QP CODE: 26212

3 Hours **(Total marks: 80)**

N.B. 1. All questions are compulsory
2. Figures to right indicate full marks.
3. Draw neat labelled diagrams wherever necessary.
4. Attempt answer of each main question on new page.

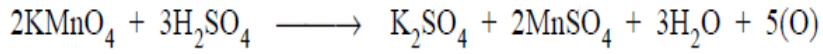
Q.1 A. Explain the terms: **(8)**

i. Cerimetry : **CERIC SULPHATE TITRATION METHODS:**

- Ammonium ceric sulphate serves as a powerful oxidizing agent in an acidic medium.

ii. Permanganometry:

- The vital application of potassium permanganate as a potential oxidizing agent in an acidic medium



Permanganate Methods :
(a) Direct Titration Methods,
(b) Indirect Titration Methods, and
(c) Residual Titration Methods.

iii. Overvoltage:

- ☐ The electrochemical cell is polarized if its actual potential is different than that expected according to Nernst equation.
- ☐ In electrochemistry, overpotential is the potential difference (voltage) between a half reaction's themodynamically determined reduction potential and the potential at which the redox event(oxidation or reduction) is experimentally observed/determined.
- ☐ The extent of polarization is measured **as overpotential** η
- ☐ $\eta = E_{applied} - E_{reversible(equilib)}$

iv. Electrogravimetry:
Electrogravimetry is a method that uses electrolysis to plate out the analyte on a tared electrode, and weighing the electrode to obtain the mass of material deposited.

It is dynamic electrochemical method of analysis.

- ☐ **Electrogravimetry** is a method used to separate and quantify ions of a substance, usually a metal.
- ☐ In this process, the analyte solution is electrolyzed.
- ☐ Electrochemical reduction causes the analyte to be deposited on the cathode.
- ☐ The cathode is weighed before and after the experiment, and weighing by difference is used to calculate the amount of analyte in the original solution.
- ☐ Controlling the potential of the electrode is important to ensure that only the

metal being analyzed will be deposited on the electrode.

- ☐ The process is similar to electroplating

v. Ostwald's ripening:

In Digestion of the precipitate, the precipitate is left hot (below boiling) for 30 min to 1 hour in order for the particles to be digested. Digestion involves dissolution of small particles and reprecipitation on larger ones resulting in particle growth and better precipitate characteristics. This process is called **Ostwald ripening.**

The small particles of a crystalline precipitate e.g. $BaSO_4$, being more soluble than the bigger ones, dissolves readily, making the solution supersaturated with respect to larger particles.to establish equilibrium with respect to larger particles, some material should leave the solution and enter in to the larger precipitate. The ions from the solution then deposit on the bigger particles of precipitate causing these to grow further i.e., the bigger particles grow further at the expense of the smaller ones. This process is called Ostwald ripening.

Ostwald ripening is useful for increasing the particle size of some crystalline precipitates such as $BaSO_4$ and CaC_2O_4.

vi. Sequestering agent:
Complexone/ chelating agent/ligand which forms water soluble complex is called sequestering agent.
e.g. EDTA

vii. Molality (m):
Number of moles of solute per kg of solvent.
A molal solution contains 1gram molecule in 1000g of solvent.
Molality is not temperature dependant.

viii. Primary standard:

- It is a substance of highest purity (99.99 -100% purity.)
- It is used for preparing standard solution (titrants) .
- It should be stable at drying temperature, non hygroscopic, nor easily oxidisable, nor affected by CO_2.
- It should be readily available.
- To be used in titration, it should posses properties required for a titration.

e.g.
1. Acid-base titration: anhydrous sodium carbonate (for acidic titrants), potassium hydrogen phthalate , benzoic acid, oxalic acid
2. Complometry: pure zinc, granulated.
3. Precipitation titration: sodium chloride, silver nitrate
4. Redox titrations: POTASSIUM CHROMATE, arsenic trioxide, sodium oxalate, potassium iodate, potassium bromated, sodium thiosulphate, oxalic acid.

B. Answer the following questions: **(12)**

i. Balance following half cell reactions-

$MnO_4^- + Fe^{2+} \rightarrow Mn^{2+} + Fe^{3+}$

$MnO_4^- + 8H + 5e \longrightarrow Mn^{2+}$

$Fe^{2+} \longrightarrow Fe^{3+} + e^-$

$MnO_4^- + Fe^{2+} + 8H + 4e^- \rightarrow Mn^{2+} + Fe^{3+} + 4H_2O$

ii. How will you prepare 350ml solution of 0.95 N HCl from given one litre of 1.47N solution.

