Q1. Discuss the mechanism of cationic polymerisation using a suitable monomer

Ans. (i) Initiation

$$Y^+ + CH_2=CH(X) \longrightarrow Y-CH_2-\overset{+}{C}H(X)$$

An acid (Acation)

where Y is a strong lewis acid like BF_3.

(ii) Propagation

$$Y-CH_2-\overset{+}{C}H(X) + CH_2=CH(X) \longrightarrow Y-CH_2-CH(X)-CH_2-\overset{+}{C}H(X)$$

(iii) Termination

$$Y-\left[CH_2-CH(X)\right]_n-CH_2-\overset{+}{C}H(X) \xrightarrow{Z^-} Y-\left[CH_2-CH(X)\right]_n-CH_2-CH(X)-Z$$

Q2. Write a short note on coordination polymerisation using a suitable monomer.

Ans. Ziegler-Natta discovered that in presence of combination of transition metal halide (like $TiCl_4$ or $TiCl_3$ --) with an organo-metallic compounds (like triethyl aluminium trimethyl aluminium), stereospecific polymerisation can be carried out.

Initiation:

$$\underset{\text{Complex Catalyst}}{Cat-R'} + CH_2=CHR \longrightarrow Cat-CH_2-CH(R)R'$$

Propagation:

$$Cat-CH_2-\underset{R}{CH}-R' + n\,CH_2=CHR \rightarrow Cat-CH_2-\underset{R'}{CH}\left(CH_2-\underset{R}{CH}\right)_n-R'$$

Termination: (with active hydrogen compound)

$$Cat-CH_2-\underset{R}{CH}\left(CH_2-\underset{R}{CH}\right)_n-R' + HX \rightarrow Cat-X + CH_3-\underset{R}{CH}\left(CH_2-\underset{R}{CH}\right)_n-R'$$

Q3. A polymer has been found to possess the population of various molecules as follows.

(i) 10 molecules → 20,000
(ii) 20 molecules → 24,000
(iii) 40 molecules → 40,000
(iv) 40 molecules → 60,000
(v) 20 molecules → 100,000

Ans. Number average molecular mass $= \frac{\sum N_i M_i}{\sum N_i}$

$= 51,384.61$

Weight Average Molecular Mass $(M_w) = \frac{\sum N_i M_i^2}{\sum N_i M_i}$

$= 63,401.19$

Polydispersive Index $= \frac{M_w}{M_n} = 1.23.$

Q2. List and explain 10 important properties of batteries.

Ans. 1. Batteries convert chemical energy directly to electrical energy such that $\Delta G < 0$

2. Redox reactions power the battery.

3. Galvanic cells work on spontaneous, reversible and thermodynamically controlled reactions.

4. Battery consists of some no. of voltaic cells.

5. The electrodes do not touch each other but are electrically connected through electrolyte.

6. A separator allows ions to flow b/w half cells.

7. Each half cells has an emf. determined by its ability to drive electric current from the interior to exterior of cells, the net emf is difference b/w reduction potentials of half reactions.

8. Ideal cells/ batteries don't internal resistance.

9. In actual cells, the internal resistance increases under discharge.

10. Batteries are used to power hearing aids, watches, cars, etc.

Q5. Write notes on

(a) Fuel cells

Ans. In a fuel cell, electric energy is obtained without combustion from oxygen and a gas that can be oxidized.

Fuel + Oxygen → Oxidation products + Electricity

It consists essentially of an electrolytic solution. Such as 25% ~~KO~~ KOH solution., and two inert porous electrodes.

Anode: $2H_2(g) + 4OH^-(aq) \longrightarrow 4H_2O(l) + 4e^-$

Cathode: $O_2(g) + 2H_2O(l) + 4e^- \rightarrow 4OH^-(aq)$

$$2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$$

Standard emf. = 1.23V.

Applications: Hydrogen-oxygen fuel cells are used as auxiliary energy source in space vehicles. In case of H_2/O_2 fuel cells, the product water proved to be valuable source of fresh water for astronauts.

(b) Lithium Batteries

It comprises of many types of cathodes and electrolytes but all with metallic lithium as anode.

