# Maximum Marks:70 Time Allowed: 3 hours

### **General Instructions:**

- a. All questions are compulsory.
- b. Section A: Q.no. 1 to 16 are very short answer questions (objective type) and carry 1 mark each.
- c. Section B: Q.no. 17 to 23 are short answer questions and carry 2 marks each.
- d. Section C: Q.no. 24 to 30 are long answer questions and carry 3 marks each.
- e. Section D: Q.no. 31 to 33 are also long answer questions and carry 5 marks each.
- f. There is no overall choice. However an internal choice has been provided in two questions of two marks, two questions of three marks and all the three questions of five marks weightage. You have to attempt only one of the choices in such questions.
- g. Use log tables if necessary, use of calculators is not allowed.

### **Section** A

1. Vapour pressure of a liquid or a solution is the pressure exerted by the vapour in equilibrium with the liquid or solution at a particular temperature. It depends upon the nature of the liquid and temperature. The non-volatile solute in solution reduces the escaping tendency of the solvent molecules in the vapour phase because some of the solute particles occupy the positions of the solvent molecules on the liquid surface. The relative lowering of the vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute in the solution. This is also known as Raoult's law. However, for solutions of volatile solutes, the vapour pressure of a component in a solution at a given temperature is equal to the mole fraction of that component in the solution multiplied by the vapour pressure of that pure component. The solutions in which each component obeys Raoult's law is called an ideal solution. For ideal solutions  $\Delta H_{mixing}$  and  $\Delta V_{mixing}$  are also zero. Practically

no solution is ideal. A non-ideal solution is that solution in which solute and solvent molecules interact with one another with a different force than the forces of interaction between the molecules of the pure components. There are two types of non-ideal solutions, showing positive deviations and negative deviations from ideal behaviour. If for the two components A and B, the forces of interaction between A and B molecules are less than the A-A and B-B interactions, the non-ideal solutions have positive deviations. On the other hand, if the forces of interaction between A and B molecules are more than the A-A and B-B interactions, the non-ideal solutions have negative deviations.

# Answer the following questions:

- i. If a liquid is in equilibrium with its vapour at its boiling point. On average, what type of energy is equal in two-phase?
- ii. What is the mole fraction of A in solution obeying result's low if the vapour pressure of a pure liquid A is 40 mm of Hg at 300 K. The vapour pressure of this liquid in solution with liquid B is 32 mm of Hg?
- iii. Vapour pressure of a solution of heptane & octane is given by the equation:
   P(sol.)(mm Hg) = 35 + 65x, where x is the mole fraction of heptane. Calculate the vapour pressure of pure octane.
- iv. What is the value of  $\Delta V_{mixing} \& \Delta H_{mixing}$  for non-ideal solution showing negative deviation?
- v. Acetic acid + pyridine, the mixture is an example of which type of solution?
- 2. State one limitation of Ellingham diagrams.
- 3. Name the base that is found in nucleotide of RNA only.
- 4. What are the products of hydrolysis of sucrose?
- 5. Name a polymer which is used for making non-stick utensils.
- 6. Write structural formula of 1-phenyl pentan-1-one.
- 7. Alcohols undergo dehydration (removal of a molecule of water) to form alkenes on treating with

- a. conc.  $H_2SO_4$  and  $ZnCl_2$
- b.  $conc.H_2SO_4$
- c. conc. HCl
- d. conc. HCl and  $ZnCl_2$
- 8. Conversion of ore to oxide is generally carried out by the process of
  - a. Smelting
  - b. Calcination
  - c. Roasting
  - d. Both calcination and roasting
- 9. The product of oxidation of  $I^-$  with  $MnO_4^-$  in acidic medium is
  - a. I<sub>2</sub>
     b. IO<sub>3</sub><sup>-</sup>
  - c. IO<sup>-</sup>
  - d. IO<sub>4</sub>-
- 10. Tetraaminecopper(II) ion is a square planar complex with one unpaired electron. According to valence bond theory, the hybrid state of copper should be
  - a. dsp<sup>2</sup>
  - b.  $sp^3d^2$
  - c.  $d^2sp^3$
  - d. sp<sup>3</sup>

- 11.  $[-CH CH(C_6H_5) -]_n$  is a polymer obtained from?
  - a. styrene
  - b. propylene
  - c. terylene
  - d. ethylene glycol
- 12. Assertion: Uracil is present in DNA. Reason: DNA undergoes replication.
  - a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
  - b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
  - c. Assertion is CORRECT but, reason is INCORRECT.
  - d. Assertion is INCORRECT but, reason is CORRECT.
- 13. **Assertion:** The nucleophilic substitution of vinyl chloride is difficult than ethyl chloride.