Data:

N_1=Strength of stock solution = 1.47N

V_1 = Volume of stock solution to be diluted = ---------mL

N_2=Strength of dilute solution= 0.95N

V_2 = desired Volume of dilute solution = 350 mL

$N_{1*} V_1 = N_{2*} V_2$

$1.47N * V_1 = 0.95N * 350Ml$

$V1 = 332.5 / 1.47$

$V1 = 226.19$ Ml.

Therefore , 226.19 Ml of stock solution (1.47N HCl) should be diluted with distilled water to make 350 mL of 0.95 N HCl.

iii. Give reasons:

a. Mohr' determination is carried out within a pH range of 6.5 to 9: because in acidic condition chromic acid is formed and in alkaline conditions AgOH is formed.

b. Mohr's method is not suitable for determination of iodides (I^-) and thiocyanates (SCN^-): because when iodides (I^-) and thiocyanates (SCN^-) ions react with Ag+ ions, AgI and AgSCN are formed respectively, which strongly adsorbs chromate ions (indicator ions) and false end point is obtained.

iv. Calculate how much quantity of substance will remain in aqueous phase, if a single extraction of 1g solute having partition coefficient K=7 between chloroform and water is carried out with equal volumes (20ml) of each solvents.

Data:

Quantity of solute= 1g

Volume of solvents= 20 ml

K= 7

-→
(Concentration in chloroform/concentration in water)= k

Since k=7
Therefore,

$$\frac{\text{Concentration in chloroform}}{\text{concentration in water}} = K = \frac{7}{1}$$

then if x g dissolves and extracted in the chloroform

$$\frac{(X/20)}{\{(1-X)/20\}} = \frac{7}{1}$$

$$\frac{(X)}{(1-X)} = \frac{7}{1}$$

Therefore,
X = 7(1-X)

X = 7-7X

8x= 7

X= 8/7

X= 0.875

Therefore,
The quantity of substance remaining in aqueous phase after extraction = total quantity – quantity extracted

The quantity of substance remaining in aqueous phase after extraction = 1g – xg

The quantity of substance remaining in aqueous phase after extraction = 1g – 0.875g

The quantity of substance remaining in aqueous phase after extraction = 0.125g.

v. Name indicator and titrant used in –
i. Assay of dried ferrous sulphate:
- Indicator: ferroin sulphate solution
- Titrant : 0.1N cerric ammonium sulphate

ii. Assay of ascorbic acid API:
- Indicator: starch
- Titrant : 0.1M iodine

vi. State Faraday's first law of electrolysis:
-→ According to of Faraday's first law of electrolysis, the mass of asubstance liberated at the electrodes during electrolysis is directly

proportional to the quantity of electrical charge (Q) that passes through the electrolyte.

If m is mass of a substance deposited by a current of I amperes in time of t seconds , then according to of Faraday's first law of electrolysis:

$$m \alpha Q$$

OR

$$m \alpha I * t$$

OR

$$m = Zit$$

where z is proportionality constant.

Thus first law correlates the quantity of current passed and the extent of chemical change that took place.

Q. 2 A What is Aquametry? Write principle and reactions involved in Karl Fischer Titration. **(4)**
Reference: "A textbook of pharmaceutical analysis", K. Connors, 3rd edition, pg 499-500

OR

Discuss in detail method used for determining organically bound halogens.
Reference: "Vogel's Textbook of Quantitative Chemical analysis", 6th edition, pg 135-136 (or Kasture, Mahadik)

B. i. Explain differentiating and levelling effects exerted by solvents in non aqueous titration. **(4)**
Reference: "Vogel's Textbook of Quantitative Chemical analysis", 6th edition, pg 381-382 (or "A textbook of pharmaceutical analysis", K. Connors, 3rd edition, pg 49-51)

ii. Complete the following table:

Compound	Titrant used in its assay	Indicator
Sodium benzoate	Perchloric acid	Crystal violet
Acetazolamide	Lithium methoxide or sodium methoxide or tertabutyl ammonium hydroxide	Potentiometric/ Azo violet

(4)

C What is fractional precipitation? Discuss the estimation of halides using adsorption indicators.
Reference: "A textbook of pharmaceutical analysis", K. Connors, 3rd edition, pg 69-70 (for Fractional precipitation), pg 73 (for Adsorption indicators).

