SRI RAMAKRISHNA INSTITUTE OF TECHNOLOGY,CBE -10

ENGINEERING CHEMISTRY-II

ELECTROCHEMISTRY

1. What is a cell? Mention its types.

A cell is a device consisting of two half cells. Each half cell contains an electrode dipped in an electrolytic solution. The two half cell are connected through one wire. The followings are two types of cells.

1) Electrolytic cells
2) Electrochemical cells (or) Voltaic cells (or) galvanic cells

2. Describe the construction of a glass electrode. How it is significant in its applications?

A glass electrode consists of thin walled glass bulb containing a Pt wire dipped in 0.1M-HCl. It is represented as

Pt, HCl (0.1M)│Glass

The pH of the solution, especially coloured solutions containing oxidizing or reducing agents can be determined by using glass electrode.

3. What is salt bridge? Explain its functions.

It consists of a U-tube containing saturated solution of KCI or NH_4NO_3 in agar-agar gel. It connects the two half cells of the galvanic cells.

Functions of salt bridge.

i) It eliminates liquid junction potential.
ii) It provides the electrical continuity between the two half cells.

4. Define Single electrode potential. What is the value of electrode potential of Standard Hydrogen Electrode?

It is the measure of tendency of a metallic electrode to gain or loose electrons, when it is in contact with a solution of its own salt. The Electrode potential of Standard Hydrogen Electrode is found to be Zero.

5. Why does Ag │Ag^+(0.01M) ‖ Ag^+(1.0M) │Ag constitute a cell?

Ag │Ag^+(0.01M) ‖ Ag^+(1.0M) │Ag
(C_1) (C_2)

This constitutes a cell since concentration of Ag^+ differs (i.e) **(C_1) < (C_2)**. Hence in this cell, Oxidation takes place in the left hand side and Reduction takes place in the right hand side.

6. Why can glass electrode not be used for a solution of high alkalinity?

At above 12 pH (high alkalinity), cations of the solution affect the glass and make the elecrode useless.

7. What are reversible and irreversible cells?

A cell is said to be reversible if it obeys the following three conditions of thermodynamic reversibility.

(i) If the external emf is equal to the actual emf of the cell, no current will flow.

(ii) If the external emf is smaller than the actual emf of the cell, current will flow.

(iii) If the external emf is greater than the actual emf of the cell, current will flow in the opposite direction. Example: Daniel cell, Secondary batteries.

If the cell does not obey the above condition, then the cell is called irreversible cell. Example: Zinc-Silver cell, Dry cell (primary cell).

8.How will you predict the spontaneity of any redox system using emf?

If the std.emf of the cell calculated is positive value, the cell reaction is spontaneous. It is well know that for a reaction to be spontaneous, the std free energy change (ΔG^o) of the reaction must be negative. Since in a cell

$$\Delta G^o = - nFE^0 \text{ J}$$

It is evident that if E_0 is positive, ΔG^o would be negative. Hence the cell reaction would be spontaneous.

9. Zinc reacts with dilute Sulphuric acid to give Hydrogen but silver does not. Explain .Given that $E^o_{Ag^+/Ag}$ =+ 0.80V and $E^o_{Zn^{2+}/Zn}$ =-0.76V.

The metal with positive reduction potential (ie., the metals placed below H_2 in the emf series) will not displace the hydrogen from an acid solution.

$$Zn + H_2SO_4 \longrightarrow Zn\,SO_4 + H_2\uparrow$$

$$Ag + H_2SO_4 \longrightarrow \text{No reaction}$$

10. What is electrochemical series? What is its significance?

When various metals are arranged in the order of their increasing values of standard reduction potential on the hydrogen scale, then the arrangement is called electrochemical series or electromotive series.

Significance:

Standard emf of the cell can be calculated.

Equilibrium constant can be calculated.

11. Give the construction of SHE.

The standard hydrogen electrode can be constructed by dipping a platinum wire with a platinum foil, in a H^+ ion solution (i.e. HCl) of 1M concentration, and hydrogen gas is passed through the solution at 1 atmospheric pressure. Under these standard conditions, the potential of SHE is arbitrarily taken as Zero Volts.

The electrode is represented as

Pt,H_2 (1atm) $\mid$ H^+(1M)

12. What is the principle involved in Conductometric titration?

Conductometric titration is a volumetric method based on the measurement of conductance of the solution during the titration.The conductance of the solution depends on the number and charge of the free ions and the mobility of the ions.

13. Define a reference electrode. Give one example.

Reference electrode is the one, the potential of which is known (or) arbitrarily fixed as zero. It is used to measure the electrode potential of another unknown electrode by combining with it.

Ex: Standard. Hydrogen electrode, Calomel electrode.

14. Write the construction and representation of Saturated Calomel Electrode.

Calomel electrode consists of a glass tube containing mercury at the bottom over which a paste of mercurous chloride is placed. The remaining portion of the tube is filled with a saturated solution of KCl. The bottom of the tube is sealed with a platinum wire. The side tube is used for making electrical contact with a salt bridge.

Cell representation is

$Hg/Hg_2Cl_2/KCl_{(Sat)}$

15. What is electrode concentration cell? Give one example

Two identical electrodes of different concentrations are dipped in the same electrolytic solution of the electrode metal**.**

Example**:** Amalgam concentration cell.

16. What is electrochemical cell or Galvanic cell? Give example

A cell which converts chemical energy produced in a redox reaction in to electrical energy. Eg. Daniel cell.

17. Write Nernst equation and explain the terms involved.

$$E = E^{o} + \frac{2.303RT}{nF} \log [M^{n+}] \text{ (Oxidation Potential)}$$

E^o = Std. emf of the cell. **R** = gas constant (8.314J mol^{-1} K^{-1})

T = Temperature **n** = No of electrons involved in the cell reaction

F = 1 Faraday (96500coloumbs) **M^{n+}**= Concentration of the ions.

18. What are the advantages of conductometric titration?

1. It gives more accurate end point.
2. It is used in the case of coloured solutions, where colour change of the indicator is not clear.
3. It is also used for the analysis of dilute solutions and weak acids.
4. Since end point is detected graphically, no keen observation is necessary

near the end point.

19. Distinguish between galvanic cell and electrolytic cell

S.No	Galvanic Cell	Electrolytic cell
1	Chemical energy is converted to electrical energy.	Electrical energy is converted to chemical energy.
2	The anode carries negative charge.	The anode carries positive charge.
3	Amount of electricity passed during electrolysis is measured by coulometer	The emf produced in the cell is measured by potentiometer.

20. Define emf of a cell.

It is defined as the "difference of potential which causes flow of current from one electrode which is at higher potential to the other electrode which is at a lower potential is called the Electromotive force."

21. Calculate the oxidation potential of the cadmium electrode constituting the following cell.

$Cd / Cd^{2+}_{a=1}$ // KCl $_{(sat)}$,$Hg_2Cl_{2\ (s)}$ / Hg- pt.

Emf of the above cell is 0.6445Vand the reduction potential of saturated Calomel Electrode is 0.2415V . Cadmium undergoes oxidation.

Emf of the cell $= E_{RHE} - E_{LHE}$

$0.6445 = 0.2415 - E_{Cd}$

$E_{Cd} = 0.2415 - 0.6445$

$= -0.403$ V

Oxidation Potential = +0.403 v

22. The Standard reduction potential of Cu and Zn are 0.34V and -0.76V respectively. Will Zinc displace Cu from its salt solution.

Yes. Metals with high negative reduction Potential in the emf series can displace those with less negative or more positive potential from their solution. Since Zn has high negative reduction potential than Cu, Zn will displace Cu from its salt solution.

23. Can we use a Cu vessel to store 1M $AgNO_3$ Solution?

[$E^o_{Cu^{2+}|Cu}$ = +0.34V & $E^o_{Ag^+|Ag}$ = +0.80V]

Yes. Since the reduction potential of $Ag^+|Ag$ electrode is higher than that of $Cu^{2+}|Cu$ electrode.