Reason: Vinyl group is electron donating group.

- a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
- b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
- c. Assertion is CORRECT but, reason is INCORRECT.
- d. Assertion is INCORRECT but, reason is CORRECT.
- 14. **Assertion:** F<sub>2</sub> has low reactivity.

**Reason:** F-F bond has low bond dissociation enthalpy.

- a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
- b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
- c. Assertion is CORRECT but, reason is INCORRECT.
- d. Assertion is INCORRECT but, reason is CORRECT.
- 15. Assertion: o- and p- nitrophenols can be separated by steam distillation.
   Reason: o- isomer is steam volatile due to chelation while p-isomer is not steam volatile due to association of molecules by intermolecular H-bonding.
  - a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
  - b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
  - c. Assertion is CORRECT but, reason is INCORRECT.
  - d. Assertion is INCORRECT but, reason is CORRECT.
- 16. **Assertion:** The micelle formed by sodium stearate in water has COO<sup>-</sup> groups at the surface.

Reason: Surface tension of water is reduced by addition of stearate.

- a. Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.
- b. Both assertion and reason are CORRECT but, reason is NOT THE CORRECT explanation of the assertion.
- c. Assertion is CORRECT but, reason is INCORRECT.
- d. Assertion is INCORRECT but, reason is CORRECT.

### Section **B**

- 17. Define polymers.
- 18. Show that for a first order reaction, the time required for half the change (half-life period) is independent of initial concentration.
- 19. State two advantages of  $H_2$   $O_2$  fuel cell over ordinary cell.
- 20. Write the IUPAC name of the following:
  - i.  $[Mn(H_2O)_6]^{2+}$ ii.  $[Cr(NH_3)_6]^{3+}$
- 21. Account for the following:
  - a. Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines.
  - b. On reaction with benzene sulphonyl chloride, primary amine yields product soluble in alkali whereas secondary amine yields product insoluble in alkali.

What is the charge on metal atom in a complex ion?  $[CO(NH_3)_3(H_2O)Cl]^{2+}$ 

22. Why is the leaching of gold by metal cyanides carried out in presence of oxygen? Name the metal used as reducing agent in the extraction of gold by leaching.

OR

What is the role of cryolite in the metallurgy of aluminium?

- 23. How would you obtain
  - i. picric acid from phenol?
  - ii. 2-methyl propanol from 2-methyl propene?

### Section C

24. What is understood by a normal hydrogen electrode? Give its significance?

25. The data given below is for the reaction,  $2N_2O_5(g) 
ightarrow 4N0_2(g) + O_2(g)$ 

S. No.	N <sub>2</sub> O <sub>5</sub> (mol L <sup>-1</sup> )	Rate of disappearance of N <sub>2</sub> O <sub>5</sub> (mol L <sup>-1</sup> min <sup>-1</sup> )
1.	$1.13 \times 10^{-2}$	34 ×10⁻⁵
2.	$0.84 \times 10^{-2}$	25 × 10 <sup>-5</sup>
3.	$0.62 \times 10^{-2}$	$18 \times 10^{-5}$

Determine for this reaction,

- i. Order of reaction
- ii. Rate law
- iii. Rate constant

OR

Define activation energy of reaction.

26. For the cell,

 $\mathrm{Zn}(s)\left|\mathrm{Zn}^{2+}(2\mathrm{M})\|\mathrm{Cu}^{2+}(0.5\mathrm{M})\right|\mathrm{Cu}(s)$ 

- i. Write the equation for each half reaction.
- ii. Calculate the cell potential at 25°C.

[Given, 
$$E^\circ_{{
m Zn}^{2+}/{
m Zn}}$$
= -0.76 V ,  $E^\circ_{{
m Cu}^{2+}/{
m Cu}}$ = + 0.34 V]

- 27. Why is  $H_2O$  a liquid and  $H_2S$  a gas?
- 28. Discuss the mechanism of  $S_N 1$  reaction of haloalkanes.
- 29. Complete each synthesis by giving missing starting material, reagent or products.