The most common type is lithium as anode and MnO_2 as cathode with a salt of lithium dissolved in organic solvent.

$$MnO_2 + Li^+ + e^- \rightarrow Li\,MnO_2 \quad \text{(cathode)}$$

$$Li \rightarrow Li^+ + e^- \quad \text{(Anode)}$$

$$EMF = 3 - 3.3V$$

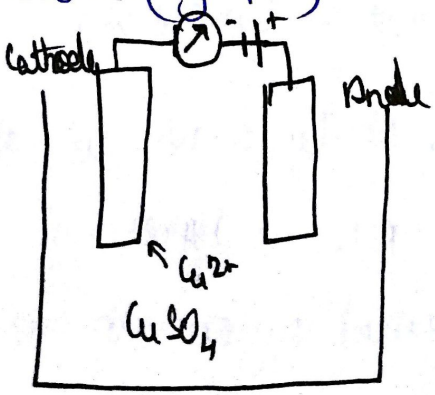
Li - MnO_2 batteries are suitable for low drain, long life, low-cost applications.

Applications: clocks, toys, cameras etc.

(c) Electroplating

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

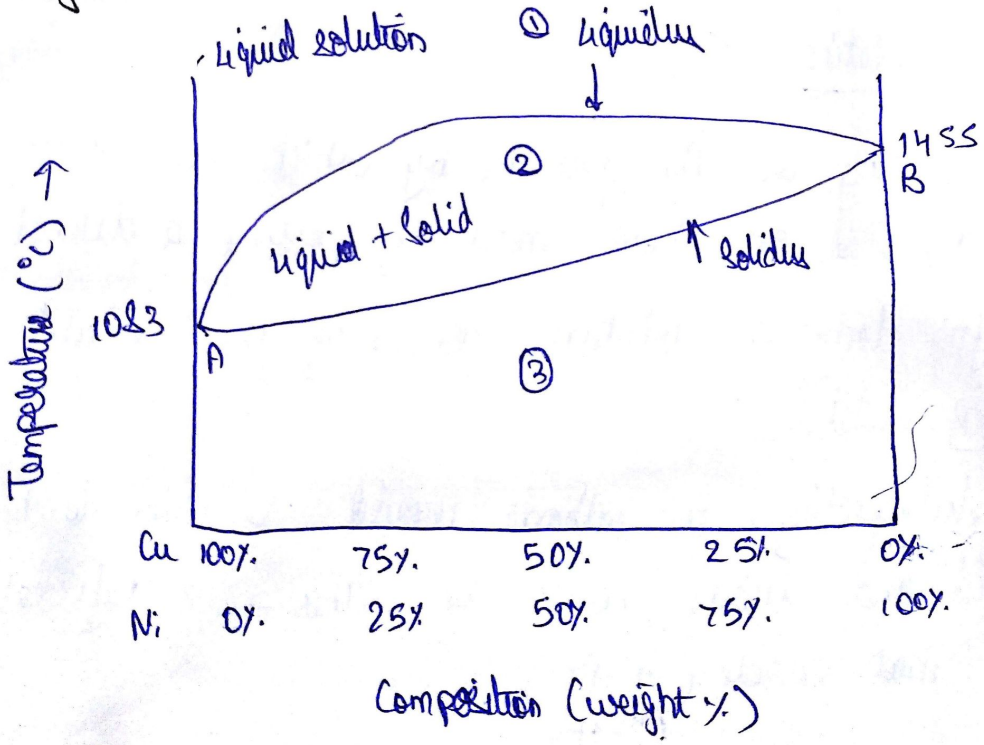
In electroplating, the cathode would be price to be plated and anode would be either a sacrificial anode/ an inert anode. (Eg Pt)



The cations associate with anions in solutions. These cations are reduced at anode to deposit in metallic zero valence state. For g- in copper plating, Cu is oxidized at anode to Cu^{2+} by losing $2e^-$. The Cu^{2+} associates with anion SO_4^{2-} in solution to form $CuSO_4$. At cathode Cu^{2+} is reduced to Cu.

Q6. Explain the phase diagram of a two component Cu-Ni system.

Ans.



Region 1: Any mixture of Cu & Ni in molten state represented by region 1 has 2 degree of freedom, since its a two component system in on phase:

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

Region 2: This system has two phases (one solid & other liquid. Hence $F = 2-2+1 = 1$ i.e., univariant or its temperature cannot be changed with affecting concentration.