24. What is a galvanic cell?

Galvanic cell is generally represented as

Anode /Anodic solution // Cathodic solution / Cathode

Ex. Daniel Cell. $Zn / ZnSO_4 // CuSO_4$

25. What are the advantages and limitations of glass electrode?

Advantages:

1. It is simple and can be easily used.
2. Equilibrium is rapidly achieved.
3. The results are accurate.
4. It is not easily poisoned.

Limitations:

1. The glass electrode can be used in solutions with pH range 0 to 10. However above pH 12, cations of solution affect the glass interface and render the electrode useless.
2. Although the glass membrane of the electrode is very thin, yet its resistance is extremely high which cannot be measured by ordinary potentiometers.

26. What is an ion selective electrode? Give example.

An ion selective electrode is an electrode that will detect only a particular type of ions present in the solution. The potential of such an electrode will depend on the concentration of a particular ion. Example: Glass electrode.

27. Define reduction potential.

The tendency of an electrode to loose electrons when it is contact with solution of its own ions.

28. Define emf.How an emf of a cell can be measured?

Emf is defined as the difference of potential which causes the flow of current from an electrode having higher potential to another having lower potential. It can be measured using potentiometer which is based on Pogendroffs compensation principle.

29. What is electrode potential?

It is the measure of tendency of a metallic electrode to loose or gain electrons when it is in contact with a solution of its own salt.

30.Can we use a salt bridge made from KCl solution for a cell made of Ag and Pb half cells?

No, because chloride ions (from the salt bridge) will react with Ag+ ions to form $AgCl_{(s)}$ and with Pb2+ ions to form $PbCl_{(2)}$. Both of these ($AgCl_{(s)}$ & $PbCl_{(2)}$ are insoluble , so the concentration of the solutions of the two half cells will change. Thus, the cell will no longer be in the initial conditions.

31.What is oxidation Potential?

The tendency of an electrode to gain electrons when it is in contact with solution of its own ions.

32.Why do we use NH_4NO_3 or KCl for preparing salt bridges?

Because the transport numbers of NH_4^+ and NO_3^- or (k^+ & Cl^-) are nearly equal to 0.5 each, so there is no net transfer of these ions during the operation of a cell.

33. What is standard electrode potential (E^o)?

It is a measure of tendency of a metallic electrode to loose or gain electrons when it is in contact with a solution of its own ions of 1M concentration at 25^oC**.** .

34.Write the applications of Nernst equation.

- To calculate unknown electrode potentials (half cell potential)
- Prediction of corrosion tendency of metals in a given set of environmental conditions.
- To construct electromotive force series.
- To calculate E.M.F and polarity of electrodes in an electrochemical cell.

35. What is meant by galvanic series?

Oxidation potential of various metals and alloys are measured by immersing them in sea water using saturated calomel electrode as the reference electrode. These values are arranged in the decreasing order of activity. This series is known as galvanic series.

36. Can we use nickel spatula to stir a solution of copper sulphate?

No. Since the reduction potential of Ni^{2+}/Ni electrode is less than (-0.25V) that of Cu^{2+}/Cu electrode (+0.34V).Nickel will otherwise displace copper from copper sulphate solution as below.

$$Ni_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Cu_{(s)} + Ni^{2+}_{(aq)}$$

37. Write about Conductivity of electrolyte.

Electrolyte like $CuSO_4$ is completely ionized in solution as

$CuSO_4 \rightarrow Cu^{2+} + SO_4^{2-}$

The ions formed travel towards the oppositely charged electrodes & conduct electricity.

38. Mention the factors which affect electrode potential.

i) The nature of the metal
ii) The temperature
iii) The concentration of metal ions in solution.

39. $Zn + H_2SO_4 \rightarrow ZnSO_4 + H_2$. Justify whether this cell is an irreversible cell (or) not.

This is an irreversible cell since one of the products of the normal cell reaction namely hydrogen gas, has already escaped. Hence it doesnot obey the three conditions of thermodynamic reversibility.

40. Write the basics principles of potentiometric titration.

The potentiometric titration involves the measurements emf between reference electrode and an indicator electrode with the addition of the titrant (burrette solution).

PART-B

1)a. Derive Nernst equation for emf of a cell?
b. Discuss in detail any two applications of Nernst equation.
2)a.What is single electrode potential?
b. Describe standard hydrogen electrode and calomel electrode with their diagram, electrode notation and electrode reaction.
3) Describe a glass electrode.How can it be used for determining the pH of a solution?
4) Describe the construction and working of a galvanic cell.
5) What is electrochemical series. Give its application.
6) What are reference electrode? Describe any two reference electrodes with neat diagram and mention their uses.
7)a. How is emf of a galvanic cell measured by poggendorff's compensation method?
b. How is pH of a solution determined from emf measurement?
8) Define electromotive force.How is it measured by potentiometric method?
9) a. What is the principle behind conductometric titration? What are its advantages and disadvantages.
b. Explain acid-base titrations conductometrically.
10) What are the reversible and irreversible cells? Explain.
11) Explain the potentiometric redox titrations of $FeSO_4$ and $K_2Cr_2O_7$ with neat diagram.
12) What are ion selective electrodes? Mention its applications.
13) Calculate the half cell potential at 298 K for the reaction.

$Zn^{2+}_{(aq)} + 2e \rightarrow Zn_{(s)}$ If $[Zn^{2+}]$ is 0.5 M and $E_{Zn2+/Zn} = -0.76V$

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ENGINEERING CHEMISTRY-II

CORROSION AND CORROSION CONTROL-UNIT II

1) Define corrosion?

The destruction of metals or alloys by the action of gaseous atmosphere, water or any other reactive liquid medium is known as corrosion.

2) What is pilling bedworth rule?

If the volume of the oxide is greater than the volume of the metal than the oxide film is protective (or) non-porous.

If the volume of the oxide film is less than the volume the metal, then the oxide film is porous and non-protective.

3) Mention the condition for wet corrosion to take place?

i)When two dissimilar metals are in contact with each other in the presence of aqueous solution or moisture, wet or electrochemical corrosion occurs.

ii)When a metal is exposed to an electrolyte with varying amount of oxygen, then also wet corrosion takes place.

4) Write the possible reactions at the cathode of an aqueous corrosion cell?

i)If the environment is acidic, hydrogen is evolved.

$2H^+ + 2e^- \rightarrow H_2$

ii)If the environment is neutral or slightly alkaline, oxygen is absorbed.

$½\ O_2 + H_2O + 2e^- \rightarrow 2OH^-$

5) What is galvanic corrosion?

When two dissimilar metals are electrically connected and exposed to an electrolyte, the metal higher in electrochemical series undergoes corrosion.

6) Distinguish between dry corrosion and wet corrosion.

S.No	Dry or chemical corrosion	Wet or electrochemical corrosion
1	It occurs in dry state.	It occurs in presence of moisture or electrolyte.
2	It involves direct chemical attack of the metal by gases.	It involves setting up of large number of tiny galvanic cells.
3	It follows adsorption mechanism	It follows electrochemical reaction
4	Corrosion products accumulate on the same spot where corrosion occurs.	Corrosion occurs at anode while products gather at cathode.

7) What is meant by rusting of iron?

The atmospheric corrosion of iron & steel, leading to the formation of a layer of reddish scale & powder of iron oxide on the surface is known as rusting.

Its chemical formula is $Fe_2O_3.3H_2O$

8) What type of corrosion would you expect when a lead pipeline is passing through clay to cinders?

Differential aeration corrosion occurs. Since the lead pipeline under cinders is more aerated, it get corroded easily.

9) What is concentration cell corrosion? Give an example.

Concentration cell type of corrosion occurs when a metal is exposed to an electrolyte with varying amount of oxygen.