Give reasons for the following:

- a. Carboxylic acids do not give characteristic reactions of carbonyl group.
- b. Treatment of benzaldehyde with HCN gives a mixture of two isomers which cannot be separated even by careful fractional distillation.
- c. Sodium bisulphite is used for the purification of aldehydes and ketones.
- 30. a. Pick out the odd one from the following on the basis of their medicinal properties: Equanil, Seconal, Bithional, Luminal
  - b. What type of detergents are used in dish washing liquids?
  - c. Why is the use of aspartame limited to cold foods?

#### Section D

31. What is the difference between multimolecular and macromolecular colloids? Give one example of each. How are associated colloids different from these two types of colloids?

#### OR

Explain how rusting of iron is envisaged as setting up of an electrochemical cell.

32. An aromatic compound 'A' of molecular formula C<sub>7</sub>H<sub>6</sub>O<sub>2</sub> undergoes a series of reactions as shown below. Write the structures of A, B, C, D and E in the following reactions.

$$(C_{7}H_{6}O_{2})A \xrightarrow{\text{NH}_{3}/\text{Heat}} C_{6}H_{5}CONH_{2}$$

$$\xrightarrow{\text{NaOH} Br_{2}} B \xrightarrow{(CH_{3}CO)_{2}O} C$$

$$\downarrow Br_{2}(aq)$$

$$E$$

#### OR

Give one chemical test to distinguish between the following pairs of compounds:

i. Methylamine and dimethylamine

- ii. Secondary and tertiary amines
- iii. Ethylamine and aniline
- iv. Aniline and benzylamine
- v. Aniline and N-methyl aniline
- 33. a. Account for the following :
  - i. Manganese shows maximum number of oxidation states in 3d series.
  - ii.  $E^{0}$  value for  $Mn^{3}+/Mn^{2}+$  couple is much more positive than that for  $Cr^{3}+/Cr^{2}+$ .
  - b. Write the chemical equations for the preparation of KMnO<sub>4</sub> from MnO<sub>2</sub>.

For  $M^{2+}/M$  and  $M^{3+}/M$  systems, the  $E^{\Theta}$  values for some metals are as follows: Cr<sup>2+</sup>/Cr = -0.9 V, Cr<sup>3+</sup>/Cr = -0.4 V, Mn<sup>2+</sup>/Mn = -1.2 V,Mn<sup>3+</sup>/Mn<sup>2+</sup> = +1.5 V, Fe<sup>2+</sup>/Fe= -0.4 V, Fe<sup>3+</sup>/Fe<sup>2+</sup> = +0.8 V. Use this data to comment upon:

- i. The stability of  $Fe^{3+}$  in acid solution as compared to that of  $Cr^{3+}$  or  $Mn^{3+}$
- ii. The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

# CBSE Class 12 - Chemistry Sample Paper - 05 (2019-20)

# Solution

### Section A

1. i. The total energy is equal in two-phase.

ii. 
$$P_A = x_A \times P_A^\circ$$
  
 $32 = x_A \times 40$   
 $x_A = \frac{32}{40}$   
 $x_A = 0.8$ 

- iii. For pure octane, x = 0
  - $\therefore$  p(sol.)(mm Hg) = P (octane) = 35 + 65  $\times$  0 = 35 mm of Hg
- iv. The value of  $\Delta V_{mixing}$  &  $\Delta H_{mixing}$  is negative.
- v. It is an example of Non-ideal solution.
- 2. Ellingham diagrams only tell us about the feasibility of a reaction. They do not tell anything about the reaction kinetics.
- 3. Uracil.
- 4. Sucrose on dydrolysis gives equimolar mixture of D-glucose and D-fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$
  
 $Glu \cos e + C_6H_{12}O_6$   
 $Fructose$ 

- 5. Teflon is used for making non-stick utensils.
- 6. The structural formula of 1-phenyl pentan-1-one.

7. (b) conc. $H_2SO_4$ 

**Explanation:** The dehydration reaction of alcohols to generate alkene proceeds by heating the alcohols in the presence of a strong acid, such as sulfuric or phosphoric

acid, at high temperatures.



