ASSIGNMENT

① Describe the mechanism of cationic polymerisation using a suitable monomer.

A. The intermediate that carries the chain reaction during Polymerisation can be a positive ion, cation. In this case, cationic polymerisation in initiated by adding a strong acid to an alkene to form a carbocation.

Initiation:

$$CH_2 = CH(R) + H^+ \longrightarrow CH_3\,CH^+(R)$$

Propogation: The ion produced in this reaction add manomers to produce a growing polymer chain.

$$CH_3 - CH^+(R) + CH_2 = CH(R) \longrightarrow CH_3 - CH(R) - CH_2 - CH^+(R)$$

Thermination: The chain reaction is terminated when the carbonium ion reacts with water that contaminates the solvent in which the polymerisation is run.

$$CH_3 - CH(R) \left(CH_2 - CH(R)\right)_n CH_2 - CH^+(R) + H_2O \longrightarrow CH_3\,CH(R)\,(CH_2\,CH(R))_n\,CH(R)OH + H^+$$

② Write a short note on coordination polymerisation.

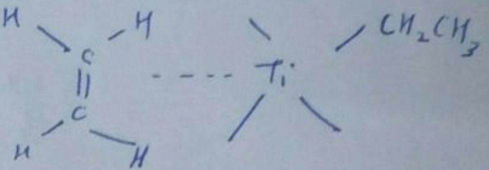
A. It is a form of addition polymerisation in which monomer adds to a growing macromolecule through an organometallic active center. The Ziegler - Natta catalysts provide the opportunity to control both the linearity and tacticity of the polymer.

Free-radical polymerisation of ethylene produces a low-density, branched polymer with side chains of one to five carbon atoms on up to 3% of the atoms along the polymer chain. Ziegler-Natta catalysts produce a more linear polymer, which is more rigid, with a higher density and a higher tensile strength. Polypropylene produced by free-radical reactions, for e.g., is a soft, rubbery, atactic polymer with no commercial value.

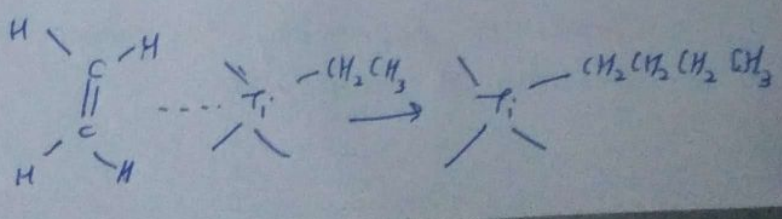
Ziegler-Natta catalysts provide an isotactic polypropylene, which is harder, tougher, and more crystalline.

A typical Ziegler-Natta catalyst can be produced by mixing solutions of titanium(IV) chloride ($TiCl_4$) and triethylaluminium ($Al(CH_2CH_3)_2$) dissolved in a hydrocarbon solvent from which both oxygen and water have been rigorously excluded. The product of this reaction is an insoluble olive-coloured complex in which titanium has been reduced to Ti(III) oxidation state.

The catalyst formed in this reaction can be described as coordinately unsaturated because there is an open coordination site on the titanium atom. This allows an alkene to act as a Lewis base toward titanium atom, donating a pair of e^- to form a transition-metal complex.



The alkene is then inserted into a $Ti-CH_2CH_3$ bond to form a growing polymer chain and a site at which another alkene can bond.



Thus, the titanium atom provides a template on which a linear polymer with carefully controlled stereochemistry can grow.

③ A polymer has been found to possess population of various molecules as follows:

i) 10 molecules → 20k
ii) 20 molecules → 24k
iii) 40 molecules → 40k
iv) 40 molecules → 60k
v) 20 molecules → 100k

Calculate No. average molecular weight, Weight average molecular weight and P.D.I.