Ex: pipeline corrosion, pitting corrosion, crevice corrosion

10) What is pitting corrosion?

Pitting is a localized attack which results in the formation of a hole around which the metal is relatively unattacked.

The mechanism of pitting corrosion involves setting up of differential aeration cell.

11) Name the factors which affect corrosion.

i) Air and moisture
ii)Electrolyte in water
iii)presence of impurities in metal
iv)presence of gases like SO_2 and CO_2 in its vicinity
v) presence of strains in the metal
vi) Differential aeration.

12) Corrosion of water filled steel tanks occurs below the water line. Explain.

The area above the water line is highly oxygenated and acts as cathode. The fully immersed part is poorly oxygenated and acts as anode. Hence, the anodic part (below the water line) gets corroded due to electrochemical corrosion. The cathodic part (above the waterline) remains completely unaffected by corrosion.

13) Bolt and nut made of the same metal is preferred in practice. Why?

This is because only such a combination will not permit galvanic corrosion to take place.

14) Explain why zinc is more readily corroded when coupled with copper than with lead.

When two metals are in contact with each other in presence of an electrolyte, the more active metal or metal having negative reduction potential undergoes corrosion.

The extent of corrosion depends on the difference on their position in the emf or electrochemical series. Greater the difference, faster is the corrosion rate. Since, the difference of Zn-Pb couple in the electrochemical series, zinc gets corroded vigorously when coupled with copper than with lead.

15) How does a drop of water, oil or dirt resting on an iron surface lead to corrosion of the metal?

The area covered by a drop of water is less oxygenated and becomes anodic with respect to other areas which are freely exposed to air. This result in setting up of differential aeration cell and corrosion occurs at the less oxygenated part.

16) In electrochemical corrosion, what is the general anodic reaction of a metal, M? what is the cathodic reaction in basic aqueous solution containing dissolved oxygen?

Anodic reaction : $M \rightarrow M^{n+} + ne^-$

Cathodic reaction : $\frac{1}{2} O_2 + H_2O + 2e^- \rightarrow 2OH^-$

17) What is sacrificial anode? How does it protect a submerged pipeline?

In this method, the metallic structure to be protected from corrosion is made cathode by connecting it with more active (anodic) metal. Hence, all the corrosion will concentrate only on the active metal. The parent structure is thus protected.

18) Give the importance of pilling-bedworth rule?

i) The rate of corrosion can be predicted

ii) The protective and non-protective nature of oxide films can be found out.

19) Explain cathodic protection. Mention its two applications.

Cathodic protection is the reduction or prevention of corrosion by making metallic structure as cathode in the electrolytic cell. This can be done by either using sacrificial anode or impressed current method.

They give protection to cables, pipelines, ship hulls.

20) What are corrosion inhibitors? Give examples.

A corrosion inhibitor is a substance which reduces the corrosion of a metal, when it is added to the corrosive environment.

Anodic inhibitors – phosphates, chromates.

Cathodic inhibitors- mercaptans, aniline and its derivatives.

Vapour Phase Inhibitors – Dicyclohexylammonium nitrate.

21) The rate of metallic corrosion increases with increase in temperature. Give reason.

With increase of temperature of the environment, the rate of reaction as well as rate of diffusion of ions increase, thereby corrosion rate increases.

22) Impure metal corrodes faster than pure metal under identical conditions. Give reasons.

Impurities in a metal generally cause heterogeneity, and form minute Electrochemical cells at the exposed parts, whereby the anodic parts get easily corroded.

23) Wire mesh corrodes faster at the joints. Why?

The joints of wire mesh are stressed (due to welding), so these becomes anodic with respect to unjoined wires. At these anodic parts, oxidation takes place and the metal is corroded fast, while the cathodic parts remain unaffected.

24) What is differential aeration corrosion?

When one part of the metal is exposed to a different air concentration from the other part, then poor-oxygenated part becomes anodic and undergoes corrosion, while the highly oxygenated parts (cathodic) remain unaffected by corrosion.

25) Why should Nickel plated steel articles be free from pores and pin holes?

Iron is anodic with respect to Nickel. Presence of pores and pin holes in Nickel plated steel articles expose the anodic metal (steel) to atmosphere at these point. A galvanic cell is set up and an intense localized corrosion at these small exposed parts occurs, thereby resulting in pitting and perforation of the base metals. (steel)

26) Why does a steel pipe in a large copper tank corrode causing rapid destruction?

Iron or steel is anodic with respect to copper. When a steel pipe fitted in a large copper tank is exposed to atmosphere, galvanic corrosion starts and the anodic metal (iron or steel) starts corroding. Moreover, small sized steel pipes (anode) in a large sized copper tank (cathode) causes rapid and intense corrosion (or destruction) of steel pipe.

27) Which of the following metals could provide cathodic protection to iron : Al, Zn, Cu,Ni

Al and Zn

28) Formation of which type of metal oxide film i) causes rapid corrosion ii) prevents corrosion.

i) Volatile oxide film & porous oxide film causes rapid corrosion

ii) Fine grained, tightly adhering, impervious oxide film and highly stable oxide film prevents corrosion.

29) Iron is corroded faster than aluminium even though Fe is placed below Al in electrochemical series. Why?

Al forms a thin, non-porous, tightly protective film of Aluminium oxide on its surface and this film does not allow Al to undergo further corrosion.

30) What is decarburisation?

The process of decrease in carbon content in steel is termed as decarburisation of steel.

31) What is meant by hydrogen embrittlement?

The process of formation of cracks and blisters on the metal surface, due to high pressure of hydrogen gas is called hydrogen embrittlement.

32) What is meant by Impressed current cathodic method?

In this method, current is taken from a direct source (battery) and supplied to an insoluble anode (like graphite,iron,stainless steel) burried in the soil and connected to the metallic structure to be protected. The anode is a backfill and increases the electrical contact with the soil.

33) A steel screw in a brass marine hardware corrodes. Give reasons.

This is due to galvanic corrosion. Iron (higher in series than brass) becomes anodic and is attacked and corroded. Brass which is present lower in series act as cathodic and is not attacked at all.

34) Small anodic area results in intense corrosion. Give reason.

If the anodic area is small, the corrosion is more rapid, intense and highly localized. This is because, the current density at a smaller anodic area is very large and the demand for electrons by the large cathodic area can be met by the small anodic area only by undergoing corrosion more effectively.

35) Explain crevice corrosion with examples.

If a crevice (a crack forming a narrow opening) between metallic and non-metallic material is in contact with a liquid,the crevice becomes anodic region and undergoes corrosion. Hence oxygen supply to the crevice is less. The exposed area has high oxygen supply and acts as cathode.

Ex: Bolts, Nuts

36) What are the factors which influences the corrosion rate of a metal?

- Purity of the metal
- Relative area of electrodes
- Position of the metal in the galvanic series
- Over voltage
- Nature of surface film

37) What are the factors which influences the corrosion rate of a environment?

- Temperature
- Humidity
- pH
- Impurities in the environment
- Presence of suspended particles

38) What is the effect of carbon dioxide on electrochemical corrosion?

Carbon dioxide increases the rate of corrosion. This is because CO_2 gets dissolved in water producing an acidic electrolyte, H_2CO_3.

39) Distinguish between the corrosion of Al & Mg.

Al forms non-porous, tightly adhering oxide film, which stops further corrosion. While Mg forms stable but porous oxide film, thereby more oxygen can diffuse inside the film. Hence, the corrosion in Mg continues.

40) Corrosion of a metal is higher at the metal junction in a galvanic couple. Give reasons.

In metal junctions air cannot easily diffuse. Hence, it is less aerated and becomes cathodic. Thus, the corrosion concentrates at the metal junction in a galvanic couple.

41) State the basic design rules in controlling corrosion?

i)Avoid crevices
ii)Avoid galvanic corrosion
iii)Avoid sharp bends and corners
iv) Provide proper and complete drainage system
v) provide cathodic protection.

