

Internal Assessment Test 2 – August 2022

Sub:	Engineering Chemistry				Sub Code:	21CHE22	Branch:	CSE, ISE, Mech & Civil	
Date:	06-08-2022	Duration:	90 min's	Max Marks:	50	Sem / Sec:	II / A to G		OBE

Question no. 1 is COMPULSORY and answer any THREE FULL Questions from the rest.

	MARKS	OBE	
		CO	RBT
1 (a) Explain the theory, instrumentation and applications of potentiometry with a neat sketch.	[7]	CO5	L3
(b) What is electroless plating? Illustrate electroless plating of copper with suitable reactions.	[7]	CO2	L3
2 (a) Explain the theory, instrumentation and applications of colorimetry with a neat diagrams.	[6]	CO5	L3
(b) Define BOD & COD. In a COD test, 22.7 cm ³ and 12.5 cm ³ of 0.05 N FAS solutions were consumed for blank & sample titration respectively. The volume of test sample used was 20 cm ³ . Calculate the COD of the sample solution.	[6]	CO5	L4
3 (a) Define the following terms i) Molarity ii) Normality iii) mole fraction	[6]	CO5	L2
(b) What are nanomaterials? Explain the synthesis of nanomaterials by precipitation method.	[6]	CO3	L3

4 (a) Discuss any 3 size dependent properties of nanomaterials.	[6]	CO3	L2
(b) What is potable water? Explain the determination of hardness of water by EDTA complexometric method.	[6]	CO5	L3
5(a) Explain the theory, instrumentation and applications of flame photometry.	[6]	CO5	L3
(b) What is electroplating? Explain the electroplating of chromium in detail.	[6]	CO2	L3
6 (a) Write a note on carbon nanotube. Discuss their properties and applications.	[6]	CO3	L3
(b) 20 cm ³ of hard water sample titrated against 0.01M EDTA solutions consumed 17.4 cm ³ of EDTA solution. 20 cm ³ same sample of hard water was boiled, filtered and titrated against 0.01 M EDTA solution consumed 8.2 cm ³ EDTA solution. Calculate total, permanent and temporary hardness of the water sample.	[6]	CO5	L4
7 (a) Write the principles and requirement of titrimetric analysis.	[6]	CO5	L3
(b) Illustrate the theory, instrumentation and applications of conductometry in the case of mixture of acids with strong base with a neat diagram?	[6]	CO5	L3

Answer 1a: Theory, Instrumentation and applications of Potentiometry

Theory : The procedure of using measurement of emf to determine the concentration of ionic species in solution is called as potentiometry also known as potentiometric titration.

When a metal M is immersed in a solution containing its own ions M^{n+} , the electrode potential is given by Nernst equation.

$$E = E^{\circ} + \frac{0.0591}{n} \log [M^{n+}]$$

Thus, the concentration can be calculated, provided E° of the electrode is known. The principle involved in potentiometric titration is the measurement of emf between two electrodes, an indicator electrode, (the potential of which is function of the concentration of the ion to be determined) and a reference electrode of constant potential. In this method, the measurement of emf is made while the titration is in progress. The equivalence point of the reaction is revealed by a sudden change in potential in the plot of emf readings against the volume of titrant.

Instrumentation: A potentiometer consists of: (i) Calomel electrode as a reference electrode, (ii) Platinum electrode as an indicator electrode, (iii) a device for measuring the potential and (iv) Magnetic stirrer.

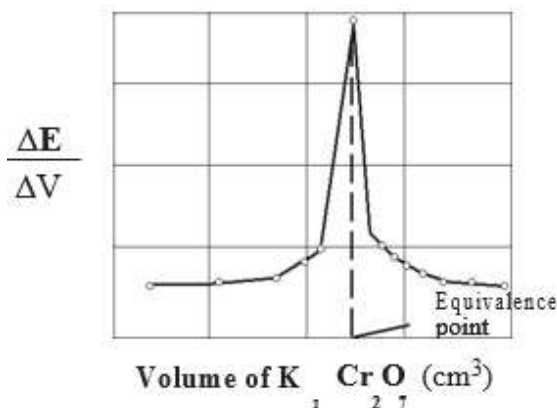
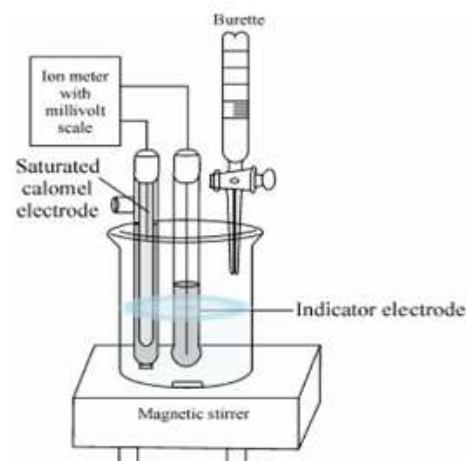
Application: (1) Analysis of pollutants in water