A. No. average molecular weight $= \frac{\Sigma NM}{\Sigma N} = \bar{M}_n$

$$= \frac{(2\times1 + 2\times2.4 + 4\times4 + 4\times6 + 2\times10)\times10^5}{10+20+40+40+20}$$

$$= \frac{66.8\times10^5}{130} = 51384.6154$$

Weight average molecular weight, $= \frac{\Sigma NM^2}{\Sigma NM} = \bar{M}_w$

$$= \frac{(1\times4 + 2\times5.76 + 4\times16 + 4\times36 + 2\times100)\times10^9}{66.8\times10^5}$$

$$= \frac{423.52}{66.8}\times10^4$$

$$= 6.3401197\times10^4$$

$$= 63401.197$$

P.D.I. = Poly dispersity Index $= \frac{\bar{M}_w}{\bar{M}_n} = 1.23$

④ List and explain 10 important properties of batteries.

A. 1. Batteries are electrochemical devices which are an excellent emergency power source.

2. They have plates usually metallic, and either a solution or a moist compound between plates.

3. A chemical reaction takes place in the battery when it is discharged that produces a flow of electrons, out one plate on the negative side and into another plate on positive side.
4. A single unit of a battery is a cell. Each cell will have a characteristic voltage range between charged and discharged that is set by the electrochemical nature of the metals used and the reactions that go on in the solution, gel, wet powder etc. between the plates
5. Some non-rechargable batteries contain other chemicals to absorb waste by products from the chemical reaction that moves the electrons along.
6. This is what an "alkaline" battery is and why it lasts longer and costs more than a standard carbon/zin cell. It has an excess of these chemicals to absorb more byproducts before cell becomes poisoned.
7. Some cells or batteries can be recharged. In this case a power supply in hooked up to run the chemical reaction backwards and restore the chemical makeup of the battery back to its uncharged state.
8. Not all batteries can be recharged andattempting to recharge some non-rechargeable batteries can be quite dangerous, as pressure will develop inside the case and cause an explosion.
9. An example of a rechargeable battery is a lead/acid cell. Here lead plates and sulphuric acid are used and lead sulphate is generated and destroyed as the battery discharges and then gets recharged.
10. A "gel cell" is usually a lead/acid battery that has something in the sulphuric acid solution to make it less sloshy or gelled. Because they have more trouble dissipating heat and outgassing, these gell cells should be charged slower than regular lead /adcid batteries.

5) Write detailed notes on:

a) Fuel Cells b) Lithium Batteries c) Electroplating

A. a) Fuel Cells

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

Fuel + Oxygen ⟶ Oxidation products + Electricity

It could consist essentially of an electrolytic solution. such as 25% KOH solution, and two inert porous electrodes.

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

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

$$\underset{(g)}{2H_2} + \underset{(g)}{O_2} \rightarrow 2H_2O(l)$$

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.

$MnO_2 + Li^+ + e^- \longrightarrow LiMnO_2$ (cathode)

$Li \rightarrow Li^+ + e^-$

E.M.F. = 3 − 3.3V

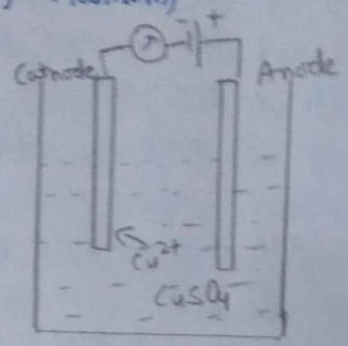
$Li-MnO_2$ batteries are suitable for low drain, long life, low cost applications.

Application: clocks, toys, cameras etc.