42) What is meant by the term passivity?

The phenomenon in which a metal or alloy exhibits a much higher corrosion resistance than expected from the position in the galvanic series is called passivity.

43) Which type of oxide film is more protective against corrosion? Give one example of a metal which produces such an oxide film.

Non porous oxide film.
Aluminium is the metal which produces non porous oxide film.

44) How do the inhibitors resist corrosion?

Anodic inhibitors form a sparingly soluble compound with newly produced metals ions and absorb on the corroding metal and thereby retarding further corrosion of metals.

Cathodic inhibitors retard the rate of corrosion of metal by blocking the active metal sites, participating electrode reaction or by forming a diffusion barrier.

45) Give the principle of electro deposition (or) electroplating.

It is the process by which the coating metal is deposited on the base metal by passing a direct current through an electrolytic solution containing the soluble salt of the coating metal.

46) What do you understand by acid pickling?

It is a method of removing scale from the surface of the metal to be electroplated. It is usually carried out by immersing the metal in acid pickling solution consisting of warm dilute sulphuric acid or cold HCl. This treatment provides clean and smooth surface.

47) What is the principle involved in electroless plating?

It is a process of depositing a noble metal from its salt solution on a catalytically active surface of the metal by using a suitable reducing agent without using electricity.

48) What are advantages of Electroless plating over Electro plating?

i) No electricity is required
ii) Complicated parts can also be plated uniformly
iii) Electroless plating can be carried out on non-metals like glass and plastics.

49) What are the types of corrosion?

Based on the environment, corrosion is classified into,

(i) Dry or Chemical corrosion
(ii) Wet or electrochemical corrosion

50) What are organic inhibitors? What will be the reason for the increase in inhibiting power of aliphatic amines in the following order? $NH_3<RNH_3<R_2NH<R_3N$

Organic inhibitors are the inhibitors forming protective layers on the cathodic part of the metal surface by adsorption. The efficiency of inhibition depends on charge, size and number of alkyl group present in the inhibitor.

Inhibiting power of various aliphatic amines

$$NH_3<RNH_3<R_2NH<R_3N$$

REASON

(i) +ve charge on nitrogen atom increases from left to right due to increase in number of alkyl groups, so it readily attaches to cathodic part.
(ii) Size of amines increase from left to right.

PART-B

1) **What is Corrosion of metals? Explain the mechanism of oxidation.**
2) **What are the factors that affect electrochemical corrosion rate? Discuss.**

3) **a) Differentiate between chemical and electrochemical corrosion.**
   b) Mention any four factors that affect electrochemical corrosion.
4) **Describe the mechanism of electrochemical corrosion by hydrogen evolution and oxygen adsorption.**
5) **Explain waterline corrosion.**
6) **State and explain pilling-Bedworth rule.**
7) **How does galvanic corrosion occur?**
8) **What is sacrificial anode? Mention its role in prevention of corrosion.**
9) **Deposition of oil or dust on metal surfaces for a long period is undesirable. Give reasons.**
10) **Describe the mechanism of differential aeration corrosion taking pitting as example.**
11) **Write short notes on corrosion control by impressed current method.**
12) **What are the corrosion inhibitors? How do they function?**
13) **What are the constituents of a paint? Explain the various functions.**
14) **Describe the mechanism of drying of an oil paint.**
15) **What are the main objectives of electroplating? Give a detailed account?**
16) **Explain the effects of pH, current density and electrolytic composition on the quality of an electrodeposit.**

SRI RAMAKRISHNA INSTITUTE OF TECHNOLOGY

ENGINEERING CHEMISTRY II

FUELS AND COMBUSTION-UNIT III

1) Define a chemical fuel?

A combustible substance containing carbon as the main constituent, which on proper burning liberates large amount of heat, which can be used economically for domestic purposes.

2) What is meant by calorific value of fuel?

It is the total quantity of heat liberated when a unit mass (or volume) of the fuel burnt completely in presence of sufficient quantity of air or oxygen.

3) Distinguish between gross and net calorific value of a fuel?

Gross calorific value is the total quantity of heat liberated, when one unit of fuel has been burnt completely and the products of combustion have been cooled to room temperature. On the other hand, net calorific value is the net heat evolved when one unit fuel is burnt completely and products of combustion are allowed to escape.

4) What is the importance of fixed carbon in coal?

Higher the percentage of fixed carbon, higher is the calorific value and better the quality of coal. Moreover the percentage of fixed carbon helps in designing the furnace and the shape of the fire-box

5) What are the characteristics of a good quality coal?

- Low moisture
- Low volatile matter
- Low ash and
- High fixed carbon content

6) Why coke is preferred than coal in metallurgical processes?

Coke possesses

- Higher strength
- Higher porosity
- Lesser sulphur content

- Low reactivity
- High calorific value

So coke is preferred to coal in metallurgical purposes

7) What is meant by term cracking?

The decomposition of high boiling hydrocarbons of high molecular weight into simpler, low boiling hydrocarbons of low molecular weight.

8) What is synthetic petrol?

The preparation of liquid fuels from solid coal is called synthetic petrol or hydrogenation of coal.

9) What is meant by knocking?

Knocking is a kind of explosion due to rapid pressure rise occurring in an IC engine.

10) What is meant by Octane number of a gasoline?

The octane number is defined as the percentage of isooctane in a mixture of isooctane and n-heptane.

11) What is meant by Cetane number of a gasoline?

The percentage of hexadecane present in a mixture of hexadecane and α-methyl naphthalene, which has the same ignition lag as the fuel under test.

12) Gasoline containing tetra ethyl lead is used in internal combustion engines. Why?

Due to the inherent presence of some constituent in gasoline, its use in internal combustion engine causes knocking, thereby resulting in loss of efficiency. In order to improve efficiency of petrol used in internal combustion engine its octane number is raised by adding tetra ethyl lead. This so called leaded-gasoline possesses less knocking tendency and Improved efficiency as internal combustion fuel. Hence, leaded-gasoline is used in internal combustion engines.

13) Why a good fuel must have low ash content?

Ash is useless, non-combustible matter present in a fuel. It reduces the calorific value and causes hindrance during the flow of air and heat thereby reducing the temperature. Moreover, it often causes trouble during firing by forming clinkers. hence, lower the ash content better quality of fuel.

14) Why is net calorific value less than gross calorific value?

Gross calorific value is the total amount of heat liberated, including latent heat of steam, when one unit of coal is burnt completely. On the other hand net calorific value is the net amount of useful heat liberated, excluding the latent heat of steam, when one unit of fuel is burnt completely. In other words net calorific value is less than gross calorific value by the amount of latent heat of steam formed during the complete combustion of one unit of the fuel.

15) Why are gaseous fuel more advantages than solid fuels?

Gaseous fuels possess advantages over solid fuels

- They can be distributed and transport easily through pipelines
- They can be ignited at moments notice
- Their combustion can be controlled easily
- They burn without producing smoke and ash
- They possess high calorific value
- Their thermal efficiency is high
- They do not affect the quality of metal , when used in metallurgical as fuel etc.,

16) Why is a small quantity of ethyl bromide added to petrol along with ant knocking agent, TEL?

TEL, used to improve the anti-knocking characteristics of an internal combustion engine fuel gets converted into finely divided lead oxide particles which react with knocking causing hydrocarbon peroxides formamide in the cylinder. This in turn decreases the chances of any early detonation. However deposit of these lead oxide particles inside the cylinder is harmful to the engine life. Consequently, a small quantity of ethyl bromide is also added to gasoline and this helps in the simultaneous elimination of lead oxide in the form of volatile lead bromide in the form of volatile lead bromide along with the exhaust gases

17) What is meant by ignition temperature?

The lowest temperature at which the fuel must be preheated so that it starts burning smoothly.

18) What is coal? How it is classified?