The required range of reaction temperature decreases with increasing substitution of the hydroxy-containing carbon:

- 1° alcohols: 170° 180°C
- 2° alcohols: 100°– 140 °C
- 3° alcohols: 25°– 80°C

If the reaction is not sufficiently heated, the alcohols do not dehydrate to form alkenes, but react with one another to form ethers.

8. (d) Both calcination and roasting

**Explanation:** Calcination is employed for carbonate ores to convert into respective oxide ores. Roasting is employed for sulphide ores for conversion to oxide ores.

9. (a) I<sub>2</sub>

**Explanation:** Iodine is liberated from potassium iodide.

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10I^{-} + 2MnO_{4}^{-} + 16H^{+} \rightarrow 2Mn^{2+} + 8H_{2}O + 5I_{2}
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10. (a)  $dsp^2$ 

**Explanation:** Tetraaminecopper(II) ion is square planar. Square planar complexes have dsp<sup>2</sup> hybridisation. So hybridization is dsp<sup>2</sup>.

11. (a) styrene

**Explanation:** This is an addition polymer obtained from monomer styrene  $CH_2 = CH(C_6H_5)$ . The addition polymers are formed by the repeated addition of monomer molecules possessing double or triple bonds.

12. (d) Assertion is INCORRECT but, reason is CORRECT.

**Explanation:** Assertion is INCORRECT but, reason is CORRECT.

- 13. (c) Assertion is CORRECT but, reason is INCORRECT.Explanation: Assertion is CORRECT but, reason is INCORRECT.
- 14. (d) Assertion is INCORRECT but, reason is CORRECT.Explanation: Assertion is INCORRECT but, reason is CORRECT.
- 15. (a) Both assertion and reason are CORRECT and reason is the CORRECT explanation of

the assertion.

**Explanation:** Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

16. (a) Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

**Explanation:** Both assertion and reason are CORRECT and reason is the CORRECT explanation of the assertion.

### Section **B**

- 17. Polymers are defined as the very large molecules having high molecular mass which are formed by joining of repeating structural units on a large scale.
- 18. For a first order reaction, rate constant,

$$egin{aligned} &k = rac{2303}{t} \log rac{[R]_0}{[R]} \ & ext{When} \ t = t_{1/2'}[R] = rac{[R]_0}{2} \ &t_{1/2} = rac{2303}{k} \log rac{[R]_0}{[R]_0/2} \ &t_{1/2} = rac{2303}{k} \log 2 = rac{2303 imes 03010}{k} \ t_{1/2} = rac{0693}{k} \end{aligned}$$

For a first order reaction, half-life period is constant. It is independent of initial concentration of the reacting species.

- 19. Two advantages of  $H_2$   $O_2$  fuel cell over ordinary cell are.
  - i. It do not cause any pollution.
  - ii. It has high efficiency of 60-70%.
- 20. i. Hexaaquamanganese(II) ion
  - ii. Hexaaminechromium(II) ion
- 21. a. Gabriel phthalimide synthesis is not preferred for preparing aromatic primary amines because aryl halide does not undergo nucleophilic substitution reaction.
  - b. On reaction with benzene sulphonyl chloride, primary amine yields product soluble in alkali whereas secondary amine yields product insoluble in alkali because of the absence of acidic hydrogen attached to nitrogen (N-H) in the product of secondary amine.

CO has +3 charge in the complex ion.

22. The leaching of gold by metal cyanides is carried out in presence of oxygen to convert gold into oxidised state from  $Au \rightarrow Au^+$ . Here Zinc metal used as reducing agent.

OR

$$egin{aligned} 4Au(s)+8CN^{-}(aq)+2H_2O(aq)+O_2(g)&
ightarrow 4[Au(CN)_2]^{-}(aq)+4OH^{-}(aq)\ 2[Au(CN_2]^{-}(aq)+Zn(s)&
ightarrow [Zn(CN)_4]^{2-}(aq)+2Au(s)\ \mathbf{OR} \end{aligned}$$

Cryolite (Na<sub>3</sub>AlF<sub>6</sub>) reduces melting point of Al<sub>2</sub>O<sub>3</sub> and increases electrical



24. It is used as reference electrode. Its electrode potential is taken as 0.00 volt. Hydrogen electrode consists of platinum wire coated with finely divided platinum black containing pure hydrogen gas at 1 atm and solution of HCl (1 M) so as to maintain equilibrium between  $H^+$  ions and  $H_2(g)$ .