(2) Drug Analysis in Pharmaceutical industry

(3) Food industry for analysis of quality

(4) Potentiometric estimation of FAS using standard $K_2Cr_2O_7$ solution: Pipette out 25ml of FAS into a beaker. Add 1 t.t dil H_2SO_4 , immerse calomel electrode + platinum electrode into it. Connect the assembly to a potentiometer and measure the potential by adding $K_2Cr_2O_7$ in the increments of 0.5ml.

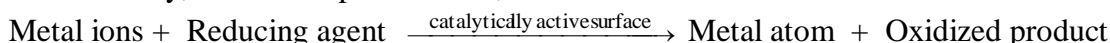
Plot graph $\Delta E / \Delta V$ against volume of $K_2Cr_2O_7$, and determine the equivalence point. From the normality and volume $K_2Cr_2O_7$, solutions calculate the normality and the weight of FAS in the given solution.



Answer 1b: *Electroless-plating:*

Deposition of metal or alloy over a conducting or non-conducting substrate surface by **chemical reduction of the metal ions by use of reducing reagent** and without the use of electrical energy is called electroless-plating.

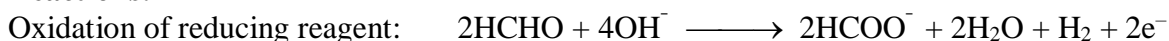
Schematically, it can be represented as,



Electroless-plating of Copper:

Substrate surface needs to be cleaned by suitable cleansing methods (solvent degreasing, acid pickling, alkali pickling, mechanical polishing, etc.). However, when the object is non-conducting or insulator material such as, plastics, PCBs, glass, etc. it needs to be activated by treatment with acidified $SnCl_2$ and then with acidified $PdCl_2$. Following bath compositions are used for plating.

Reactions:



Reduction of metal ion over object surface: $\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}$

Overall reaction: $\text{Cu}^{2+} + 2\text{HCHO} + 4\text{OH}^- \longrightarrow \text{Cu} + 2\text{HCOO}^- + 2\text{H}_2\text{O} + \text{H}_2\uparrow$

Constituents	Amount	Purpose
CuSO ₄	12 g/L	Provides metal ions
H-CHO	8 g/L	Reducing reagent
Rochelle salt	14 g/L	Complexing agent
NaOH	15 g/L	Provides alkaline medium
EDTA	20 g/L	Exaltant & complexing agent
pH	11.0	
Temperature	25°C	

Applications:

1. Metalizing PCBs.
2. Producing through-hole connections.
3. For plating on non-conductors.
4. As a base before electroplating.

Answer 2a. Theory, Instrumentation and applications of Colorimetry

Theory: Colorimetry is a scientific technique that is used to determine the concentration of colored compounds in solutions.

When a beam of incident light of intensity I_0 passes through a solution, a part of the incident light is reflected (I_r), a part is absorbed (I_a) and rest of the light is transmitted (I_t)

Thus, $I_0 = I_r + I_a + I_t$

In colorimeter, I_r is eliminated. For this purpose, the amount of light reflected (I_r) is kept constant by using cells that have identical properties. (I_0) & (I_t) is then measured.

Colorimetry measurements are based on Beer-Lambert's law which states that when a monochromatic light passes through a transparent medium, the amount of light absorbed is directly proportional to the concentration and path length of the solution.

$$A = \epsilon ct$$

Where A is absorbance, ϵ is the molar extinction coefficient, c is the concentration, t is the path length. If t, the path length is kept constant, then, $A \propto c$. Hence a plot of absorbance against concentration gives a straight line.

