)d- and ns-orbitals. Since there is very little energy difference between these orbitals, electrons from both the energy levels can be used for bond formation. As a result, transition elements exhibit variable oxidation states.

Valence shell electronic configuration for Mn (Z = 25): $3d^5\ 4s^2$

In the 3d series, Mn has the maximum number of unpaired electrons present in the d-subshell (5 electrons). Hence, Mn exhibits the maximum number of oxidation states, ranging from +2 to +7.

Question 11

Calculate the mass of NaCl (molar mass = 58·5 g mol^{-1}) to be dissolved in 37·2 g of water to lower the freezing point by 2^0C, assuming that NaCl undergoes complete dissociation. (K_f for water = 1·86 K kg mol^{-1}) [3]

Answer:

NaCl undergoes complete dissociation as:

$NaCl \rightarrow Na^{+} + Cl^{-}$

The Van't Hoff factor, *i* is given as:

$$i = \frac{\text{Number of particles after dissociation}}{\text{Number of particles before dissociation}}$$

$$\Rightarrow i = \frac{2}{1} = 2$$

The depression in freezing point of a solution is given by

$$\Delta T_f = iK_f \frac{w_S \times 1000}{M_S \times W} \quad .....(i)$$

Given: K_f for water=1.86 K kg mol^{-1}

Molar mass of solute, *M*s=58.5 g mol^{-1}

Mass of water, *W* = 37.2 g

ΔT_f = 2 °C =2 K

Mass of solute, w_s = ?

Substituting the above values in (i), we get

$$2 = 2 \times 1.86 \times \frac{w_S \times 1000}{58.5 \times 37.2}$$

w_s=1.17 g

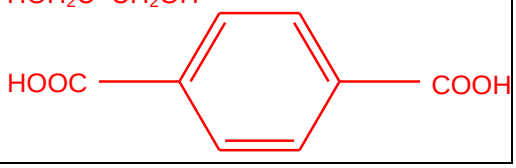
Hence, the required mass of NaCl is 1.17 g.

Question 12

Write the names and structures of the monomers of the following polymers: [3]

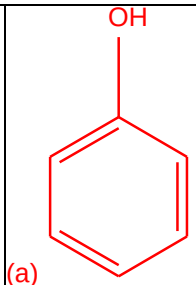
i. Terylene

Answer:

Polymer	Monomers	Structures of Monomers
Terylene	(a) Ethylene glycol (b) Terephthalic acid	(a) HOH_2C-CH_2OH  (b)

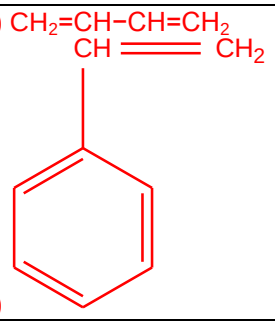
ii. Bakelite

Answer:

Bakelite	(a) Phenol (b) Formaldehyde	 (a) (b) HCHO

iii. Buna-S

Answer:

Buna-S	(a) 1,3-Butadiene (b) Styrene	(a) $CH_2=CH-CH=CH_2$ (b) 

Question 13 [3]

i. Which one of the following is a monosaccharide: starch, maltose, fructose, cellulose?

Answer:

Among the given carbohydrates, fructose is a monosaccharide.

ii. What is the difference between acidic amino acids and basic amino acids?

Answer:

Amino acids that have more number of carboxyl groups than amino groups are referred to as acidic amino acids. Example: Aspartic acid

Amino acids that have more number of amino groups than carboxyl groups are referred to as basic amino acids. Example: Lysine.

iii. Write the name of the vitamin whose deficiency causes bleeding of gums.

Answer:

Deficiency of vitamin C (ascorbic acid) causes the bleeding of gums (scurvy).

Question 14 [3]

i. Indicate the principle behind the method used for the refining of Nickel.

Answer:

The method of vapour phase refining is employed to refine nickel. It is based on the principle of converting a metal into a volatile compound using a suitable reagent that can be readily decomposed elsewhere to give back the pure metal.

ii. What is the role of dilute NaCN in the extraction of gold?

Answer:

In the extraction of gold, dilute NaCN is used as a leaching agent. Gold is converted into a cyanide complex from which the metal is extracted later by replacement.

iii. What is 'copper matte'?

Answer:

During extraction of copper from cuprous oxide in a reverberatory furnace, cuprous oxide is mixed with silica and heated. This leads to separation of iron oxide as iron silicate (slag) and the copper obtained after this procedure is known as copper matte. It contains Cu_2S and FeS. It is then put in a silica-lined converter to remove the remaining FeO and FeS present in the matte as slag ($FeSiO_3$).