Q3. A Write a note on normal pulse polarography and differential pulse polarography. **(4)**
Reference: "Vogel's Textbook of Quantitative Chemical analysis", 6th edition, pg 575-577.

B. What is the difference between iodometric and iodimetric titration? Give the equations involved in the assay of potassium iodide. **(4)**

1. Direct titrations with iodine are called as Iodimetric titrations. These make use of the oxidising power of iodine in aqueous solutions. A standard solution of iodine is used as a titrant. The analyte should be a substance that

is oxidizable.

2. Titrations involving liberated iodine are called as iodometric titrations. Here, iodine is liberated in the reaction flask by the use of KI and concentrated acid. A standard solution of sodium thiosulphate is used as a titrant. The analyte should be a substance that is reducable.
3. Equations:
   Beckett and Stenlake, fourth edition, pg: 191

C. Write principle, chemical reactions and end point determination involved in the assay of calcium gluconate injection **or** assay of aspirin API. **(4)**

Ca-Gluconate + EDTA ⟶ Ca- EDTA complex
$MgSO_4$ + EDTA ⟶ Mg- EDTA complex
Mg^{2+} + Mordant black ⟶ Mg^{2+}- Mordant black complex

1. Calcium gluconate is assayed by complexometric titration (replacement or substitution titration) using disodium EDTAte as the titrant and mordant black as the indicator at a pH of 10 buffered by ammonia-ammonium chloride buffer.
2. Since the stability of the calcium ion- indicator complex is less than stability of the Ca-EDTA complex, the titration cannot be performed under these conditions. Therefore, a known amount of standard Magnesium sulphate solution is added. Magnesium ions form a stable complex with mordant black under the maintained pH conditions.
3. Towards the end point, all of the Calcium is in the form of Ca- EDTA complex. The last drops of disodium EDTAte will break the Mg^{2+}- Mordant black complex (pink/ reddish colour) and convert it to Mg- EDTA complex, releasing the free indicator (blue colour) and thus signalling the end point.

OR

The determination of aspirin depends upon the alkaline hydrolysis of aspirin to acetic acid and salicylic acid and titrating the excess of alkali with standard acid using phenol red as the indicator. A blank determination is essential because alkali is being heated and then cooled.

Reference: Beckett and Stenlake, fourth edition, pg: 147

Q. 4 A. Explain the neutralisation curve for titration of strong acid with strong base by taking suitable example. **(4)**

Reference: "Vogel's Textbook of Quantitative Chemical analysis", 5th edition, Page 267-271

-X vs Y axis, Shape of curve,

-Calculation of (equations only) pH at each poin

-significance of curve, choosing indicators

-factors affecting (strength and concentration)

B. What is gravimetry? Explain organic and inorganic precipitants with suitable examples and reactions. **(4)**

Reference: "Vogel's Textbook of Quantitative Chemical analysis", 5th edition, pg 417-18,424,437

C. Give the role of: **(4)**

i. Sulphuric acid in permanganometry : **i) assists in 5e transfer, stable solution**

ii. Ferroin in cerimetry : **internal indicator**

iii. Starch in iodimetry : **indicator**

iv. Sodium thiosulphate in iodometry : **titrant/secondary standard**

Q. 5 A. A series of extract assays yielded the following values in terms of mg of total alkaloid per 100mL. **(4)**

33.40 mg	32.99 mg	33mg	31.95mg	32.35mg
33.5 mg	33.33mg	32mg	31mg	

Calculate mean, median, R.S.D and variance for the recorded values.

Mean = 32.61333

Median = 32.99 (5th observation)

SD = 0.843979 , Variance = SD^2 = 0.7123

relative standard deviation (RSD)= SD/mean = 0.025878

B. Explain how pH is an important factor in complexometric titrations. Write structure and properties of EDTA as a complexing agent. **(4)**

Reference: "Vogel's Textbook of Quantitative Chemical analysis", 5th edition, pg 321-23, 329

pH: 1) each metal forms stable complex at specific pH

2) pH might change during titration as YH4---> Y-4, hence buffer should be used to stabilize and fix pH

Structure, molecular wt, sequestering agent, hexa-coordinated, solubility issues therefore disodium salt used

C. What is separatability factor? Write a note on counter current extraction. **(4)**

- The effectiveness of separation increases with the magnitude of the separation coefficient (β*) or* separatability factor

$$\beta = \frac{[A]_o/[B]_o}{[A]_w/[B]_w} = \frac{[A]_o/[A]_w}{[B]_o/[B]_w} = \frac{D_A}{D_B}$$

- A & B, and both tend to be extracted , then a separation coefficient or factor

β can be defined:

Thus, if Da = 10 and Db= 0.1, a single extraction will remove 90.9% of A, but only 9.1 % of B (ratio 10:1).