c) Electroplating

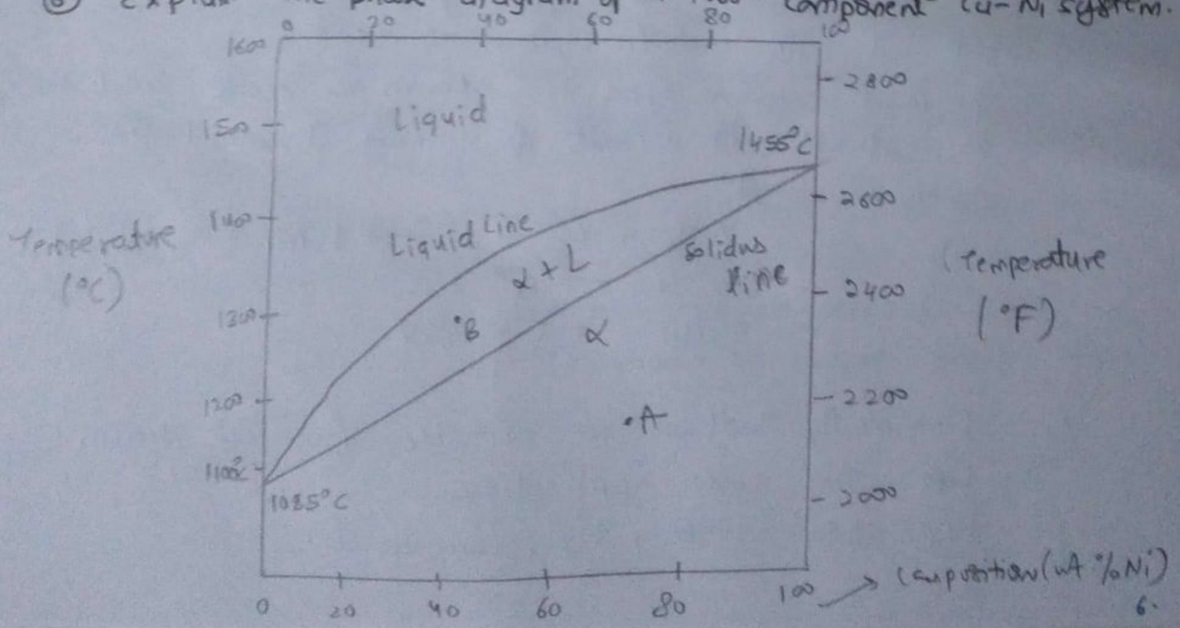
It is the process by which the coating metal is deposited on base metal by passing a direct current through electrolytic solution, containing the soluble salt of coating metal.

In electroplating, the cathode would be piece to be plated and anode would be either a sacrificial anode / an inert anode (eg. Platinum)



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

⑥ Explain the phase diagram of a two-component Cu-Ni system.



The above figure contains the Cu-Ni phase system. Its system is termed as being isomorphous.

The diagram has 3 different phase regions, the alpha region, the liquid region, and the liquid + alpha region, which are defined by specific compositions and temperatures. Both points A and B are located in the alpha and the alpha + liquid regions respectively. The phase boundaries are seperated by two lines. The line seperating the alpha and the alpha + liquid regions is the solidous line. The intersection of these 2 lines signify the melting temperatures of the two constituent's individually. The Cu-Ni system is especially noted for its complete liquid and solid solubility of its constituents, and is thusly identified as an isomorphous system.

7) What is Green Chemistry? Discuss its principles with suitable examples.

A. Green chemistry, also called sustainable chemistry is a philosphy of chemical research and engineering that encourages the design of products and processes that minimise the use & generation of hazardous substances. The principles are:

1) It is better to prevent waste than to treat or clean up waste after its formed. e.g. pollution should be stopped at source.
2) Synthetic methods should be designed to maximise the incorporation of all materials used in process into the final product.
   e.g. diels alder reaction is 100% atom economic reactor.
3) Chemical products should be designed to preserve efficiency of function while reducing toxicity. e.g. properties of super critical CO_2 make it possible

to be used as a good effective solvent.

4) The use of auxillary substances (e.g. solvents etc.) should be made unnecessary wherever possible and innocuous when used.

5) Energy requirements should be recognised for their environmental and economic impacts and should minimise synthetic processes.

6) A raw material or feed stock should be renewable rather than depleted wherever technically & economically practicable.

7) Catalytic reagents (as selective as possible) are superior to stochiometric reagents.

8) 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.

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

10) 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.

(8) 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 the % atom economy for the synthesis of 1-chlorohexane.