Region 3: This system now has only 1 phase (solid phase) $F = C - P + 1 = 2$.

Q7. What is Green chemistry 2. Discuss the principles of green chemistry with suitable examples.

Ans. Green chemistry, also called sustainable chemistry is a philosophy of chemical research and engineering that encourages the design of products and processes that minimize the use & generation of hazardous substances

the principles are:

→ It is better to prevent waste than to treat or clean up waste after it is formed. Eg- Pollution should be stopped at source.

→ Synthetic methods should be designed to maximize the incorporation of all materials used in process into the final product.

Eg- Diel Alder reaction is 100% Atom economic reaction

→ Chemical products should be designed to preserve efficiency of function while reducing toxicity.
Eg- properties of super critical CO_2 make it possible to used as a good effective solvent.

→ The use of auxiliary substances (eg- solvents, etc) should be made unnecessary wherever possible and innocuous when used.

→ Energy requirements should be recognized for their environmental and economic impacts and should minimize synthetic processes should be conducted at ambient temp. & pressure.

→ A raw material or feed stock should be renewable rather than depleting wherever ~~them~~ technically & economically praticable.

→ Reduce derivatives - unnecessary derivatization (blocking group, modification) should be avoided wherever possible.

→ Catalytic reagents (as selective as possible) are superior to ~~the~~ stoichiometric reagents.

→ Chemical products should be designed so that at the end of their function they don't persist in the environment and break down into

innocuous degradation products.

→ Analytical methodologies need to be further developed to allow real time in process monitoring and control prior to the formation of hazardous substances.

→ Substances and the form of a substance used in a chemical process should be chosen to minimise potential for chemical accidents including releases, explosions and fires.

Q8. 1-chlorohexane can be prepared by the following substitution reaction.

$$CH_3(CH_2)_4CH_2OH + SOCl_2 \longrightarrow CH_3(CH_2)_4CH_2Cl + SO_2 + HCl$$

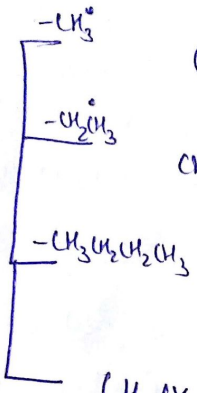
Calculate % atom economy.

Ans. % Atom economy = $\frac{\text{Formula mass of desired product}}{\text{Sum of formula mass of all reactants}}$

$$= \frac{120.5}{221} \times 100 = 54.52\%.$$

Q9. (a) How will you distinguish n-pentane, 2 methyl butane and neopentane using mass spectrometry 2. Explain.

n-pentane:



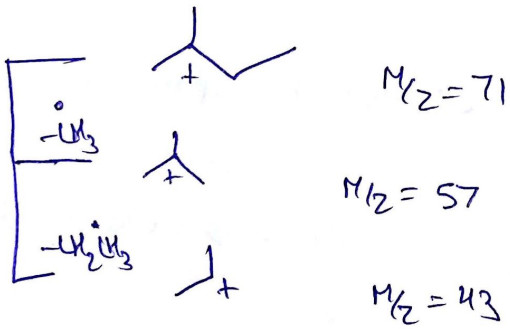
$CH_3CH_2CH_2^+CH_2 \rightarrow CH_3-CH_2-\overset{+}{C}H-CH_3$ $M/z = 57$

$CH_3CH_2CH_2^+ \longrightarrow$  $M/z = 43$

CH_3 $M/z = 15$

$CH_3CH_2CH_2\overset{+}{C}HCH_3$ $M/z = 71$

2- methyl butane:

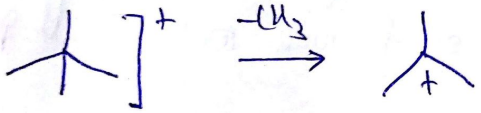


$M/z = 71$

$M/z = 57$

$M/z = 43$

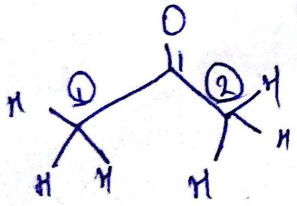
neopentane



$M/z = 57.$

(b) How will you distinguish propanone & propanol using NMR ~~spectroscopy~~ ? Explain.