Coal is an important primary solid fuel. It has been formed as a result of alteration of vegetable matter under some favourable conditions. The process of conversion of coal is called coalification or metamorphism of coal.

Various types of coal are-

Wood →Peat→Lignite→Bituminous coal→Anthracite

19) Distinguish between proximate and ultimate analysis of coal

SNo	Proximate Analysis	Ultimate Analysis
1	It involves the determination of weight percentage of moisture, volatile matter, fixed carbon and ash in coal	It involves the determination of weight percentage of Carbon, Hydrogen, Sulphur and oxygen of the pure coal free from moisture and inorganic constituents.
2	It gives the approximate composition of the main constituents of coal.	It gives the elementary constituents

20) What are the drawbacks of presence of sulphur in coal?

The presence of sulphur in coal is undesirable because

i) The combustion product of coal is harmful and has the corrosion effects on equipments.

ii) During the combustion of sulphur in coal, produces harmful gases like sulphur dioxide, sulphur trioxide and they cause air pollution.

21) What is meant by hydrogenation of coal?

The preparation of liquid fuels from solid coal is called synthetic petrol or hydrogenation of coal.

22) What is meant by carborisation? How it is classified?

When coal is heated strongly in the absence of air known as destructive distillation, it is converted into lustrous, dense, porous and coherent mass known as coke. This process of conversion of coal to coke is called carbonization.

Carbonization is classified into the following two types on the basis of temperature.

- Low temperature carbonisation (LTC) 500-700^{o}C
- High temperature carbonisation (HJTC) 900-1200^{0}C

23) Give the characteristics of metallurgical coke.

- Purity: Low moisture and ash content are desirable for metallurgical coke. It must contain minimum percentage of sulphur and phosphorus.
- Porosity: High porosity id\s desirable to obtain high rate of combustion.
- Strength: The coke should be hard and strong.
- Calorific value: The calorific value of coke is high.

24) Define LPG. What are its uses?

- It is used as domestic and industrial fuel.
- It is also used as a motor fuel.

25) What is meant by refining of petroleum?

The process of removing impurities and separating the crude oil into various fractions having different boiling points is called refining of petroleum.

26) How will you improve the octane number?

Octane number of petrol is improved by adding additives like tetraethyl lead.

27) What is leaded petrol? Mention its advantages and disadvantages.

When tetraethyl lead is added to petrol, it is called leaded petrol. Leaded petrol prevents knocking in engines. Leaded petrol when used in engines produces lead bromide which pollutes atmosphere.

28) Why should the leaded petrol not be used?

- Lead deposits on the spark plug and on cylinder walls which is harmful to engines.
- This creates atmospheric pollution due to the formation of lead bromide.

29) How cetane number be improved?

It can be increased by adding certain additives called dopes.

Example: Ethyl nitrate, Isoamyl nitrate.

30) Distinguish between petrol and diesel.

S.No	Petrol	Diesel

1	It is the low boiling fraction of petroleum	It is the high boiling fraction of petroleum.
2	It contains C_5-C_9 hydrocarbons.	It contains C_{15}-C_{18} hydrocarbons.
3	It is used as fuel for spark ignition engine.	It is used as fuel for compression ignition engine
4	Knocking is due to premature ignition and is measured by octane number.	Knocking is due to ignition delay and is measured by cetane number.
5	Anti knocking is improved by the addition of TEL.	Anti knocking is improved by addition of dopes.

31) What is water gas? What are its composition and uses?

Water gas is essentially a mixture of CO and H_2. The average composition of water gas is as follows

S.No	Constituents	Percentage
1	H_2	51
2	CO	41
3	N_2	4
4	CO_2+CH_4	4

Water gas has high calorific value than producer gas.

- Water gas is a good source of hydrogen. Hence, it is use in Haber's process to produce ammonia.
- Since water gas contains 51% H_2, it can be used as reducing agent in metallurgical industries.

32) What is producer gas? What are its composition and uses?

Producer gas is a mixture of CO and N_2 with small amount of H_2. The average composition of producer gas is as follows

S.No	Constituents	Percentage
1	H_2	10
2	CO	30
3	N_2	50
4	CO_2+CH_4	rest

The calorific value of producer gas is 1800 kcal/m^3.

- It is cheap, clean and easily producible gas and is used for heating open-hearth and muffle furnaces.
- It can be used as reducing agent in metallurgical industries.

33) What is compressed natural gas (CNG)?

When natural gas is compressed, it is called compressed natural gas. It is derived from natural gas. Hence the primary component of CNG is methane.

34) Mention the properties of CNG.

- CNG is expected to be less polluting.
- It is lighter than air.
- CNG requires a much higher ignition temperature of 540^0C.
- It has low inflammability.

35) Select the compound which possesses highest octane number and highest cetane number out of n-heptane, n-hexadecane, n-octane and iso-octane.

Highest octane number- iso-octane.

Highest cetane number- n-hexadecane

36) Differentiate between thermal cracking and catalytic cracking.

When cracking is carried out higher temperature and pressure without any catalyst, it is known as thermal cracking.

When cracking is carried out at lowest temperature and pressure in the presence of suitable catalyst, it is known as catalytic cracking.

37) What is Cottrell's process in crude oil refining?

The crude oil from oil well is an extremely stable emulsion of oil and salt water. The crude oil is allowed to flow between two highly charged electrodes, where colloidal water droplets combine to form large drops, which is then separated out from the oil.

38) In catalytic cracking process, catalyst requires regeneration. Give reason.

The catalyst loses its activity due to deposition of carbon. Therefore it is reactivated by burning off the deposited carbon.

39) Name the reagents used for adsorbing Carbondioxide, Carbon monoxide and oxygen during flue gas analysis by orsat apparatus.

CO_2- KOH solution

CO – Ammoniacal cuprous chloride solution

O_2 – Alkaline pyrogallol solution

40) Mention the uses/ significance of flue gas analysis.

- It gives an idea about the complete or incomplete combustion
- The presence of high percentage of CO in the flue gas shows incomplete oxidation of the fuel and also indicates the short supply of oxygen.

41) Write the various units of calorific values.

- Calorie
- Kilocalorie
- British thermal Unit
- Centigrade Heat unit

PART B

1) **How are fuels classified? Give the advantages of gaseous fuels over other forms of fuel.**
2) **Describe the proximate and ultimate analysis of coal and its significance.**
3) **How is metallurgical coke manufactured? What are their special properties and uses?**
4) **What is meant by crude petroleum? Discuss the principle steps in the refining of crude petroleum.**
5) **How synthetic petrol is obtained by Fischer Tropsch process?**

6) **How will you obtain synthetic petrol by Bergius process?**
7) **Describe the Otto Hoffmann method of coke manufacture.**
8) **How is producer gas manufactured? State its composition and uses.**
9) **How the flue gas analysis is carried out with neat diagram?**
10) **What are LPG and CNG? Discuss the advantage of LPG over gaseous fuel and CNG over LPG.**
11) **Explain the physico chemical methods involved in the manufacture of water gas.**
12) **Explain the fixed bed catalytic cracking for the manufacture of gasoline.**
13) **Give a brief account of refining of petroleum and the products obtained and their uses.**

SRI RAMAKRISHNA INSTITUTE OF TECHNOLOGY,CBE -10

ENGINEERING CHEMISTRY-II

PHASE RULE AND ALLOYS-UNIT IV

1. State phase rule.

The phase rule is a generalization which explains the heterogeneous equilibria. Mathematically it is stated as F = C-P+2 where,

P = the number of phases present in equilibrium.

C = the number of components of the system.

F = the number of degrees of freedom for the equilibrium,

2.Define phase (P).

A phase is defined as any homogeneous and physically distinct part of a system which is mechanically separable from other parts of the system by a boundary surfaces. A phase may be a gas, liquid or solid.

3.Define component. (C).