Instrumentation: Photoelectric colorimeter consists of

- (i) Tungsten lamp as the light source.
- (ii) A filter which provides the desired wavelength range wherein the solution gives the maximum absorbance.
- (iii) A sample cell
- (iv) A photocell detector: Detector are photosensitive elements which converts light energy into electrical energy

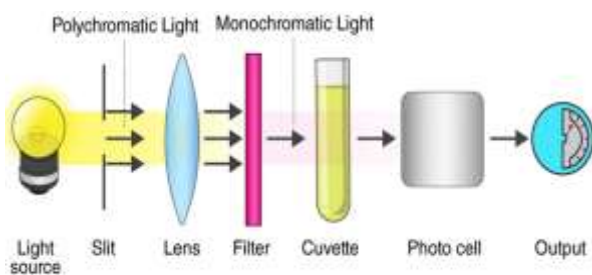


Fig: Schematic layout of colorimeter

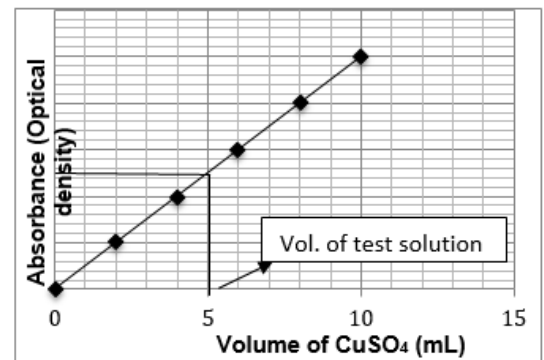
Application: (i) Colorimetry is versatile method of determining the concentration of metals and nonmetals present in small quantities in ores, soil, samples and alloys.

(ii) For the determination of the course of the reaction by measuring the rate of formation and disappearance of the light-absorbing compound

(iii) A compound can be identified by determining the absorption spectrum in the visible region of the light spectrum

(iv) For determination of the concentration of a colored compound

(v) **Colorimetric estimation of Cu in CuSO₄.** Draw out 2, 4, 6, 8, and 10 ml cm³ of the Copper sulphate solution into 50cm³ volumetric flask. Add 5cm³ of ammonia solution to each of them and dilute upto the mark with distilled water and mix well. Prepare a blank solution by diluting 5cm³ of ammonia solution in 50cm³ volumetric flasks. For test solution add 5ml of NH₃ and make up to the mark. Measure the absorbance of each of these against blank solution at 620 nm. Plot a graph of absorbance (OD) against volume of copper sulphate solution and determine the volume of copper sulphate solution in the test sample as shown in the figure and find the amount of copper present in it.



Answer 2b. Definition of Biological Oxygen Demand (BOD): Biological oxygen demand, BOD is defined as the amount of oxygen required by microorganisms to oxidize the organic wastes present in one liter of waste water at 20°C over a period of 5 days. It is expressed in mg dm⁻³.

Chemical Oxygen Demand (COD): COD is defined as the amount of oxygen consumed in the complete chemical oxidation of organic and inorganic wastes present in 1 litre of waste water by using strong oxidizing agent, such as acidified K₂Cr₂O₇. It is represented in mg dm⁻³ or ppm.

$$\begin{aligned} \text{COD of sample} &= \frac{N_{\text{FAS}} \times (b-a) \times 8}{V_s} \text{ g.dm}^{-3} \\ &= \frac{N_{\text{FAS}} \times (b-a) \times 8000}{V_s} \text{ mg.dm}^{-3} \end{aligned}$$

$$\text{COD} = \frac{0.05 \times (22.7 - 12.5) \times 8000}{20} = 204 \text{ mg of O}_2/\text{dm}^3$$

Answer 3a.