Question 15

Calculate the emf of the following cell at 25^0C: [3]

Zn | Zn^{2+} (0.001 M) | | H^+ (0.01 M) | H_2(g) (1 bar) | Pt(s)

$E^0_{\frac{Zn^{2+}}{Zn}} = -0.76\,V$, $E^0_{\frac{H^+}{H_2}} = 0.00\,V$

Answer:

For the given cell representation, the cell reaction will be

$Zn(s) + 2H^+(aq) \rightarrow Zn^{2+}(aq) + H_2(g)$

The standard emf of the cell will be

$E^o_{cell} = E^o_{\frac{H^+}{H_2}} - E^o_{\frac{Zn^{2+}}{Zn}}$

$E^o_{cell} = 0-(-0.76)=0.76\ V$

Question 16

Give reasons for the following observations: [3]

i. A delta is formed at the meeting point of sea water and river water.

Answer:

When river water (a colloidal solution of clay) comes in contact with sea water (rich in electrolytes), the clay coagulates from the colloidal solution and starts depositing leading to the formation of delta over time.

ii. NH_3 gas adsorbs more readily than N_2 gas on the surface of charcoal.

Answer:

Higher the critical temperature of a gas, more readily it can get adsorbed on the surface of an adsorbent due to stronger van der Waal's forces at this temperature. NH_3 (132°C) has a higher critical temperature than dinitrogen (−147°C). Thus, NH3 gas adsorbs more readily than N2 gas on the surface of charcoal.

iii. Powdered substances are more effective adsorbents.

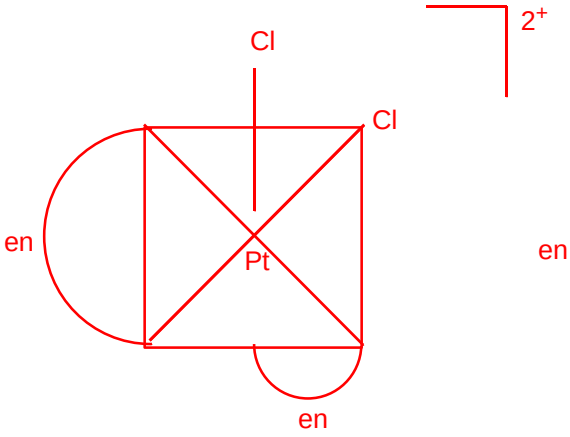
Answer:

Adsorption is a surface phenomenon. Therefore, the process of adsorption is directly proportional to the surface area available for adsorption to take place. Both physisorption and chemisorption increase with an increase in the surface area. Powdered substances have large surface areas. Hence, powdered substances are more effective adsorbents.

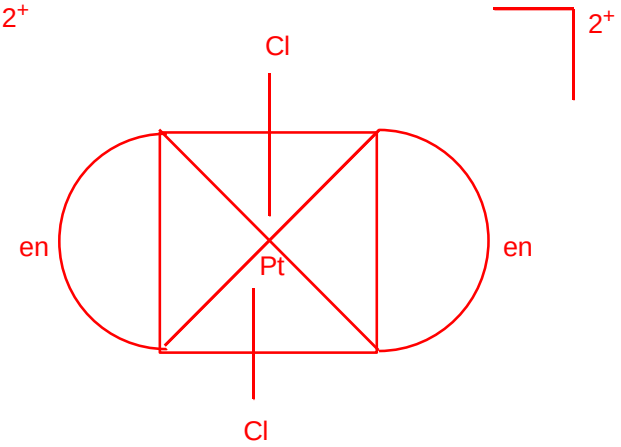
Question 17 [3]

i. Draw the geometrical isomers of complex $[Pt(en)_2Cl_2]^{2+}$.

Answer:



cis



trans

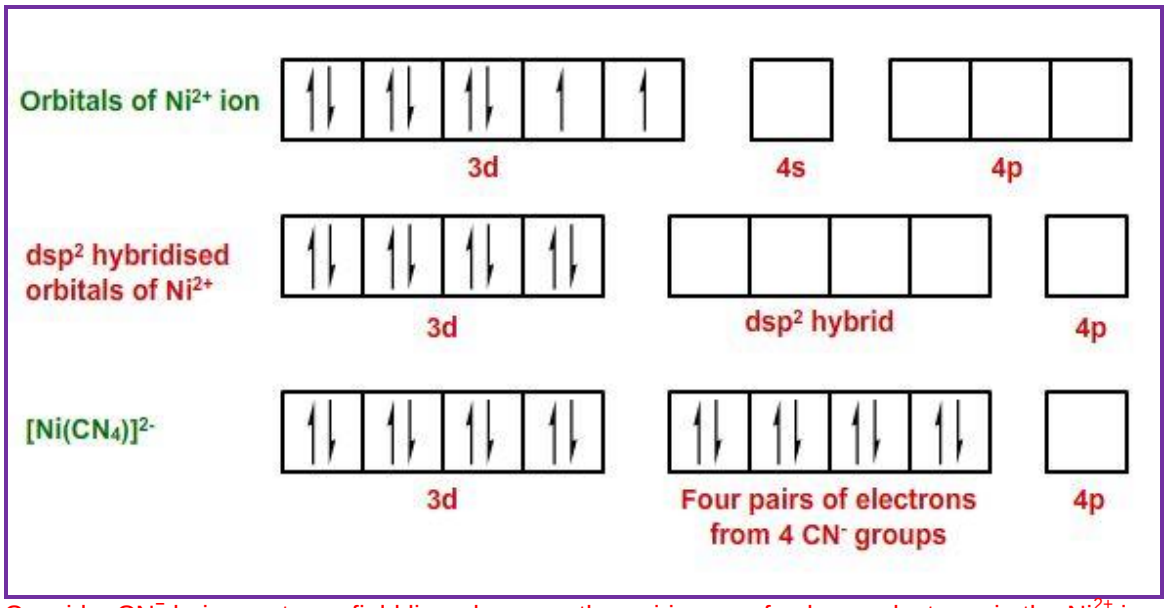
ii. On the basis of crystal field theory, write the electronic configuration for d4 ion, if $\Delta_o > P$.