Component is defined as, "the smallest number of independently variable constituents, by means of which the composition of each phase can be expressed in the form of a chemical equation".

4. Define degree of freedom. (F)

Degree of freedom is defined as,"the minimum number of independent variable factors such as pressure, temperature and concentration, which must be fixed in order to define the system completely.

5. How many phases and components are present in the system,

$CaC0_3(s) \dashrightarrow CaO(s) + C0_2(g)$?

The system consists of two solid phases and one gaseous phase.

Hence, P=3. It is a two component system only as per the definition.:.P=3,C=2

6. $NH_4C1(s) \leftrightarrow NH_3(g)+HCI(g)$"Write the values of P, F and C for this system.

The system consists of two phases. P=2 and is a one component system. C= I.

F = C-P+2 = 1-2+2 = I

7. What is phase diagram?

A phase diagram is a graph obtained by plotting one degree of freedom against another.

8. Mention the uses of studying phase diagram.

They help in studying and controlling the various processes such as phase separation, Solidification of metals, change of structure during heat treatment.

9. Mention the merits of phase rule.
(i) The phase rule takes no account of the nature or amount of substances.
(ii) It gives information about the behavior of systems when theyare subjected to changes in variables like temperature, pressure, concentration.

10. What are the limitations of phase rule?
(i) The phase rule takes into account only the variables like temperature, pressure and concentration. The influence of factors such as electric, magnetic, gravitational forces etc. are ignored.
(ii) The phase rule is applicable only to heterogeneous system in equilibrium.

11. What is "the effect of pressure on the melting point of ice?
The melting point of ice decreases with increase of pressure.

12. What is a triple point?
It is the point at which all the three phases (solid,liquid,gas) are present simultaneously in equilibrium.

13. Is it possible to have a quadruple point in phase diagram component system?
Quadruple point means, 4 phases are present.

P =4; C = 1;
F = C - P + 2 = 1 - 4 + 2 =-1
Since, the degree of freedom, F =-1, it is not possible.

14. How many phases, components and degrees of freedom are present in
(i) Water at 0.0075°C and 4.58 mm Hg.
(ll) Water ↔ Water vapour at 30° C.
(i) Water at 0.0075^{O}C and 4.58 mm Hg indicates the triple point of water system. Here, P=3; C= 1.
F = C-P+2 = 1 - 3 + 2 = 0
(ii) Water ↔ Water vapour at 30°C.
Here, P =2 ; C =1 F =C - P + 2 = I - 2 + 2 =1

15. In the phase diagram of water, point out the phase in equilibrium with
(i) F=I and (ll) F=O.
(i) F=I ; C=1 P = C - F + 2 =1 - 1+ 2 = 2
Two phases should be in equilibrium. It may be anyone of the following:
(a) ice ↔ water;
(b) ice ↔ water vapour.
(c) water ↔ water vapour
(ii) F=O;C=1 P = 0-F+2 = 1-0+2 =3
All the three phases are present simultaneously in equilibrium(triple point).
ice↔ water↔ water vapour

16. State reduced phase rule.
A solid-liquid equilibrium of an alloy has no gaseous phase. Hence,the effect of pressure is negligible on this type of equilibrium. Hence, to construct the usual phase diagram with two axis, the vapour phase is neglected. Such solid-liquid system is called condensed system. In

condensed system, measurements are made at constant pressure. This reduces the degree of freedom of the system by one. Thus, the phase rule equation for two component alloy system is written as, F = C - P + 1. This equation is known as reduced or condensed phase rule equation.

17. Define eutectic point.
It is the point at which two solid and one liquid phases are in equilibrium.

18. What is eutectic temperature?
It is the lowest possible temperature at which a mixture of two solids simultaneously melts.

19. Write the differences among melting point, triple point and eutectic point.
* At the melting point, a solid and a liquid having the same composition are in equilibrium.
* At the triple point, three phases are in equilibrium.
* At the eutectic point, two solids and a liquid are in equilibrium

20. State the conditions under which two substances can form a simple eutectic.
(i) They must be completely miscible in the liquid state, but completely immiscible in the solid State.
(ii) They should not chemically react with each other.

21. Eutectic is a mixture and not a compound. Explain.
Eutectic is an unique mixture of two solids which has the lowest melting point. Since it is completely immiscible in the solid state, it is a mixture and not a compound.

22. Mention the uses of eutectic mixture.
(i) It is used in preparing solder (an alloy of Pb-Sn)
(ii) Desilverisation (Pattinson process) of lead is based on the formation of eutectic mixture.

23. What is an eutectic alloy?
It is an unique composition of two solids which has the lowest melting point when compared to the melting point of two solids. Since, it has the same composition both in liquid and solid states, it behaves like a pure solid substance.

24. How are the two component systems classified?
Based on mutual solubility and reactive ability, the two component system is classified into the following three types -
(i) Simple eutectic formation.
(ii) (a) Formation of compound with congruent melting point.
(b) Formation of compound with incongruent melting point.
(iii) Solid solution formation.

25) Calculate the number of phases present in the following systems.

a) $MgCO_{3(s)} \rightarrow MgO_{(s)} + CO_2$ three phases

b) Rhombic sulphur$_{(s)}$ → Monoclinic sulphur$_{(s)}$ two phases

c) Ice$_{(s)}$ → water$_{(l)}$ → water vapour$_{(g)}$ three phases

d) An emulsion of oil in water two phases

26) Comment on the degree of freedom.

The degree of freedom of the system can have values 0 1 2 3 etc

If the degree of freedom of the system is Zero it is nonvarient or

.. invariant system One it is monovarient or univarient system

Two it is bivarient system

27) How many components are present in the following system.

$KCl + H_2o \rightarrow KCl. H_2o$

Two

28) Discuss the significance of triple point.

A triple point is invariant .For a given substance, the triple point occurs at a unique Set of values of the temperature and pressure. If either temperature or pressure (Volume) is altered even slightly , one of the three phases disappears and the system changes from invariant (F= 0) to univariant (F=1).

29) What is metastable equilibrium?

Sometimes water can be cooled below 0^0C without the formation of ice . This Water is called super cooled water. The equilibrium between super cooled water and the vapour is known as metastable equilibrium. In the phase diagram of water system, the curve OA, represents it.

30) What is an invariant system? Give an example.

The system which has degree of freedom as zero is called invariant system. It means that no condition is required to be specified to define the system.

Example:A system consisting of ice, water and water vapour in equilibrium as F=C-P+2=1-3+2=0.

31) What is the value of triple point of water system?

When water System is at 0.0075^0C and 4.58 mm Hg pressure, it is called triple point.

32) In the phase diagram of water,the melting curve is almost a straight line and it Slopes slightly backwards. Does an increase in pressure increases or decrease the melting point point of ice?

The melting point of ice decrease,(i.e)., an increase in pressure turns ice into water.

33) State the number of degrees of freedom for the following systems:

a) $PCl_{5(s)} \rightarrow PCl_{3(g)}+Cl_{2(g)}$

b)$CaCO_3(s) \rightarrow CaO_{(s)}+CO_{2(g)}$

Ans

a) F=C-P+1; 2-3+1=1
b) F=C-P+1; 2-3+1=1

34) A System consist of benzene and water. What is the number of phases?

Two liquid phases and one vapour phases.

35) What are types of phase diagram?

i) P-T diagram

If the diagram is plotted between temperature against pressure, the diagram is called P-T diagram.P-T diagram is used for one-component system.

ii)T-C diagram

If the diagram is plotted between temperature against composition, the diagram is called T-C diagram. T-C diagram is used for two component system.

36) Mention any two advantages of alloy making.

- To increase the hardness of the metal.
- To resist the corrosion of the metal.

37) What is meant by quenching in heat treatment of metals?

It is the process of heating steel beyond the critical temperature and then cooling suddenly in oil or brine water or some other fluid.

38) What is the use of studying phase diagram?