At cathode  $2H^+ + 2e o H_2$ 

At anode $H_2 o 2H^{2+} + 2e^-$ significance: In the measurement of electrode potential. 25. For the reaction  $2N_2O_5(g) o 4NO_2(g) + O_2(g)$ 

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Assume rate law expression as
Rate = k[N_2O_5]^x
According to question
34	imes 10^{-5} = k [1.13	imes 10^{-2}]^x... (i)
25	imes 10^{-5} = k[0.84	imes 10^{-2}]^x...(ii)
18	imes 10^{-5} = k[0.62	imes 10^{-2}]^x...(iii)
From eq.(i) and eq.(ii)
rac{34 	imes 10^{-5}}{25 	imes 10^{-5}} = rac{k [1.13 	imes 10^{-2}]^x}{k [0.84 	imes 10^{-2}]^x}
[1.36] = [1.36]^x
x = 1
 i. Order of reaction=1
ii. Rate law expression
     Rate = k[N_2O_5]
iii. Rate constant
     k=rac{[Rate]}{[N_2O_5]}=rac{34{	imes}10^{-5}}{1.13{	imes}10^{-2}}
     k = 30.09 \times 10^{-3}
     k=3.0	imes10^{-2}\mathrm{min}^{-1}
```

# OR

Activation Energy (E<sub>a</sub>) is the least amount of energy required to activate atoms or molecules to a state in which they can undergo a chemical reaction. Activation energy may also be defined as the minimum energy required to start a chemical reaction. It is independent of temperature and expressed in units of kilojoules per mole (kJ/mol) or kilocalories per mole (kcal/mol).

26. i. For the cell;  $Zn(s)|Zn^{2+}(2M)||Cu^{2+}(0.5M)|Cu(s)$ . The cell reactions are: Oxidation half cell reaction;  $\operatorname{Zn}(s) \to \operatorname{Zn}^{2+}(aq) + 2e^-$  (At Anode) Reduction half cell reaction;  $\operatorname{Cu}^{2+}(aq) + 2e^- \to \operatorname{Cu}(s)$  (At Cathode) ii.  $E_{\text{cell}}^{\circ} = E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$   $E_{\text{cell}}^{\circ} = 0.34 \text{ V- (-0.76 V)} = 1.10 \text{ V}$ By applying Nernst equation;  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log \frac{[\operatorname{Zn}^{2+}]}{[\operatorname{Cu}^{2+}]}$  $E_{\text{cell}} = 1.10 - \frac{0.0591}{2} \log \frac{2}{25}$ 

$$E_{\text{cell}} = 1.10 - \frac{2}{2} \log_{0.5} \frac{100}{2} \times 0.6021$$
$$E_{\text{cell}} = 1.10 - 0.0178 = 1.0822 \text{ V}$$

27. Due to greater electronegativity of O than S, H<sub>2</sub>O undergoes extensive intermolecular H-bonding. As a result, H<sub>2</sub>O is a liquid at room temperature. In contrast, H<sub>2</sub>S does not undergo H-bonding. It exists as discrete molecules which are held together by weak Vander Waals forces of attraction. To break these forces of attraction, only a small amount of energy is required. Therefore, H<sub>2</sub>S is a gas at room temperature.

$$H_{\delta^{+}}^{\delta^{+}} \xrightarrow{H_{\delta^{+}}} O_{\delta^{-}}^{H_{\delta^{+}}} O_{\delta^{-}}$$

28. Tertiary halides undergo nucleophilic substitution through  $S_N 1$  mechanism. It is a two step mechanism. First step involves formation of carbocation by loss of halide ion.

$$CH_3 - egin{array}{c} CH_3 \ dots \ CH_3 \ \$$

2<sup>nd</sup> Step: Second step involves attack of nucleophile which can happen from either side of the plane of the molecule



Thus, the compound which gives the most stable carbocation on losing the halide ion

will preferably undergo nucleophilic substitution by  $S_N 1$  mechanism.

29. The reaction between an aldehyde/ketone and an aromatic carbonyl compound lacking an  $\alpha$ -hydrogen is called Claisen–Schmidt condensation.



a. This is due to the lone pairs on oxygen atom attached to the hydrogen atom in the -COOH group, are involved in resonance and hence making the carbon atom less electrophilic. Hence, carboxylic acids do not give their action of carbonyl groups