Answer:

On the basis of the crystal field theory, for a d^4 ion, if $\Delta_o > P$, then the complex is a low-spin complex formed by the association of strong-field ligands with the metal ion. As a result, it becomes energetically more favourable for the fourth electron to occupy a t_{2g} orbital and, thereby, exhibit the electronic configuration $t_{2g}^4 e_g^0$.

iii. Write the hybridization type and magnetic behaviour of the complex $[Ni(CN)_4]^{2-}$. (Atomic number of Ni = 28)

Answer:



Cyanide, CN^- being a strong-field ligand causes the pairing up of valence electrons in the Ni^{2+} ion against the Hund's rule of maximum multiplicity. This results in the formation of an inner orbital complex, $[Ni(CN)_4]^{2-}$ having diamagnetic character and dsp^2 hybridisation.

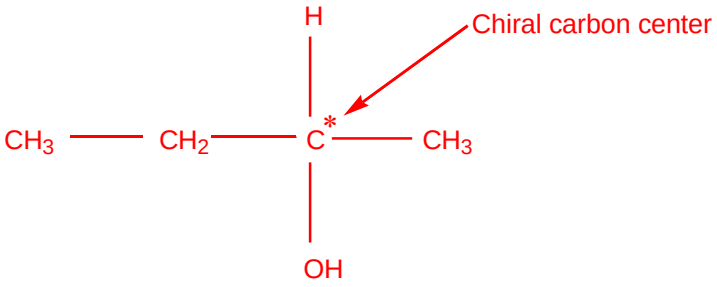
Question 18 [3]

i. Why are alkyl halides insoluble in water?

Answer:
Alkyl halides are very slightly soluble in water. This is because the interaction of haloalkane and water molecules is not as strong as the interaction among water molecules. When alkyl halides dissolve in water, the energy released is not sufficient to overcome the attractions between the alkyl halides molecules and to break the hydrogen bonds between water molecules. Thus, alkyl halides are insoluble in water.

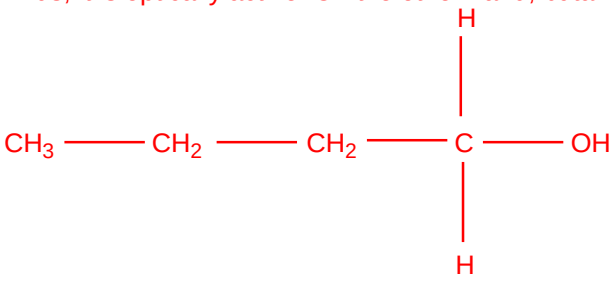
ii. Why is Butan-1-ol optically inactive but Butan-2-ol is optically active?

Answer:
Butan-2-ol has a chiral centre, that is, butan-2-ol has a carbon atom bonded to four different substituents.



Butan - l - ol

Thus, it is optically active. On the other hand, butan-1-ol does not have any chiral carbon atoms.



Butan - l - ol

Therefore, it is optically inactive.