From the phase diagram, it is possible to predict whether an eutectic alloy or solid solution is formed on cooling a homogeneous liquid containing mixture of two metals.

39) Define an alloy.

Alloys are the homogeneous mixture of a metal with metal, metal with non metal, metal with metal and non metal.

40) What is the basic difference between brass and bronze?

Brass is an alloy of copper and zinc while bronze is an alloy of copper and tin.

41)What is meant by 18/8 stainless steel?

Stainless steel having 18% Cr and 8% Ni is known as 18/8 stainless steel.

42)Write the chemical composition of Dutch metal and Gun metal.

Dutch metal : Cu= 80% Zn=20%

Gun metal: Cu= 85% Zn=20% Sn=8% Pb=3%

43) Distinguish between annealing and hardening.

S.No	Annealing	Hardening
1.	Involves heating a metal to High temperature followed by slow cooling.	Involves heating a metal to high temperature and then sudden cooling

2.	Cooling is carried out in a furnace itself.	Cooling is carried out in oil or brine water.
3.	It increases the machinability.	it increases hardness of steel.

44) What is meant by annealing of steel?

Annealing means softening. This is done by heating the metal to high temperature, followed by slow cooling in a furnace.

45) What is meant by galvanizing?

The process of coating molten zinc over the base metal is known as galvanizing.

46)What is the effect of increasing carbon content in steel?

Increase in carbon content up to 0 .83% increases its strength and hardness, but beyond 0.83% there is decrease in strength, increase in hardness of steel.

PART B

1) **State the phase rule. Explain the terms involved in it with suitable examples.**
2) **Draw and explain the phase diagram of ice, water, vapour system. How the melting point of ice change with variation of pressure?**
3) **What is condensed phase rule? What is the number of degree of freedom at the eutectic point for a two component system?**
4) **Why is condensed phase rule used for the two component system?**
5) **Discuss in detail about lead-silver system.**
6) **Write briefly about Pattinsons process.**
7) **Draw the phase diagram of simple eutectic A-B system with the following data and discuss. Melting point of A 961^0C, Melting point of B 327^0 C , Eutectic temperature 303^0 C , Eutectic composition 2.6%**
8) **What is thermal analysis? Draw the cooling curves of a pure substance and a mixture and discuss.**
9) **What is meant by phase diagram? With the help of phase diagram explain the following terms i) Triple point ii)Eutectic point.**
10) **State the phase rule and discuss its application to Ag-Pb system.**
11) **Define the term alloy and bring out the effect of alloying of metals with example.**
12) **What are non ferrous alloys? Give their properties.**
13) **a) Write a note on Nickel alloys**
    b)What are the main purpose of alloying steel?
14) **Discuss different heat treatment methods and their effects on alloys.**

SRI RAMAKRISHNA INSTITUTE OF TECHNOLOGY,CBE -10

ENGINEERING CHEMISTRY-II

ANALYTICAL TECHNIQUES - UNIT V

1) What is meant by monochromatic radiation?

A monochromatic radiation is a narrow beam of light which belong to a specific wavelength range of light. It is produced by a special arrangement known as monochromator.

2) Mention the important region of electromagnetic radiations and their wavelengths

X- rays	:10^{-2}-10^{2} Å
Far UV region	:10-200 nm
Near UV region	: 200-400 nm
Visible	:400-750 nm
Near IR region	: 0.75-2.5 µm
Mid IR region	: 2.5 -50µm
Far IR region	: 50-1000µm
Microwaves	:0.1-100 cm
Radio waves	: 1-1000cm

3) Explain the terms "atomic and molecular spectroscopy"?

In "atomic spectroscopy", the interaction of electromagnetic radiation with atoms which are in the lowest energy state which makes them to shift to the excited state. In "molecular spectroscopy" the interaction of electromagnetic radiation with molecules are in their lower energy state that makes them to shift to the excited higher energy state.

4) Explain electronic transition?

When ultra violet or visible radiation are allowed to pass through a sample under study containing mono atomic particles, very few well defined frequencies are removed as a result of absorption. This is mainly due to the excitation of electrons to higher energy states and when the excited atom revert back to the ground state, it emits radiation in one step or in several steps in the form of photons of electromagnetic radiation. This can be recorded as spectral lines or very narrow peaks.

5) What is Born-Oppenheimer approximation?

According to Born-Oppenheimer approximation, the total energy of molecule is given by

$$E_{int} = E_{tr} + E_{rot} + E_{vib} + E_{ele} \quad \text{----------(1)}$$

Where, E_{tr} , E_{rot} , E_{vib} , E_{ele} are translational energy, rotational energy, vibrational energy and electronic energies respectively. Its order of energy is

$$E_{ele} > E_{vib} > E_{rot} > E_{tran}$$

Since E_{tra} is negligibly small equation (1) becomes

$$E_{int} = E_{rot} + E_{vib} + E_{ele}$$

6) State Beer- Lambert's law?

According to this law, " when a beam of monochromatic light radiation is passed through a solution of an absorbing substances, the rate of decrease of intensity of radiation 'dI' with thickness of the absorbing solution 'dX' is proportional to the intensity of incident radiation 'I' as well as the concentration of the solution 'C'.

It is mathematically represented as

$$-dI/dX = k I C$$

7) What are the factors, which affect the absorbance of the photons by a molecule?

The fractions of photons being absorbed by the matter depends on,

- The nature of the absorbing molecules
- The concentration of the molecules. If the concentration of the molecule are more, the absorbed photons will be more
- The length of the path of radiation through the matter. If the length of the path is long, the larger number of molecules are exposed and hence greater the photons will be absorbed.

8) What are the disadvantages of Beer-Lambert's law?

- ❖ Beer-Lambert's law is not obeyed if the radiation used is not monochromatic
- ❖ It is applicable only for dilute solutions
- ❖ The temperature of the system should not be allowed to a large extent

9) What is the relation between wavelength, frequency and wavenumber?

$$1/\lambda = \bar{\nu} = \nu / C$$

10) Name the transitions that is responsible for molecular spectra?

The molecular spectra arises from three types of transitions, namely

- ❖ Rotational transition
- ❖ Vibrational transition
- ❖ Electronic transition

11) What is meant by the term 'absorption spectroscopy'?

When a beam of electromagnetic radiation is allowed to fall on a molecule in the ground state, the molecule absorbs photon of energy hv and undergoes a transition from the lower energy level to the higher energy level. The measurement of this decrease in the intensity of radiation is the basis of absorption spectroscopy. The spectrum thus obtained is called the absorption spectrum.

12) What is meant by the term 'emission spectroscopy'?

If the molecule comes down from the excited state to the ground state with the emission of photons of energy hv, the spectrum obtained is called emission spectroscopy

13) What is colorimeter?

Colorimetry is concerned with the visible region (450-750 nm) of the spectrum. The instrument, used for measuring absorption of radiant energy in the visible region from the substances is called colorimeter

14) Mention the few application of colorimetry?

- ❖ Molar composition of complexes can be determined
- ❖ The instability constant of complexes are also determined
- ❖ Dissociation constants of an acid-base indicator can also be determined
- ❖ Structure of inorganic compounds, complexes can be determined
- ❖ Molecular weight of a compound can also be determined.

15) Write the complexes formed in the spectrometric determination of Fe and Ni ?

$$Fe^{3+} + 6KCNS \rightarrow [Fe(CNS)]^{3-} + 6K^{+}$$

Red colour complex

$$Ni^{3+} + DMG \rightarrow \text{Scarlet red colour complex}$$

16) What are the important processes that occur in the flame of flame emission spectroscopy?

- ❖ It should evaporate the solvent from the sample solution
- ❖ It should decompose the solid into atoms

- ❖ It should excite the atoms and cause them to emit radiant energy

17) What are the limitations of flame photometry?