Molarity: It is one of the most widely used unit of concentration and is denoted by M. It is defined as no. of moles of solute present in 1 liter of solution. Thus,

$$\text{Molarity} = \frac{\text{No of moles of solute}}{\text{Volume of solution (in Liters)}}$$

Normality: It is described as the number of gram or mole equivalents of solute present in one litre of a solution.

$$\text{Normality} = \frac{\text{No of gram equivalents of solute}}{\text{Volume of solution (in Liters)}}$$

Mole Fraction: The mole fraction or molar fraction (x_i) is defined as the amount of a constituent (expressed in moles), n_i, divided by the total amount of all constituents in a mixture (also expressed in moles), n_{tot}:

$$x_i = \frac{n_i}{n_{\text{tot}}}$$

The sum of all the mole fractions is equal to 1.

Answer 3b. Precipitation Method.

Nanomaterials or Nanoparticles are defined as materials which contain nano size particles with at least one dimension in the range of 1 nm to 100 nm.

In this method solid nanoparticles are obtained by careful precipitation from their solution. Precipitation method can be used to prepare nanoparticles of metal oxides, metal sulphides and metals.

- In this method, an inorganic metal salt (such as nitrate, chloride or acetate of metal) is dissolved in water (precursor solution).
- Metal cations exist in the form of metal hydrate species, for example, [Al(H₂O)₆]³⁺ or [Fe(H₂O)₆]³⁺.
- These metal hydrates are hydrolyzed by addition of precipitating agent like NaOH or NH₄OH, which causes condensation of precursor.

d) The concentration of sol increases and reaches a critical level called supersaturation. At this concentration nucleus formation is initiated. The nucleus further grows into particles, which gets precipitated.

e) The precipitate obtained is filtrated, washed with water, air dried and finally calcined at high temperature to obtain nanoparticles.

Advantages

1. The process is relatively economical.
2. Wide range of single and multicomponent of oxide nanopowders can be synthesized.

Answer 4a Nanomaterials or Nanoparticles are defined as materials which contain nano size particles with at least one dimension in the range of 1 nm to 100 nm. Nanoparticles can exhibit size-dependent properties which is different from those of bulk materials.

Size dependent properties of Nanoparticles:

1 Surface area : *Surface area increases on moving from bulk to nanoscale. The Nanomaterials have a significant proportion of atoms existing at the surface.*

For approximately 30000 atoms of the entire particle: (a) At a particle diameter of 10 nm, 20 % of the atoms are positioned on its surface; (b) At a particle diameter of 5 nm, the value increases to 40 %, and (c) at 1 nm diameter, almost all of the atoms are on the surface. Nanomaterials have high surface to volume ratio therefore they exhibit good catalytic activity.

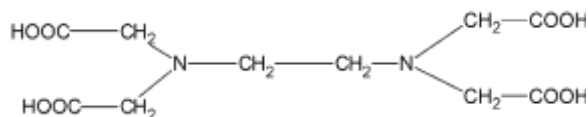
2. Catalytic Property: Surface area is enormously increased on moving from bulk to nanoscale. Nanomaterials have a significant proportion of atoms existing at the surface. *Nanomaterials have high surface to volume ratio therefore they exhibit good catalytic activity.* Example: *Bulk gold is catalytically inactive while nano gold is catalytically very active for selective redox reactions.*

3. Optical Property: It is dependent on *electronic structure*. A change in the particle size, brings about change in *electronic structure and band gap*, which leads to the *change in absorption and emission properties*. Example: *Bulk gold appears yellow in colour, where as nano gold appears red in colour.*

Answer 4b Hardness of water is determined by EDTA method, which involves complexometric titration

Principle

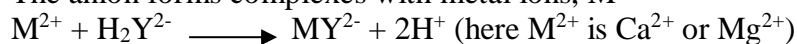
EDTA (Ethylene diamminetetra acetic acid) is a hexadentate ligand and forms complexes with Ca^{2+} & Mg^{2+} ions. EDTA commonly represented as H_4Y . It has structure,



The ionization of EDTA in solution is represented as



The anion forms complexes with metal ions, M^{2+}



The total hardness of water is determined by titrating a known volume of water against standard EDTA solution at pH 10 using Eriochrome black – T (EBT) indicator. The colour of indicator at pH 10 is blue

EBT forms a wine-red complex with M^{2+} ion. On adding EDTA, it forms a complex with free metal ions. At the end point when all the free metal ions are exhausted in the solution, added EDTA dissociates wine red coloured metal – EBT complex, consumes the metal ion and releases blue coloured free indicator. Therefore the colour changes from wine red to blue.