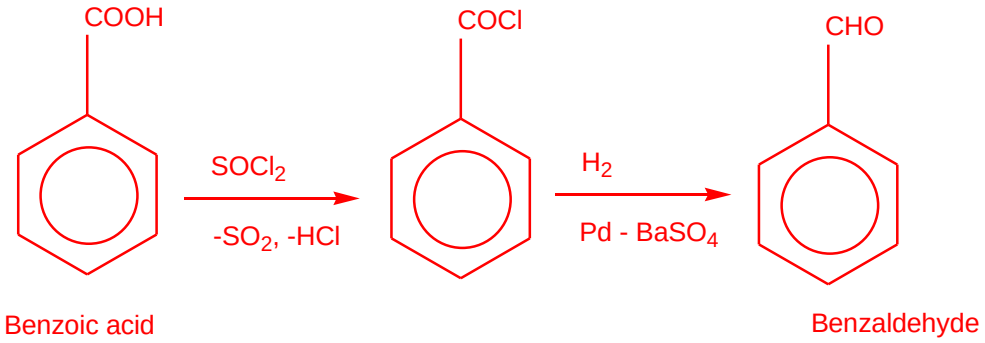
iii. Although chlorine is an electron withdrawing group, yet it is ortho-, para- directing in electrophilic aromatic substitution reactions. Why?

Answer:
Chlorine is an electron-withdrawing group, yet it is *ortho*-, *para*- directing in electrophilic aromatic substitution reactions. This is because Cl exhibits positive mesomeric effect as well. By virtue of resonance, Cl tends to stabilise the carbocation and increases the electron density more at*ortho*- and *para*- positions than at *meta*- position of the benzene ring. Thus, electrophilic aromatic substitution reactions take place at *ortho*- and*para*- positions.

Question 19
How do you convert the following? [3]

i. Benzoic acid to Benzaldehyde

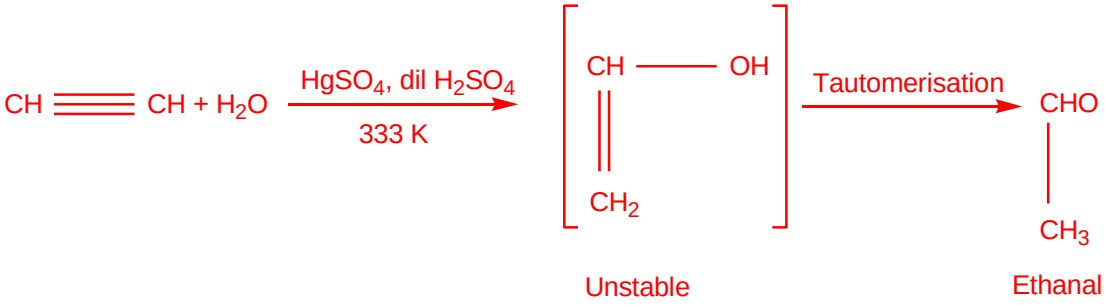
Answer:



Benzoic acid — Benzaldehyde

ii. Ethyne to Ethanal

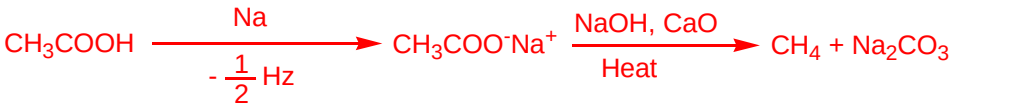
AnswerNa2NA:



Unstable — Ethanal

iii. Acetic acid to Methane

Answer:



Acetic acid — Sodium acetate — Methane — Sodium carbonate

OR

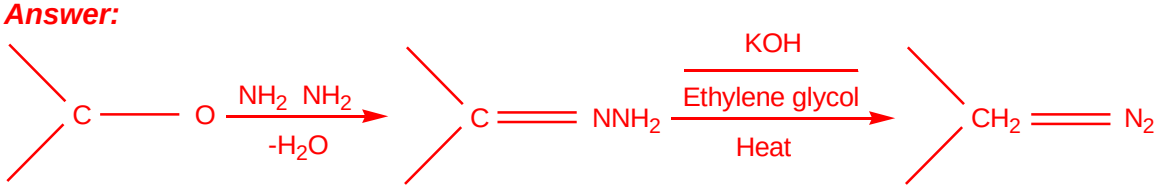
Write the equations involved in the following reactions:

i. Stephen reaction

Answer:

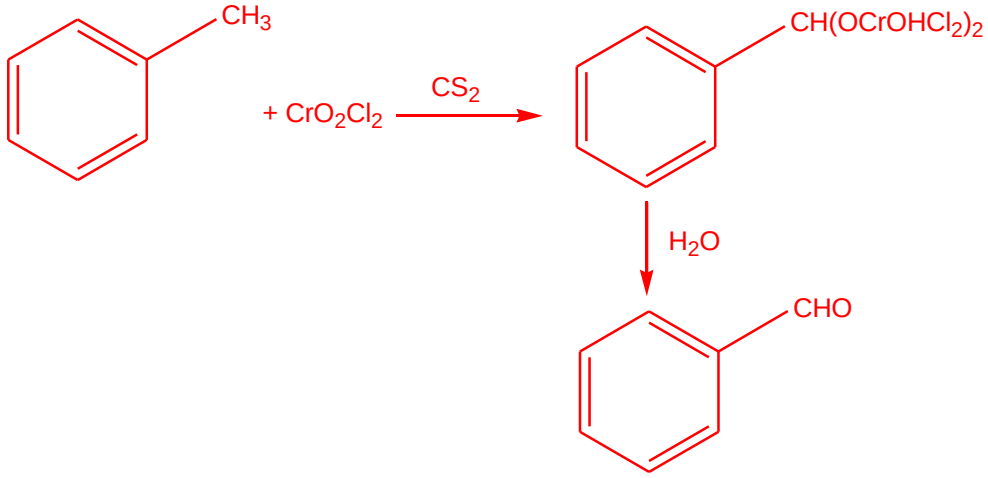
ii. Wolff-Kishner reduction

Answer:



iii. Etard reaction

Answer:



Question 20

a. How would you account for the following: [3]

i. Highest fluoride of Mn is MnF_4 whereas the highest oxide is Mn_2O_7.

Answer:

Oxygen has a greater ability than fluorine to stabilise the higher oxidation states of transition metal ions. Oxygen can also form multiple bonds with metals. Also, it is observed that the highest fluoride of Mn is MnF_4 and the highest oxide of Mn is Mn_2O_7.

ii. Transition metals and their compounds show catalytic properties.

Answer:

The catalytic activity of transition metals and their compounds can be explained by two basic facts:

1. Owing to their ability to show variable oxidation states and form complexes, transition metals form unstable intermediate compounds. Thus, they provide a new path with lower activation energy, E_a, for a reaction.
2. Transition metals also provide a suitable surface for reactions to occur.

b. Complete the following equation:

$3MnO_4^{2-} + 4H^+ \rightarrow$

Answer:

The complete equation is given below.

$3MnO_4^{2-} + 4H+ \rightarrow 2MnO_4^{2-} + MnO_2 + 2H_2O$

Question 21

Predict the products of the following reactions: [3]

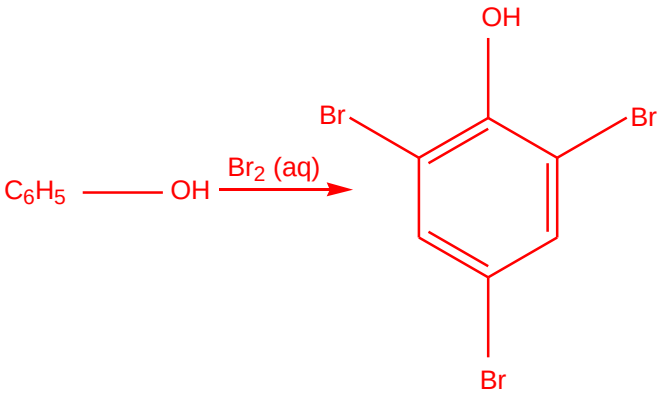
i. $CH_3 - CH = CH_2 \xrightarrow[\text{ii. } \frac{3H_2O_2}{OH^-}]{\text{i. } B_2H_6} ?$

Answer:

$CH_3 - CH = CH_2 \xrightarrow[\text{ii. } \frac{3H_2O_2}{OH^-}]{\text{i. } B_2H_6} CH_3 - CH_2 - OH + B(OH)_3$

ii. $C_6H_5-OH \xrightarrow{Br_2(aq)} ?$

Answer:



iii. $CH_3CH_2OH \xrightarrow[573K]{Cu} ?$

Answer:

$CH_3CH_2OH \xrightarrow[573K]{Cu} CH_3CHO$

Question 22

An element X (molar mass = 60 g mol^{-1}) has a density of 6.23 g cm^{-3}. Identify the type of cubic unit cell, if the edge length of the unit cell is 4×10^{-8} cm. [3]

Answer:

Molar mass (M) of element X = 60 g mol^{-1} = 0.060 kg mol^{-1}
Edge length, $a = 4 \times 10^{-8}$ cm = 4×10^{-10} m
Density, d = 6.23 g cm^{-3} = 6.23×10^{3} kg m^{-3}
Applying the relation,

$$d = \frac{Z \times M}{a^3 \times N_A}$$

Where,
Z=Number of atoms in the unit cell
N_A=Avogadro number

$$Z = \frac{d \times a^3 \times N_A}{M}$$

$$= \frac{6.23 \times 10^{23} \times (4 \times 10 - 10)^3 \times 6.022 \times 10^{23}}{0.060}$$

$=4.002 \approx 4$

Since the number of atoms in the unit cell is four, the given cubic unit cell is face-centred cubic (fcc).

Question 23 [4]

Seeing the growing cases of diabetes and depression among children, Mr. Chopra, the principal of one reputed school organized a seminar in which he invited parents and principals. They all resolved this issue by strictly banning the junk food in schools and by introducing healthy snacks and drinks like soup, lassi, milk etc. in school canteens. They also decided to make compulsory half an hour physical activities for the students in the morning assembly daily. After six months, Mr. Chopra conducted the health survey in most of the schools and discovered a tremendous improvement in the health of students.