$$\begin{array}{c} 0 \\ R - C - \overset{O}{\bigcirc} H \\ \hline \end{array} \\ R - C = \overset{O}{\bigcirc} H \\ \hline \end{array} \\ R - C = \overset{O}{\bigcirc} H \\ \hline \end{array}$$

b.  $C_6H_5CHO$  reacts with HCN to form isomeric benzaldehyde cyanohydrins because an asymmetric carbon atom is introduced

$$C_{6}H_{5}\overset{ec{l}}{C}=O~+~HCN~
ightarrow~C_{6}H_{5}-ec{l}{C}_{CN}^{ec{l}}st-OH~(Asymmetric~carbon~atom)$$

H

These two isomers are enantiomers and therefore, cannot be separated by physical methods like fractional distillation.

c. Aldehydes and ketones form addition compounds with NaHSO<sub>3</sub> whereas impurities do not. On hydrolysis, we get pure aldehydes and ketones back.

$$CH_3-\overset{O}{C}-H+\ NaHSO_3
ightarrow CH_3-CH-SO_3Na \xrightarrow{H_2O/H} CH_3-\overset{C}{O}-H$$

- 30. a. Bithional. It is a antimicrobial whereas all other are tranquilizers.
  - b. Non-ionic detergents are used in dish washing liquids.
  - c. Aspartame is unstable at cooking temperature. So, use of aspartame is limited only to cold foods.

# Section D

31. i. In multi-molecular colloids, the colloidal particles are an aggregate of atoms or

small molecules with a diameter of less than 1 nm. The molecules in the aggregate are held together by Van der Waal's forces of attraction. Examples of such colloids include gold sol and sulphur sol.

- ii. In macro-molecular colloids, the colloidal particles are large molecules having colloidal dimensions. These particles have a high molecular mass. When these particles are dissolved in a liquid, sol is obtained. For example: starch, nylon, cellulose, etc.
- iii. Certain substances tend to behave like normal electrolytes at lower concentrations. However, at higher concentrations, these substances behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called aggregated colloids or associated colloids.

#### OR

The water layer present on the surface of iron (especially in the rainy season) dissolves acidic oxides of air like  $CO_2$ ,  $SO_2$  etc. to from acids which dissociate to give

H<sup>+</sup> ions: H<sub>2</sub>O + CO<sub>2</sub> → H<sub>2</sub>CO<sub>3</sub>  $\rightleftharpoons$  2H<sup>+</sup> +  $CO_3^{2-}$  In the presence of H<sup>+</sup> ions iron starts losing electrons at some spot to form ferrous ions, i.e. its oxidation takes place. Hence, this spot acts as the anode: Fe(s) → Fe<sup>2+</sup>(aq) + 2e- .The electrons this released through the metal to reach another spot where H<sup>+</sup> ions and the dissolved oxygen takes up these electrons and reduction reaction takes place. Hence, this spot acts as the cathode: O<sub>2</sub>(g) + 4H<sup>+</sup>(aq) + 4e<sup>-</sup> → 2H<sub>2</sub>O(l) The overall reaction is : 2Fe(s) + O<sub>2</sub>(g) + AH<sup>+</sup> (aq) → 2Fe<sup>2+</sup>(aq) + 2H<sub>2</sub>O(l) Ferrous ions are further oxidized by the atmospheric oxygen to ferric ions which combine with water molecules to form hydrated ferric oxide, Fe<sub>2</sub>O<sub>3</sub>.xH<sub>2</sub>O which is rust.





i. These can be distinguished by the carbylamine test.

 $CH_3NH_2 + CHCl_3 + 3KOH \xrightarrow{\sim} CH_3NC + 3KCl + 3H_2O$  $Methyla \min e_{(1^0 A \min e)}$  Methylisocyanide (offensive smell)  $CH_3NH_{\substack{Dimethyla\min e\\(2^0) \ a\min e)}} \xrightarrow{CHCl_3/KOH(alc)} No \, reaction$ 

