

DELHI TECHNOLOGICAL UNIVERSITY

## CHEMISTRY ASSIGNMENT - 2

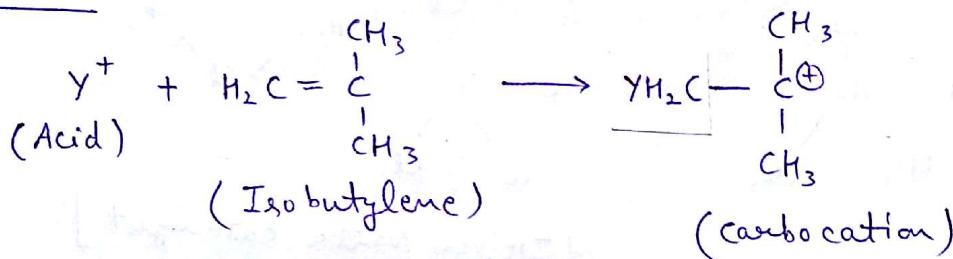
VIVEK SAHRAWAT

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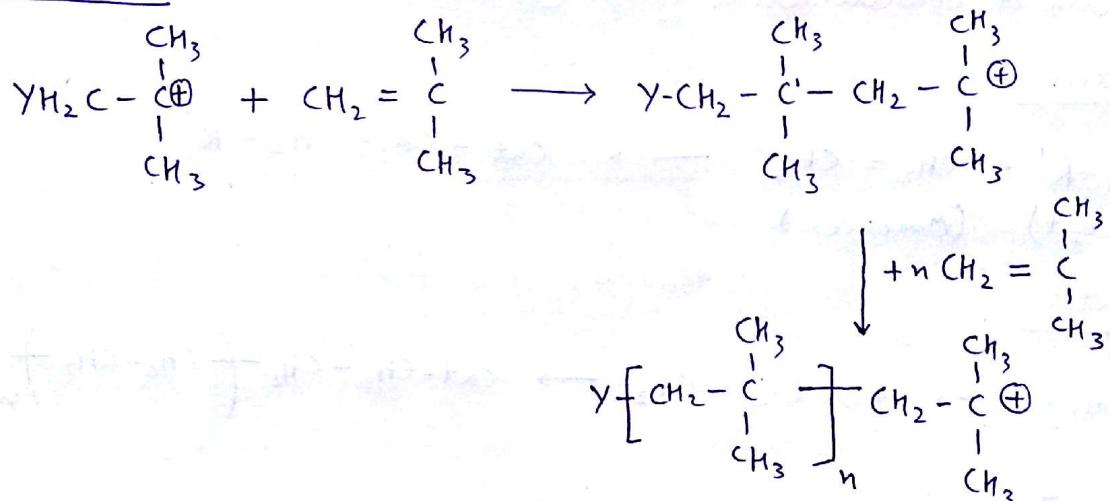
Q<sub>1</sub>

Sol Cationic polymerisation mechanism involves the following step. →  
(i) Initiation