After reading the above passage, answer the following questions:

i. What are the values (at least two) displayed by Mr. Chopra?

Answer:

The values displayed by Mr. Chopra are:

- Care - He showed concern for the health of the students.
- Selfless service - He conducted seminars and health surveys in most of the schools.

ii. As a student, how can you spread awareness about this issue?

Answer:

Awareness regarding diabetes and depression among students can be spread by seminars, health camps, debates, pamphlets, workshops by doctors, etc. to highlight the need to follow healthy eating habits and importance of physical activity in day to day life of students.

iii. Why should antidepressant drugs not be taken without consulting a doctor?

Answer:

Antidepressant drugs, when taken in doses higher than recommended, may cause harmful effects and sometimes, may even lead to death. Hence, they should not be taken without consulting a doctor.

iv. Give two examples of artificial sweeteners.

Answer:

Two examples of artificial sweeteners are saccharin and and aspartame.

Question 24 [5]

a. Define the following terms:

i. Activation energy

Answer:

According to Arrhenius theory, for any chemical reaction to take place, the reactant molecules must combine to form an activated intermediate complex. The energy required to form the activated complex is termed as activation energy. It is the energy difference between the activated complex and the reactant molecules.

ii. Rate constant

Answer:

It is the proportionality factor in the rate law expression for a chemical reaction. It is defined as the rate of a chemical reaction for which the concentration of each of the reacting species is unity.

b. A first order reaction takes 10 minutes for 25% decomposition. Calculate $t\frac{1}{2}$ for the reaction.

(Given: log 2 = 0·3010, log 3 = 0·4771, log 4 = 0·6021)

Answer:

The rate constant *k* for a first-order reaction is given by

$$k=\frac{2.303}{t}\log\frac{[R]_o}{[R]}$$

Where $[R]_o$=Initial concentration of reactant

[R]=Final concentration of reactant

At t=10 min,

$$k=\frac{2.303}{10}\log\frac{100}{100-25}=\frac{2.303}{10}\log\frac{4}{3}$$

$$\Rightarrow k=\frac{2.303}{10}(\log 4-\log 3)=\frac{2.303}{10}(0.6021-0.4771)$$

$\Rightarrow k=2.88\times10^{-2}\ \text{min}^{-1}$

For a first order reaction, half-life and rate constant are related as

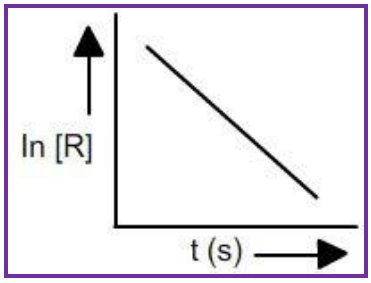
$$t_{\frac{1}{2}}=\frac{0.693}{k}$$

$$\Rightarrow t_{\frac{1}{2}}=\frac{0.693}{2.88\,x10^{-2}}=24.06\,\text{min}$$

Hence, the $t_{\frac{1}{2}}$ for the reaction is 24.06 minutes.

OR

a. For a chemical reaction R → P, the variation in the concentration, ln [R] vs. time (s) plot is given as



i. Predict the order of the reaction.

Answer:

Since the plot of *ln* [R] vs. time is a straight line with negative slope, the order of the reaction is one.

ii. What is the slope of the curve?

Answer:

The slope of the line represents the negative of the rate constant of the reaction. Slope = −k

iii. Write the unit of rate constant for this reaction.

Answer:

Since it is a first order reaction, the unit of the rate constant is s^{-1}.

$$t_1=\frac{2.303}{k}\log\frac{100}{100-99}$$

$$=\frac{2.303}{k}\log 100$$

$$=2x\frac{2.303}{k}$$

For the same reaction, the time required for 90% completion is

$$t_2 = \frac{2.303}{k} \log \frac{100}{100 - 90}$$
$$= \frac{2.303}{k} \log 100$$
$$= \frac{2.303}{k}$$

It is clear that

$t_1 = 2t_2$

Hence, the time required for 99% completion of a first-order reaction is double the time required for the completion of 90% of the reaction.

b. Show that the time required for 99% completion is double of the time required for the completion of 90% reaction.

Answer:

Assuming the reaction to follow first-order kinetics, the time required for 99% completion is given as

Question 25 [5]

a. Account for the following:

i. Bond angle in NH_4^+ is higher than NH_3.

Answer:

NH_3 has a lone pair of electrons that strongly repels the bonded pair of electrons and reduces the bond angle. On the other hand, NH_{+4} does not have any lone pair of electrons; hence, there is no lone pair–bond pair repulsion. Thus, the bond angle in NH+4 is higher than that in NH_3.

ii. H_2S has lower boiling point than H_2O.