A

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

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

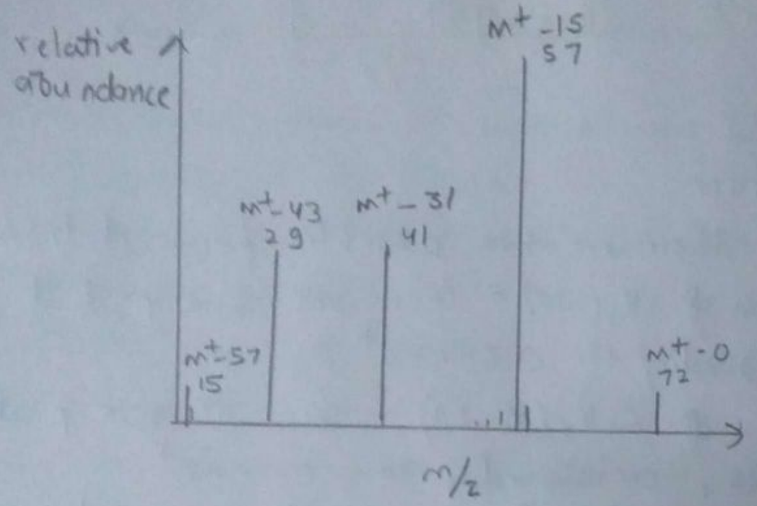
⑨ a) How will you distinguish n-pentane, 2 methyl butane & neopentane using mass spectroscopy? Explain.

b) How will you distinguish propane & propanol using NMR spectroscopy. Explain.

A. a)

- 2-2 dimethyl propane (neopentane)

The base peak should be at $m/z = 57$. This corresponds to loss of a methyl group and formation of the stable t-butyl cation, $(CH_3)_3C^+$.



- 2-Methyl butane

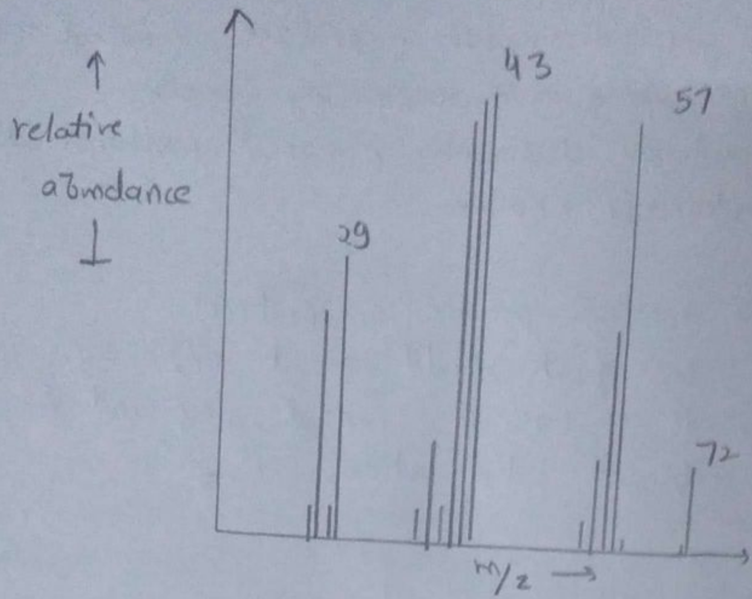
Here we have two possible fragmentations

1) Loss of CH_3 (M-15). This will give peak at $m/z = 57$, corresponding to $C-\overset{+}{C}-C-C$.

2) Loss of CH_3CH_2 (M-29). This will give peak at $m/z = 43$, corresponding to $(C)_2C^+$.

The peaks at 43 & 29 should be stronger than 57 & 13 because ethyl cation (29) is more stable than methyl cation.

The base peak is probably $\frac{m}{z} = 43$.