A second extraction of the aqueous phase will bring the total amount of A extracted to 99.2 % and B= 17.4 %. If B was an impurity then complete extraction of A would increase B.

Thus, the best situation is where the distribution factor for A is large and the distribution factor for B is small.

Counter current distribution

A method of multiple liquid-liquid extractions is countercurrent extraction, which permits the separation of substances with different distribution coefficients (ratios). A clever design known as Craig apparatus is used for this purpose (Lyman C. Craig, 1943).

- Permits separation of substances with very similar partitioning behavior.
- Consider the distribution of single solute between two immiscible liquids: fraction p distributed in upper phase with partition coefficient –K and ratio of U of upper to lower phase volumes.
- p=KU/KU+1

Craig apparatus consists of a series of glass tubes (r: 0, 1, 2..) that are designed and arranged such that the lighter liquid phase is transferred from one tube to the next. The liquid-liquid extractions are taking place simultaneously in all tubes of the apparatus which is usually driven electromechanically.

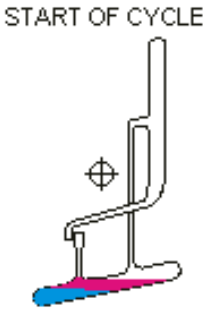
The lower (heavier) phase of the two-phase solvent system (e.g. water, blue layer in the picture) is the "stationary phase", whereas the upper (lighter) phase (e.g. hexane, red layer in the picture) is the "mobile phase".

In the beginning, tube #0 contains the mixture of substances to be separated in the heavier solvent and all the other tubes contain equal volumes of the same solvent. The lighter solvent is added to tube #0, extraction (equilibration) takes place and the phases are allowed to separate. The upper phase of tube #0 is then transferred to tube #1 and fresh solvent is added to tube #0, and the phases are equilibrated again. The upper layers of tubes #0 and #1 are simultaneously transferred to tubes #1 and #2 respectively. This cycle is repeated to carry on the process through the other tubes of the apparatus. Obviously, substances with higher distribution ratio move faster than those with a lower distribution ratio.

It is interesting to examine the distribution of a substance A in each tube after a given number of equilibration/transfer cycles.

Supposing that the volumes of each solvent are equal (V), and let W represent the weight of A in the sample, p and q represent the fraction of A with distribution ratio of D in the upper (organic solvent, o) and lower (water, w) phase, then it is

$$D = \frac{(C_A)_o}{(C_A)_w} = \frac{p\,W/V}{q\,W/V} = \frac{p}{q}$$



Since p+q = 1, we have

$$p = \frac{D}{D+1}$$

$$q = \frac{1}{D+1}$$

Q. 6 A. i. What volume of 1N H_2SO_4 would be required to neutralize 60 ml of 1.256 N NaOH. **(2)**

(2)

Data:
N_1=Strength of NaOH= 1.256N
V_1 = Volume of NaOH= 60mL

N_2=Strength of H_2SO_4= 1N
V_2 = Volume of H_2SO_4= ?

$N_{1*} V_1 = N_{2*} V_2$

1.256 * 60 =1* V_2

V_2= 75.36 mL

volume of 1N H_2SO_4 required to neutralize 60 ml of 1.256 N NaOH = 75.36 mL.

ii. How will you prepare 200 ml 0.25 N $KMnO_4$ solution. (mol.wt.158)

SOLUTION:

GIVEN –
mol. wt. of $KMnO_4$ = 158
volume to be prepared= 200ml
desired strength= 0.25 N
1M $KMnO_4$ solution contains 158 g in 1000mL.
Since for $KMnO_4$ solution,
1M=5N
Therefore,
1000ml of 5N solution will contain 158g of $KMnO_4$.

So,
1000ml of 0.25 N solution will contain 7.9 g of $KMnO_4$….(divide by 20)

Hence,
200ml of 0.25N solution will contain 1.58 g of $KMnO_4$ ……(divide by 5)

<u>To prepare 200 ml 0.25 N $KMnO_4$ solution, weigh 1.58g $KMnO_4$ dissolve in some quantity of water and then make up the volume to 200ml.</u>

B. i. In Kjeldahl's estimation of an unknown compound, ammonia obtained from 0.99 g of an organic compound was received in 98 mL M/20 HCl, the residual acid in flask required 49 mL of M/20 NaOH for complete neutralization in back titration. What is the percentage of nitrogen in the compound? **(2)**

Ans:

(2)

Data:
W= 0.99 g
Strength of std acid in receiving flask: (HCL): M/20= 0.05M=0.05N
Strength of std base used for titration of unreacted acid: (NaOH): M/20= 0.05M=0.05N

% N= ?