Answer:

H_2S molecules are involved in weaker hydrogen bonding than H_2O molecules. This is because of the lower electronegativity of sulphur than oxygen. So, less energy is required to break the hydrogen bonds in H_2S. Thus, the boiling point of H_2S is lower than that of H_2O.

iii. Reducing character decreases from SO_2 to TeO_2.

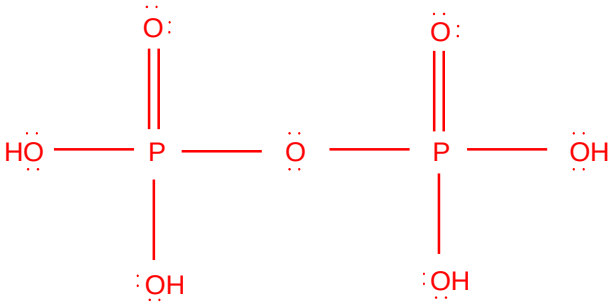
Answer:

As the size of group 16 elements increases down the group, the element–oxygen bond strength decreases from SO_2 to TeO_2. Therefore, the bond dissociation enthalpy decreases. Hence, due to increase in the tendency to release oxygen, the oxidising tendency increases and, consequently, the reducing character decreases.

b. Draw the structures of the following:

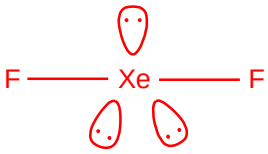
i. $H_4P_2O_7$ (Pyrophosphoric acid)

Answer:



ii. XeF_2

Answer:

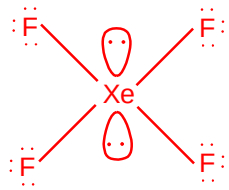


OR

a. Draw the structures of the following:

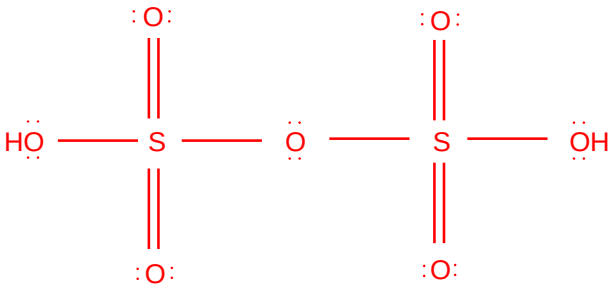
i. XeF_4

Answer:



ii. $H_2S_2O_7$

Answer:



b. Account for the following:

i. Iron on reaction with HCl forms $FeCl_2$ and not $FeCl_3$.

Answer:

The reaction of HCl with iron produces H_2.

$Fe + 2\ HCl \rightarrow FeCl_2 + H_2$

Liberation of hydrogen prevents the formation of $FeCl_3$.

ii. $HClO_4$ is a stronger acid than HClO.

Answer:

$HClO_4$ is a stronger acid than HClO. This is because ClO−4 is a weaker conjugate base than ClO^-. In ClO−4, the negative charge is spread over four oxygen atoms owing to resonance. Hence, it is more stable than ClO^-.

iii. BiH_3 is the strongest reducing agent amongst all the hydrides of group 15.

Answer:

On moving down a group, the atomic size of elements increases. Thus, the stability of their hydrides decreases due to increase in the E–H bond length. BiH_3 has the least stability among group 15 halides. Thus, it is the strongest reducing agent among all the hydrides of group 15.

Question 26 [5]

a. Illustrate the following reactions giving suitable example in each case:

i. Ammonolysis

Answer:

Ammonolysis: When an alkyl or benzyl halide is allowed to react with an ethanolic solution of ammonia, it undergoes a nucleophilic substitution reaction in which the halogen atom is replaced by an amino (−NH_2) group. This process of cleavage of the carbon–halogen bond is known as ammonolysis.

For example, the ammonolysis of chloroethane yields a substituted ammonium salt.

C_2H_5Cl + $NH_3 \rightarrow$ $C_2H_5\overset{+}{N}H_3\,\overset{-}{Cl}$

Chloroethane Ammonia Substituted ammonium salt

ii. Coupling reaction

Answer:

The reaction of joining two aromatic rings through the −N=N−bond is known as the coupling reaction. Arenediazonium salts, such as benzenediazonium salts, react with phenol or aromatic amines to form coloured azo compounds.

For example, the reaction of benzenediazonium chloride with phenol yields p-hydroxyazobenzene (orange dye).