Procedure:

- (i) Total hardness:** Pipette out 50ml of the sample of water into a clean titration flask, add 1ml of $\text{NH}_3\text{-NH}_4\text{Cl}$ buffer solution and 3-4 drops of EBT indicator. Titrate against 0.01M EDTA till the color changes from wine-red to clear blue. Let the volume of EDTA required be v_1 ml.
- (ii) Permanent hardness:** Transfer 50ml of the sample of water into a clean 500ml beaker and boil gently for 20-30 minutes. Cool and filter it directly into a 250ml conical flask. Add 1ml of buffer solution

followed by 3-4 drops of EBT indicator. Titrate against standard 0.01M EDTA. Let the volume of EDTA required be v_2 ml.

Calculations:

Total hardness

1000 ml of 1M EDTA = 100g CaCO_3 (Molecular mass of $\text{CaCO}_3 = 100$ g)

1ml of 1M EDTA = $\frac{100}{1000}$ g of CaCO_3

1000

V_1 ml of 0.01M EDTA = $\frac{v_1 \times 0.01 \times 100}{1000}$ g of CaCO_3

50 ml of water sample = $\frac{v_1 \times 0.01 \times 100}{1000}$ g of CaCO_3

10^6 (1 million parts) ml of water sample contains = $\frac{v_1 \times 0.01 \times 100 \times 10^6}{1000 \times 50}$ g of CaCO_3
 = $20 \times v_1$ ppm CaCO_3 equivalent

Permanent hardness

Permanent hardness = $\frac{v_2 \times 0.01 \times 100 \times 10^6}{1000 \times 50}$ g of CaCO_3

= $20 \times v_2$ g of CaCO_3

Temporary hardness

Temporary hardness = $20 \times (v_1 - v_2)$ ppm of CaCO_3

Answer 5a. Theory, Instrumentation and applications of Flame Photometry

Theory—Flame photometry is an **atomic emission technique** used **for detection of metals**. Emission of characteristic radiation by an element, and the correlation of the emission intensity with concentration of the element form the basis of flame photometry.

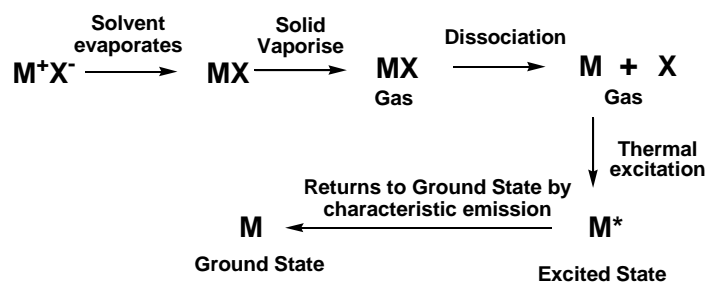
When a solution containing sample is aspirated into the flame, following changes takes place: (i) Firstly, solvent gets evaporated leaving behind salt in the flame. (ii) Then, salt gets evaporated into salt vapours, which further undergo dissociation into its constituent atoms. (iii) These gaseous atoms formed absorb energy from the flame get excited to high energy levels from the ground state. (iv) Being unstable in the excited state, they return back to ground state by emitting characteristic radiation. (v) Intensity of emitted light is proportional to number of atoms in the excited state which in which in turn is proportional to the concentration of solution fed into the flame and is given as

$$E = k \alpha c$$

E = detector response

k = constant

α = efficiency of atomic excitation; c = concentration



Instrumentation: A simple flame photometer consists of the following basic components:

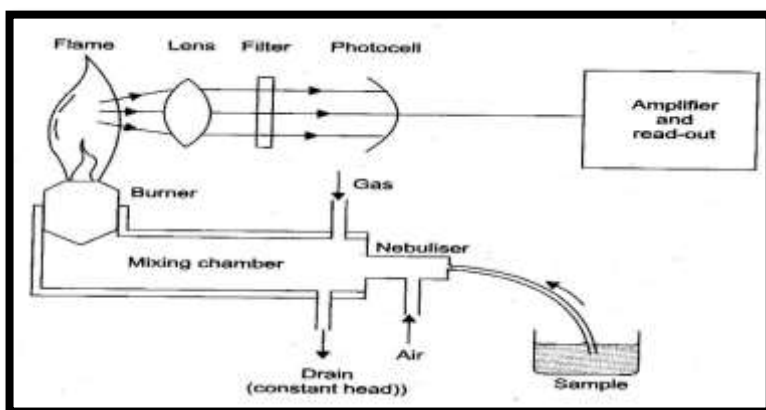
(a) **The burner:** Source of flame (Flame serves both as an atomizer and excitation source)