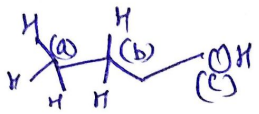
Ans



Carbons C_1 & C_2 are identical in all respects ∴ all the 6 hydrogens (3 on C_1 & 3 on C_2) show singlet

peaks at same position.

Propanol



Case I: Pure form of propanol: → 3 triplet peaks of type (a) are observed as 2 neighbouring hydrogen are present.

→ 2 pentate peaks of type (b) are observed as 4 neighbouring hydrogen are present

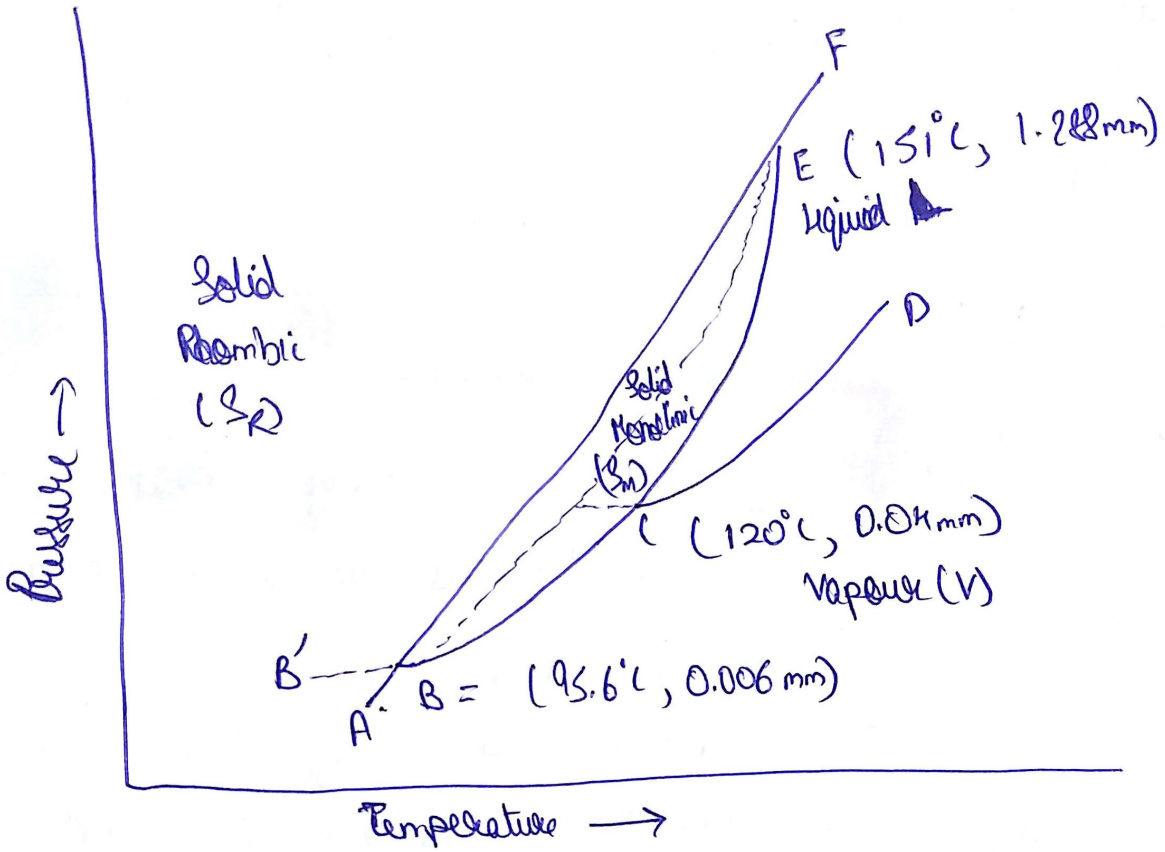
→ 1 triplet peak of hydrogen of OH group is observed.

Case II: Impure form Propanol: → 3 triplet peaks of type (a) are observed as 2 neighbouring hydrogen are present.

→ 2 quadrulet peaks of type (b) are observed.

→ 1 triplet peak of hydrogen of OH group is observed.

Q10. Draw the phase diagram of sulphur & mark the curve showing solid - solid transformation.



The curve BE represents the Solid - Solid transition curve.