$C_6H_5-N^+\equiv NCl^-$ Benzenediazonium chloride + C_6H_5-OH Phenol $\rightarrow -OH^-$ $C_6H_5-N=N-C_6H_5-OH$ p−Hydroxyazobenzene + Cl^- + H_2O

iii. Acetylation of amines

Answer:

Acetylation of amines: Acetylation is the process of introducing an acetyl group into a molecule. Aliphatic and aromatic primary and secondary amines undergo the acetylation reaction by nucleophilic substitution when treated with acid chlorides, anhydrides or esters. This reaction involves the replacement of the hydrogen atom of the −NH_2 or > NH group by the acetyl group, which, in turn, leads to the production of amides. To shift the equilibrium to the right-hand side, the HCl formed during the reaction is removed as soon as it is formed. This reaction is carried out in the presence of a base (such as pyridine), which is stronger than the amine.

For example, the reaction of benzenamine with acetyl chloride in the presence of pyridine yields *N*-phenylethanamide.

$C_6H_5-NH_2 + CH_3-CO-Cl \xrightarrow{\text{Pyridine}} C_6H_5-NH-CO-CH_3 + HCl$

Benzenamine Acetyl chloride N-Phenylethanamide(Soluble in alkali)

b. Describe Hinsberg method for the identification of primary, secondary and tertiary amines. Also write the chemical equations of the reactions involved.

Answer:

Hinsberg's method: Benzenesulphonyl chloride ($C_6H_5SO_2Cl$) (known as Hinsberg's reagent) reacts with primary and secondary amines to form sulphonamides. The method is used for the distinction of primary, secondary and tertiary amines.

- Sulphonamide formed in case of a primary (1°) amine is soluble in an alkali.

$C_6H_5-SOCl + C_2H_5-NH_2 \rightarrow C_6H_5-SO-NH-C_2H_5 + HCl$

Benzenamine Acetyl chloride N−Phenylethanamide

- Sulphonamide formed in case of a secondary (2°) amine remains insoluble in an alkali.

$C_6H_5-SO_2Cl + NH(C_2H_5)_2 \rightarrow C_6H_5-SO_2-N(C_2H_5)_2 + HCl$

N,*N*−Diethylbenzenesulphonamide(Insoluble in alkali)

- A tertiary (3°) amine does not give a positive Hinsberg test.

OR

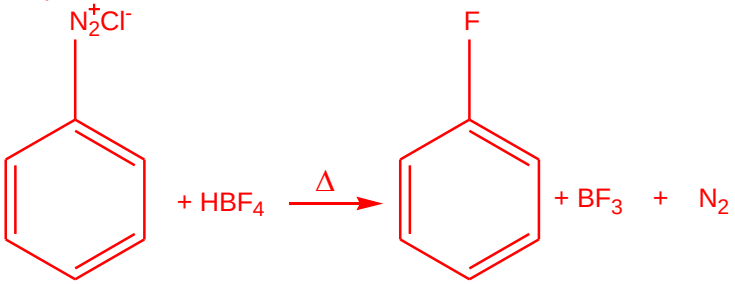
[5]

a. Write the structures of main products when benzene diazonium chloride ($C_6H_5N_2^+Cl^-$) reacts with the following reagents:

i. $\frac{HBF_4}{\Delta}$

Answer:

Main product: Fluorobenzene



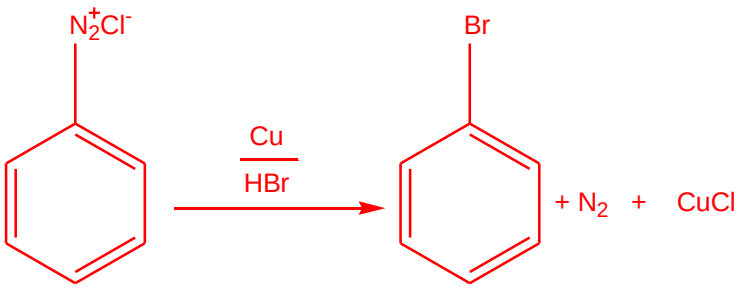
Benzendiazonium chloride

Flurobenzene

ii. $\frac{Cu}{HBr}$

Answer:

Main product: Bromobenzene



Benzendiazonium chloride

Bromobenzene

a. Write the structures of A, B and C in the following reactions:

i. $C_6H_5NO_2 \xrightarrow[HCl]{Sn} A \xrightarrow[273K]{NaNO_2} B \xrightarrow[\Delta]{H_2O} C$

Answer:

A: Ethanenitrile
B: Ethanamine
C: Ethanol

ii. $CH_3Cl \xrightarrow{KCN} A \xrightarrow{LiAlH_4} B \xrightarrow[273K]{HNO_2} C$

Answer:

$CH_3Cl \xrightarrow{KCN} \underset{A}{CH_3CN} \xrightarrow{LiAlH_4} \underset{B}{CH_3CH_2NH_2} \xrightarrow[273\ K]{HNO_2} \underset{C}{CH_3CH_2OH}$

A: Ethanenitrile
B: Ethanamine
C: Ethanol