(b) **Nebuliser and mixing chamber** (Nebuliser is used to send homogeneous solution into the flame at a balanced rate)

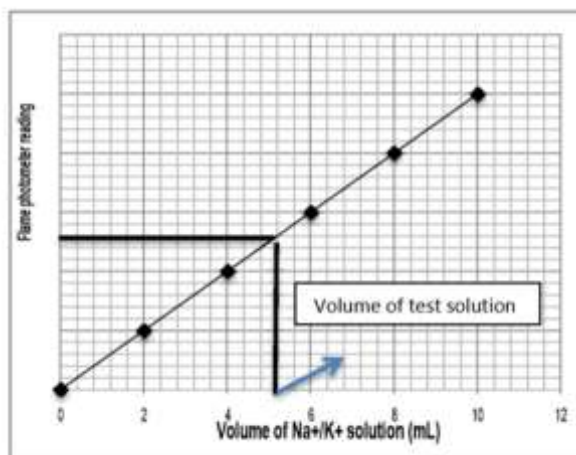
(c) **Simple colour filters:** Filters will isolate the wavelength to be measured from that of irrelevant emissions

(d) Photocell-detector: The emitted radiation is converted to an electrical signal with the help of photo detector.

The sample containing the analyte is aspirated into the flame. Radiation from resulting flame is collected by the lens and allowed to pass through an optical filter, which permits only the radiation characteristic of the element under investigation into the detector. The output from detector is read out on a display device.



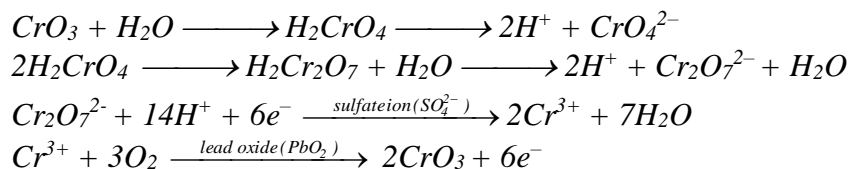
Application: 1) Flame photometer can be applied both for quantitative and qualitative analysis of elements.
 2) The presence of various alkali and alkaline earth metals in soil sample can be determined.
 3) Flame photometer can be applied for quantitative and qualitative analysis of various alkali and alkaline earth metals. A series of standard solution of analyte is prepared, passed into flame and emission of each solution is measured in flame photometer. Then calibration curve is obtained by plotting emission intensity against concentration of standard solutions. Sample solution is also properly diluted and then its emission is measured. From calibration curve, concentration of sample solution can be determined.



Answer 5b. Electroplating of Chromium: The process of deposition of a thin and uniform layer of metal or metal-alloy on to the electrically conducting object surface by electrolysis is known as electroplating. Chromium is employed for either decorative purposes (as a thinner coat) or engineering purposes (as a thicker hard coat). Mentioned below are coating specifications.

Bath composition	CrO ₃ (chromic acid) : H ₂ SO ₄ = 100: 1 ratio
Temperature	45 – 60 °C
Current density	100 – 200 mA/cm ²
Current efficiency	17 – 21 %
Anode material	Insoluble lead- Pb-Sb alloy or Pb-Sn alloy (with lead oxide coating)
Cathode material	Surface cleaned object metal
Reaction at anode	H ₂ O → ½ O ₂ ↑ + 2H ⁺ + 2e ⁻
Reaction at cathode	Cr ³⁺ + 3e ⁻ → Cr

- There is a complex sequence of reactions which control the concentration of Cr³⁺ in the plating bath. Sulfate ion is said to catalyse the conversion of Cr⁶⁺ into Cr³⁺ and PbO₂ catalyses the conversion of Cr³⁺ into Cr⁶⁺.