- ➢ It cannot be used for the determination of all metal atoms and inert gases
- ➢ Only liquid samples must be used
- ➢ It does not provide information about the molecular form of the metal present in the original sample.

18) Name the important components of UV spectroscopy?

- Light source
- Monochromators
- Sample cell and reference cell
- Detectors
- Recorder

19) What are the types of transitions involved in organic molecules?

- $n \rightarrow \pi^*$ transitions
- $\sigma \rightarrow \sigma^*$ transitions
- $n \rightarrow \sigma^*$ transitions
- $\pi \rightarrow \pi^*$ transitions

20) Define the term bathochromic shift?

Shifting of absorption to a longer wavelength is called bathochromic shift or red shift.

21) What are chromophores ? Give some examples

The presence of one or more unsaturated linkages (π- electrons) in a compound is responsible for the colour of the compound, these linkages are referred to as chromophores.

Example: C=C, -C≡C- , -C≡ N-, -N=N-, C=O, ;etc

22) What are auxochromes? Give some examples

It refers to an atom or a group of atoms which does not give rise to absorption band on its own, but when conjugate with chromophore will cause red shift

example: -OH ,-NH_2, -Cl, -Br, -I, etc

23) How are IR range subdivided?

- Near IR region : 12500-4000cm^{-1}
- IR region : 4000-667cm^{-1}
- Far region : 667-50cm^{-1}

24) How to find out number of vibrational modes of a molecule?

- For non-linear molecule

A non-linear molecule containing 'n' atoms has (3n-6) fundamental vibrational modes

Examples:

$CH_4 \rightarrow$ (3x5-6) = 9 fundamental vibrational modes

$C_6H_6 \rightarrow$ (3x12-6) = 30 fundamental vibrational modes

- For linear molecule

A linear molecule containing 'n' atoms has (3n-5) fundamental vibrational modes

Examples:

$CO_2 \rightarrow$ (3x3-5) = 4 fundamental vibrational modes

25) What is finger print region? Mention its important uses?

The vibrational spectral region at 1400-700 cm^{-1} gives very rich and intense absorption bands. This region is termed as finger print region.

It can be used to detect the presence of functional group and also to identify the compounds

26) What is inter and intra molecular hydrogen bonding? Give an example

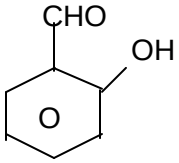
The hydrogen bond formed between the two molecules is intermolecular hydrogen bonding

Example: R-O-H -----O-H
|
R

Intermolecular hydrogen bond formed between alcohols

The hydrogen bond formed within the same molecule is intramolecular hydrogen bonding

Example:



Salicyaldehyde is an example for intramolecular hydrogen bonding, a bond is formed with in the molecule.

27) Mention any two applications of UV spectroscopy.

(i) Molecular weight can be determined

(ii) Calcium in blood serum can be determined.

(iii) Dissociation constants of acid and bases can be calculated.

(iv) Kinetics of chemical reactions can be studied.

28) State the principle involved in the colorimetric analysis.

The principle involved in the colorimetric analysis is based on the intensity of the coloured solutions. The intensity of the colour can be easily measured by using a photoelectric colorimeter from which the concentration of coloured solution can be obtained by using Beer-Lamberts law.

29) What are the difference between molecular spectra and atomic spectra?

Atomic Spectra	Molecular spectra
It is due to the interaction of atoms with electromagnetic radiation	It is due to the interaction of molecules with electromagnetic radiation
They are line spectra	They are complicated, band spectra
It is due to electronic transition from one level to other in atoms.	It is due to vibration, rotational and electronic transition in a molecule.

30) What happens to a molecule when it is irradiated with

a) IR light b) Microwave radiation?

IR light causes both vibrational and rotational transitions.

Microwave radiations cause rotational transitions.

31) What are the sources of UV light in UV-Visible spectrophotometer?

Hydrogen discharge or deuterium lamps, mercury lamp, quartz capillary are the sources of UV llight.

32) What are the factors that influence the intensity of spectral lines?

1) Collision broadening 2) Boltzmann population

3) Doppler broadening 4) transition probability

33) What is flame photometer? Name few metals which can be easily detected by this method.

Flame photometry is a method in which the intensity of the emitted light is measured when an atomized metal is introduced into the flame.

Most of the alkali metals (Li,Na,K) and alkaline earth metals (Ca, Sr,Ba) can be detected and determined using flame photometry.

34) Outline the applications of IR Spectroscopy.

- IR spectra can be used to determine the nature, structure, molecular weight of compounds.
- Type of H-bonding can be ascertained using IR.
- Purity of a sample can be confirmed using IR
- Progress of a reaction can be studied.
- Diplole moment, force constant and bond strength can be calculated.

35) State the selection rules of IR Spectroscopy.

- Molecules must have permanent dipole moment.
- The transitions are restricted to adjacent levels only.

36) Methane does not absorb IR energy. Why?

This is because the four hydrogen atoms of methane vibrate symmetrically.

37) Name the interferences that we come across in flame photometry.

- Spectral interferences
- Ionic interferences
- Cation-Anion interferences
- Cation-Cation interferences

38) Filters are invariably used in absorption spectroscopy.Why?

A given type of species absorbs light at a particular wavelength. So in absorption spectroscopy, a number of filters are provided for the proper choice of the wavelength at which the given species absorbs maximum light.

39) Express the wavelength $1A^0$ in different units.

$1A^0=1\times10^{-8}$ cm= 1×10^{-10} m=100 ppm=0.1 µm

40) What are i) one quantum ii) one Einstein?

The energy absorbed by one molecule is called one quantum and is calculated using **$E=h\nu$.**

The energy absorbed by one mole is called one Einstein and is calculated using **$E=Nh\nu$.**

41) What are the common features in absorption instruments?

The common features of all absorption instruments are the following

1) Source

2) Analyzing device
3) Detector
4) Recorder

42) How are alkali and alkaline earth metals detected in flame photometry?

The alkali and alkaline earth metals detected from the colour of the flame as given in the following table

S.No	Metal	Wavelength(nm)	Colour of the flame
1	Lithium	670	Scarlet red
2	Sodium	586	Yellow
3	Potassium	404	Red
4	Calcim	423	Brick red
5	Strontium	461	Crimson red

43) Distinguish between atomic absorption spectroscopy and flame photometry.

S.No	**Atomic absorption spectroscopy**	**Flame photometry.**
1	It is an absorption spectroscopy	It is an emission spectroscopy
2	Absorption of radiaton by the ground state gaseous atoms is measured.	Emission of radiation by the excited state gaseous atoms is measured.
3	Absorption is proportional to the concentration of atoms.	Intensity of the emitted colour is proportional to the concentration of atoms.

44) ASolution shows a transmission of 20% when taken in a cell of 2.5 cm thickness. Calculate its concentration if the molar absorption co-efficient is 12,000 dm3 mol-1 cm-1

%t=20% T=0.20 x=2.5 €=12,000 dm3 mol-1 cm-1

A=-logT=-log 0.20=0.699

We know that A=€Cx

C=A/€x

=0.669/12000×2.5

=2.33×10^{-5} mol dm^{-3}

PART B

1) What is the relation between wavelength, frequency and wave number?

2) Explain i) Atomic spectra ii) Molecular spectra

3) Derive Beer-Lamberts law and write all the limitations absorbed in the quantitative analysis

4) Explain briefly colorimetry with neat diagram.

6) How will you estimate the concentration of a solution by colorimetry.

7) Draw the block diagram of atomic absorption spectrophotometer and explain its working.

8) a) What are the differences between chromophore and auxochrome?

b) What are Red Shift and blue shift.

9) Mention the application of UV spectroscopy.

10) a) What is IR Spectroscopy? Explain the different regions of IR.

b) What are the principles and selection rules of IR spectroscopy?

11) What are the applications of IR in different fields?

12) Mention the factors which influence intensity of the spectral lines.