ii. Secondary and tertiary amines can be distinguished by Libermann nitrosoamine test. 2° amines react with nitrous acid to form N-nitrosamines while 3° do not.

 $(CH_3CH_2)_2 NH + HO - N = 0 \rightarrow (CH_3CH_2)_2 N - N = O + H_2O$ Diethyla min e (Yellow colour)

- iii. **Azo dye test:** Aniline and ethylamine can be distinguished by azo dye test. It involves the reaction of aniline with  $HNO_2$  at 273-278 K followed by treatment with an alkaline solution of  $\beta$ -naphthol, which gives a brilliant yellow, orange or red coloured dye. Ethylamine under these condition gives a brisk evolution of  $N_2$  gas with the formation of primary alcohol.
- iv. Nitrous acid test: Benzylamine reacts with nitrous acid to form a diazonium salt which being unstable even at low temperature, decomposes with evolution of  $N_2$  gas.

Aniline, on the other hand, reacts with nitrous acid to form benzene diazonium chloride which is stable at 273 - 278 K and hence does not decompose to evolve  $N_2$  gas.

- v. **Carbylamine test:** Aniline being a primary amine gives carbylamine test whereas N-methylamine being a secondary amine does not give this test. when aniline is heated with an alcoholic solution of KOH and CHCl<sub>3</sub>, it gives the offensive smell of phenyl isocyanide.
- 33. a. i. Manganese shows maximum number of oxidation states in 3d series due to the presence of maximum number of unpaired electrons.
  - ii.  $E^{0}$  value for  $Mn^{3}$ +/ $Mn^{2}$ + couple is much more positive than that for  $Cr^{3}$ +/ $Cr^{2+}$ because Cr is more stable in +3 oxidation state due to stable  $t^{3}_{2g}$  configuration whereas Mn is more stable in +2 oxidation state due to half filled  $3d^{5}$ configuration.
  - b. Preparation of  $KMnO_4$  from  $MnO_2$ :

 $2MnO_2 + 4KOH + O_2 \rightarrow 2K_2MnO_4 + 2H_2O$ 

 $2\mathrm{K}_{2}\mathrm{MnO}_{4} + 4\mathrm{HCl} \rightarrow 2\mathrm{KMnO}_{4} + \mathrm{MnO}_{2} + \mathrm{H}_{2}\mathrm{O} + 4\mathrm{KCl}$ 

Oxidation potential is measure of tendency of a chemical species to undergo oxidation. More is the tendency of substance to undergo oxidation, more will be its oxidation potential. Similarly, Reduction potential is a measure of tendency of a chemical species to undergo reduction. More is the tendency of substance to undergo reduction, more will be its reduction potential and lesser will be its oxidation potential. Oxidation potential = - (Reduction Potential) The  $E^{\Theta}$  value (Standard reduction potential value) for  $Fe^{3+}/Fe^{2+}$  is higher than that for  $Cr^{3+}/Cr^{2+}$  and lower than that for  $Mn^{3+}/Mn^{2+}$  .So, the reduction of  $Fe^{3+}to\,Fe^{2+}$  is easier than the reduction of  $Mn^{3+}$  to  $Mn^{2+}$ ,but not as easy as the reduction of  $Cr^{3+}$  to  $Cr^{2+}.$ Hence,  $Fe^{3+}$  is more stable than  $Mn^{3+}$ , but less stable than  $Cr^{3+}.$  The stability of  $Cr^{3+}$  is because of presence of half filled  $t_{2g}$  configuration in  $Cr^{3+}$ . These metal ions can be arranged in the increasing order of their stability as:  $Mn^{3+} < Fe^{3+} < Cr^{3+}$  The reduction potentials for the given pairs increase in the following order.  $Mn^{2+}/Mn < Cr^{2+}/Cr < Fe^{2+}/Fe$  So, the oxidation of Fe to  $Fe^{2+}$  is not as easy as the oxidation of Cr to  $Cr^{2+}$  and the oxidation of Mn to  $Mn^{2+}$ Thus, these metals can be arranged in the increasing order of their ability to get oxidised as: Fe < Cr < Mn.