Chromium plating is a hard, attractive coating, with low coefficient of friction exhibiting wear resistance, abrasion resistance and also good corrosion resistance (with an undercoat of nickel and copper).

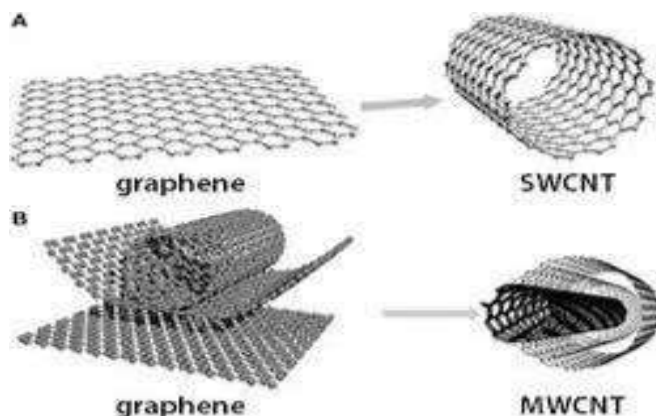
Applications :

- Decorative chromium provides a durable finish on cycles, automobiles, furniture, household fittings, aircraft, surgical and dental instruments.
- Hard chromium is mostly used in industries in the making of gauzes, dies, cutting tools, piston rings, cylinder liners, crankshafts of marine and aero engines, bearings, hydraulic rams and in printing industry.
- Black chromium is used in optical instruments, machine tools and electronic parts. It is also used in non-glare finishes on automobiles, and as an efficient coating for solar energy collectors.

Answer 6a Carbon Nanotubes (CNTs): Carbon Nanotubes (CNTs) are cylindrical tubes with a central hollow core formed by rolling up of graphene sheets. The CNT is a one dimensional material like nanowire, but with the length to width ratio greater than 1000. CNTs are categorized as Single-Walled CNTs (SWCNTs) and multi-walled nanotubes (MWCNTs).

1 **Single-Walled CNT (SWCNTs):** They are formed by rolling up of single graphene layer. The diameter of SWCNT is 1-4 nm and length can go up to few micrometers.

2. **Multi-Walled CNT (MWCNTs):** They consist of two or more concentric graphene cylinders. The diameter of MWCNTs is in the range of 30-50 nm and length can go up to few micrometers.



Properties:

- 1 CNTs exhibit high electrical and thermal conductivity. They have low density and very high mechanical strength due to these properties they are used as electrode material.
- 2 CNTs can emit electrons when subjected to high electrical field. Due to this property they are used in X-ray tubes.
- 3 The CNTs are about 20 times stronger than steel and hence find applications in making automobiles and aircraft body parts.
- 4 SWCNTs absorb radiation in the near IR range (700-1100 nm) and convert it to heat. This property is used in cancer thermotherapy to selectively kill cancer cells.
- 5 SWCNTs are used in solar panels.
- 6 CNTs are used for hydrogen storage to be used as fuel source.

Applications: In the field of

1. Biosensors, chemical sensor and gas sensors,
2. Water purification
3. Drug delivery
4. Cancer treatment
5. Battery

6. Construction with steel, 7. Fiber-optics etc.

Answer 6b Calculations:

Total hardness

1000 ml of 1M EDTA = 100g CaCO₃ (Molecular mass of CaCO₃ = 100g)

1ml of 1M EDTA = $\frac{100}{1000}$ g of CaCO₃

18 cm³ of 0.01M EDTA = $\frac{17.4 \times 0.01 \times 100}{1000} = 0.0174$ g of CaCO₃

25 cm³ of water sample = 0.0174 g of CaCO₃

10⁶ (1 million parts) ml of water sample contains = $\frac{0.0174 \times 10^6}{20}$ g of CaCO₃
= 870 ppm

Permanent hardness

1000 ml of 1M EDTA = 100g CaCO₃ (Molecular mass of CaCO₃ = 100g)

1ml of 1M EDTA = $\frac{100}{1000}$ g of CaCO₃

12 cm³ of 0.01M EDTA = $\frac{8.2 \times 0.01 \times 100}{1000} = 0.0082$ g of CaCO₃