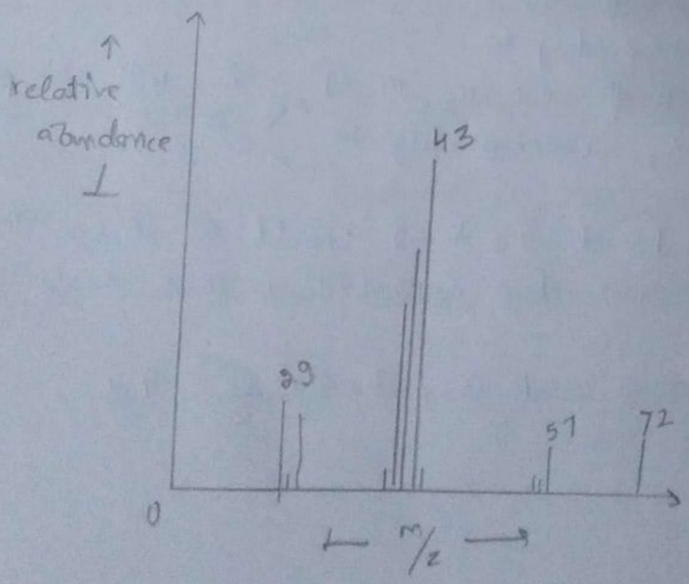


- n- pentane

  Again there are two possible fragmentations.

  1. Loss of CH_3 (-15) : This will give peak at $\frac{m}{z} = 57$, corresponding to $C-C-C-C^+$.
  2. Loss of C_2H_5 (M-27) : This will give peak at $m/z = 45$, corresponding to $C-C-C^+$.

The peaks at 43 & 27 will be more intense than those at 57 & 15, because second pair involves formation of unstable methyl cation CH_3^+.



9) Propanone & propanol using NMR spectroscopy:

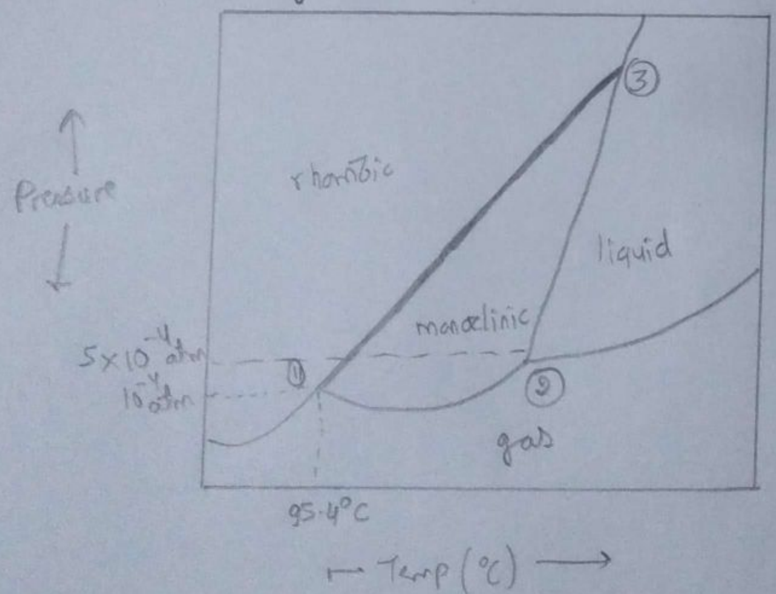
$$CH_3 - \overset{\overset{O}{\|}}{C} - CH_3$$

It would give only one peak in its NMR spectrum, because both CH_3 groups are in an identical environment - both are attached to $-COCH_3$.

$$\overset{(a)}{CH_3} - \overset{(b)}{CH_2} - \overset{(c)}{CH_2} - OH$$

- 3 triplet (2+1) peaks of type a) are observed as 2 neighbouring H 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.

(10) Draw the phase diagram of sulphur & mark the curve showing solid - solid transformation.



A phase diagram is a chart that shows the conditions of pressure and temperature at which distinct phases occur and coexist at eq^m.

The diagram is complicated by the fact that sulphur can exist in 2 crystalline forms: rhombic and monoclinic.
From the diagram it is pretty clear that,

lower left to ① = sublimation curve of rhombic S, S(rhombic) $\rightleftharpoons$ S(g)
① to ② = " " " monoclinic S, S(monoclinic) $\rightleftharpoons$ S(g)
② to upper right = vapour pressure curve of liquid S, S(l) $\rightleftharpoons$ S(g)
■ ① to ③ = transition curve, for S(rhombic) $\rightleftharpoons$ S(monoclinic)
② to ③ = melting point curve for S(monoclinic) $\rightleftharpoons$ S(l)
③ to top = " " " " S(rhombic) $\rightleftharpoons$ S(l)

Thus ① to ③ represents solid-solid transformation