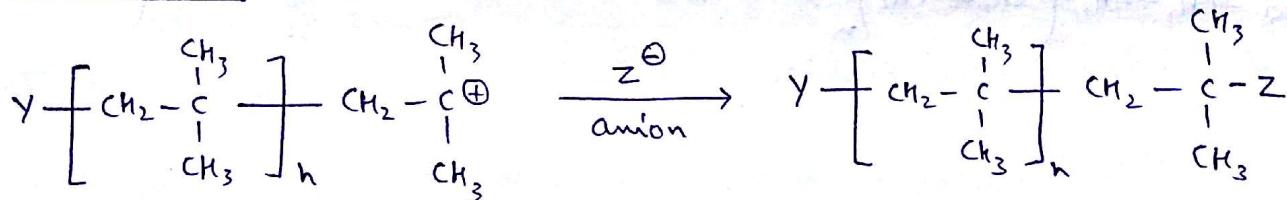
### (i) Initiation



## (ii) Propagation



### (iii) Termination

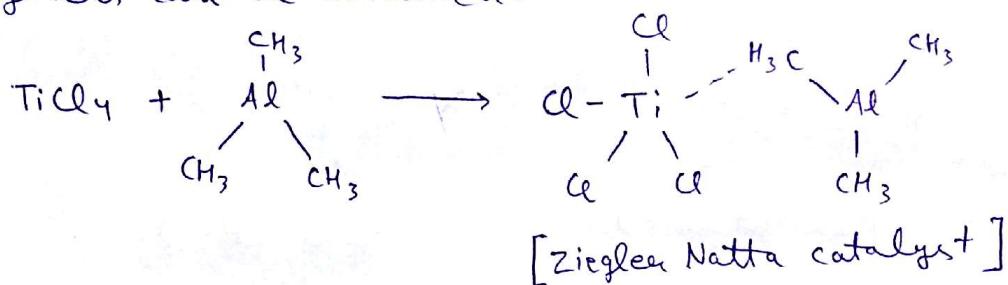


→ In cationic polymerisation any strong lewis acid like  $\text{BCl}_3$  can be used as catalyst. In this, a co-catalyst (e.g. water) is required to provide actual proton.

In certain cationic polymerisation a distinct termination step may not take place. However, chain transferred to a monomer from a polymer solvent or counter ion may occur. The choice of solvent for cationic polymerisation is important because of the relation of solvent to the intimate association between cation and counter ion.

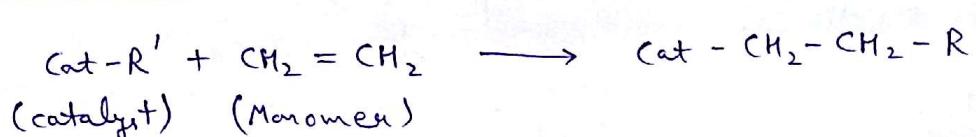
Q2.

Sol In coordination polymerisation the counter ion controls the propagation reaction by coordinating and by orienting the monomer propagation before ion insertion in the bond between counter ion and growing chain. e.g. Ziegler Natta catalyst. The importance of this method lies in the fact that "stereospecific polymers" can be obtained.

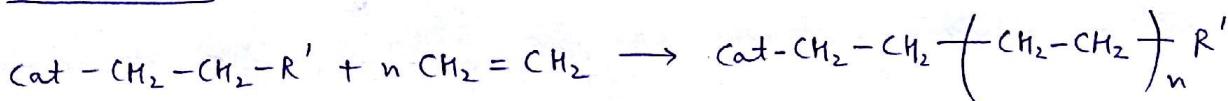


Mechanism of Coordination Polymerisation →

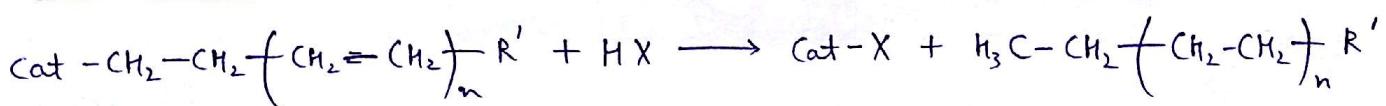
(i) Initiation



(ii) Propagation



(iii) Termination



Q3.

Sol

$M_i$ (Molecular Mass)	$N_i$ (No. of molecules)	$M_i^2$	$M_i N_i$	$M_i^2 N_i$
20000	10	$4 \times 10^8$	$2 \times 10^5$	$4 \times 10^9$
24000	20	$5.76 \times 10^8$	$4.8 \times 10^5$	$11.52 \times 10^9$
40000	40	$16 \times 10^8$	$16 \times 10^5$	$64 \times 10^9$
60000	40	$36 \times 10^8$	$24 \times 10^5$	$144 \times 10^9$
100000	20	$100 \times 10^8$	$20 \times 10^5$	$200 \times 10^9$
	130		$66.8 \times 10^5$	$423.52 \times 10^9$

$$\therefore \text{Number Average Molecular weight } (M_n) = \frac{\sum M_i N_i}{\sum N_i}$$

$$M_n = \frac{66.8 \times 10^5}{130}$$

$$M_n = 5.138 \times 10^4$$

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

$$M_w = \frac{423.52 \times 10^9}{66.8 \times 10^5}$$

$$M_w = 6.34 \times 10^4$$

$$\therefore \text{Poly Dispersive Index (PDI)} = \frac{M_w}{M_n}$$

$$PDI = \frac{6.34 \times 10^4}{5.138 \times 10^4}$$

$$PDI = 1.234$$

Q4.