25 cm³ of water sample = 0.0082 g of CaCO₃

10⁶ (1 million parts) ml of water sample contains = $\frac{0.0082 \times 10^6}{20}$ g of CaCO₃
= 410 ppm

Temporary hardness

Temporary hardness = Total Hardness – permanent Hardness
= (870 – 410) ppm
= 460 ppm

Answer 7a Principles of titrimetric analysis

1. The solution to be analyzed contains an unknown amount of chemicals.
2. The reagent of unknown concentration reacts with a chemical of an unknown amount in the presence of an indicator (mostly phenolphthalein) to show the end-point. It's the point indicating the completion of the reaction.
3. The volumes are measured by titration which completes the reaction between the solution and reagent.
4. The volume and concentration of reagent which are used in the titration show the amount of reagent and solution.
5. The amount of unknown chemical in the specific volume of solution is determined by the mole fraction of the equation.

When the endpoint of the reaction is reached, the volume of reactant consumed is measured and applied to carry volumetric analysis calculations of the analyte by the following formula,

$$C_a = C_t V_t M / V_a$$

Where,

C_a is the analyte concentration, typically in molarity.

C_t is the titrant concentration, typically in molarity.

V_t is the volume of the titrant which is used, typically in liters.

M is the mole ratio of the analyte and reactant from the balanced equation.

V_a is the volume of the analyte, typically in liters.

Many non-acid-base titrations are needed a constant pH throughout the reaction. Therefore, a buffer solution can be added to the titration chamber to maintain the pH value.

Requirement of titrimetric analysis

1. Reaction between reagent and analyte must be specific. Titrant cannot react with impurities or additions of analyte solution.
2. Reaction must be stoichiometric.
3. Titrant must react rapidly with the analyte so that the time required between additions of reagent is minimised.
4. Titrant must react more or less completely with the analyte so that satisfactory end points are realised.
5. Undergo a selective reaction with the analyte that can be described by simple balanced equation. Equilibrium constant must have high value.

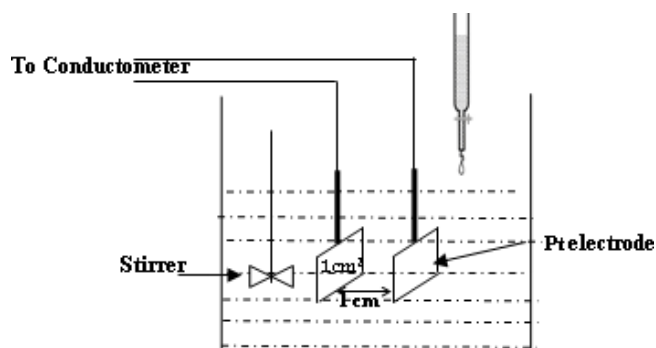
Answer 7b Theory: Conductometry is based on Ohm's law which states that the current i (amperes) flowing in a conductor is directly proportional to the applied electromotive force, E (volts), and inversely proportional to the resistance R (ohms) of the conductor.

$$i = \frac{E}{R}$$

The reciprocal of the resistance is called the conductance (Ease with which electric current flows through a conductor). Specific conductance of a solution is defined as the conductance of a solution present between two parallel electrodes which have 1cm^2 area of cross section and which have kept 1cm apart.

The conductance of solution depends on the number and mobility of ions. The substitution of ions with different ionic mobility affects the electrolytic conductivity. Therefore, the equivalence point can be determined by means of conductivity measurement for a neutralization reaction between an acid and a base. Equivalence point is determined graphically by plotting conductance against titer values.

Instrumentation: Conductometer consists of: (1) conductivity cell having two platinum electrodes; and (ii) conductometer. A simple arrangement of conductometric titration is depicted in figure. The solution to be titrated is taken in the beaker.



Application: (i) used to check water pollution in lakes as well as rivers.

(ii) used to check the alkalinity of the fresh water (iii) Purity of distilled water and de ionised water can determined. (iv)

Conductometric titrations of acids and base: Pipette out 50ml of sample (Acid mixture) into a beaker. Immerse the conductivity cell into it. Connect the conductivity cell to a conductivity meter and measure the conductance by adding NaOH from the burette by increment of 1 ml. Plot a graph of conductance against volume of NaOH. Determine the neutralization point from the graph as shown below.