FORMULA:
Volume of acid consumed by liberated ammonia= 98mL- 49 mL=49 mL

% Nitrogen = (1.4 VN)/ W

% N= (1.4 * 49*0.05)/0.99

%N= 3.43/0.99

%N = 3.4646 %W/W

ii. Explain end point determination using external indicator in assay of Sulphacetamide sodium.

Answer:
Sulphacetamide sodium is assayed by nitrite or miscellaneous type of titration. It is also referred as Sodium nitrite titration. These type of titration involves diazotization reaction which results in formation of diazonium salts of aromatic primary amine in acidic medium.

Sulphacitamide sodium which will react with standard solution of sodium nitrite in acidic medium.
After suitable intervals take a drop of reaction mixture and streak it on a drop of starch iodide paste placed on white tile.(starch iodate paste is an external indicator.)
It helps in dertermination of end point in sodium nitrite titration by liberation of iodine from iodide.
A blue colouration is produced instantaneously which makes the end point of titration.(End point is appearance of blue colouration in potassium iodide paste placed on a tile.)

In assay of Sulphacetamide sodium,

Nitrous acid is formed by the interaction of sodium nitrite and hydrochloric acid as follows :

$$NaNO_2 + HCl \longrightarrow NaCl + HNO_2$$

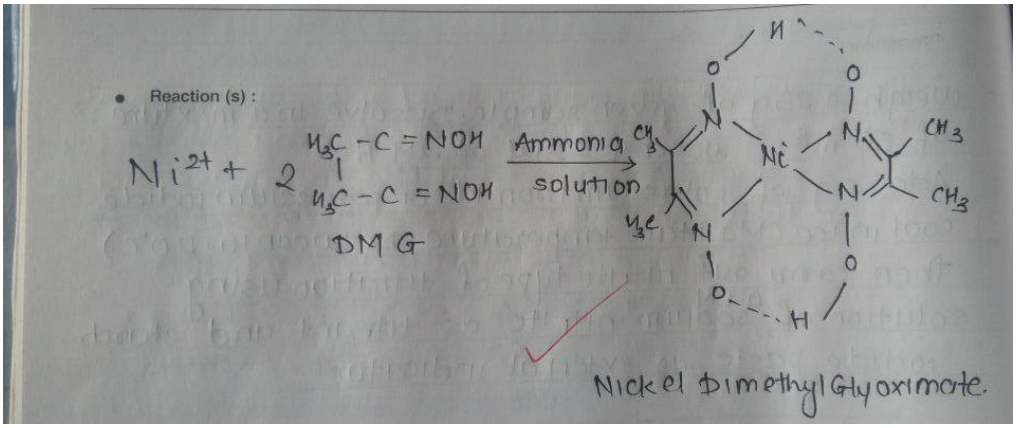
The end-point in the sodium nitrite titration is determined by the liberation of iodine from iodide which may be expressed by the following equations :

$$KI + HCl \longrightarrow HI + KCl$$

$$2HI + 2HNO_2 \longrightarrow I_2 + 2NO + 2H_2O$$

In other words, the small excess of HNO_2 present at the end-point can be detected visually by employing either starch-iodide paper or paste as an external indicator. Thus, the liberated iodine reacts with starch to form a blue green colour which is a very sensitive reaction. Besides, the end-point may also be accomplished electrometrically by adopting the dead-stop end-point technique, using a pair of platinum electrodes immersed in the titration liquid.

C . i. Give reactions involved in assay of Nickel by dimethylglyoxime. **(2)**



(2)

ii. Calculate gravimetric factor involved in gravimetric determination of sulphates as barium sulphate.
[Atomic weights: C:12, H:1, O:16, N:14, Ba: 137.33 , S:32]

Answer:
SO_4^{2-} + $BaCl_2$ ----------→ $BaSO_4$ + $2Cl^-$
formula wt of analyte: 32+4(16)= 32+64=96
formula wt of ppt: 137.33+32+4(16)= 137.33+32+64= 233.33

G.F.= [formula wt of analyte/ formula wt of ppt] *(a/b)

= [96/233.33]* (1/1)
= 0.4114