Ans - The important properties of batteries are →

- ① Energy density: Energy density is a measure of how much energy a battery contains in comparison to its weight or volume.
- ② Cell Voltage / Voltage Stability: The voltage provided to power the load is very important. Ni-Cd and Ni-MH batteries have 1.25 V nominal voltage whereas Ni-Cd has 3.6 V nominal voltage.
- ③ Peak Current: The maximum current that a battery can deliver is directly dependent on the internal equivalent series resistance of battery. The current pass through the internal resistance will reduce the terminal voltage equal to the resistance multiplied times the load current.
- ④ Self discharge: Self discharge (which occurs in all batteries) determines the "shelf life" of a battery. It is important to note that self discharge is highly dependent on temperature, increasing as the battery temperature is increased.

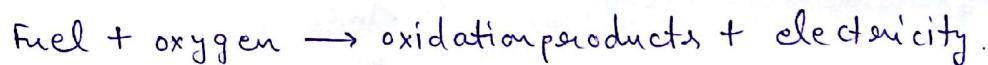
⑤ Recharge Time: The amount of time that the typical consumer finds acceptable for battery recharging is highly variable, and depends on item being powered.

⑥ Operating Temperature: Batteries are sensitive to operating temperature with respect to their charging and A-hr capacity. Most well-designed chargers have temperature sensors to assure that the battery temp. is within the allowable "window" for charging.

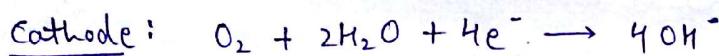
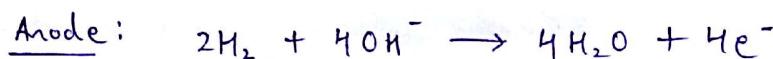
Q5.

(a) Fuel Cells.

Ans - In a fuel cell, electric energy is obtained without combustion from oxygen and gas that can be oxidized. Hence, a fuel cell converts the chemical energy of the fuel directly to electricity. The essential process in a fuel cell is →



One of the most successful fuels is hydrogen-oxygen fuel cell. It consists essentially of an electrolyte solution such as 25% KOH and two inert porous electrodes. Hydrogen and oxygen gases are bubbled through the anode and cathode compartment.



The standard emf of cell,

$$E^\circ = E_{\text{Ox}}^\circ + E_{\text{red}}^\circ = 0.83 + 0.4$$

$$\underline{\underline{E^\circ = 1.23 \text{ V}}}$$

Application → Hydrogen-Oxygen fuel cell are used as auxiliary eng source in space vehicles (e.g. Apollo spacecraft), sub-marines or other military vehicles.

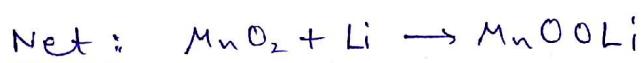
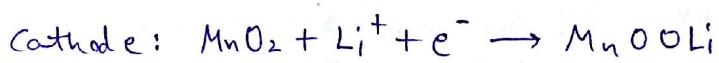
(b) Lithium Batteries.

Ans - Lithium batteries are batteries that have lithium as an anode. They stand apart from other batteries in their high charge density (long life) and high cost per unit. Depending on the design and chemical compounds used, they can produce voltages from 1.5 V to 3.7 V. The most common type of lithium cell used in consumer

application uses metallic lithium as anode and manganese dioxide as cathode, with a salt of lithium dissolved in organic solvent.

Another type of cell having large energy density is lithium-thionyl chloride cell. It is not sold to the consumer market, It is not rechargeable. The cell contains a liquid mixture of  $\text{SOCl}_2$  and  $\text{LiAlCl}_4$  which act as cathode and electrolyte respectively. A porous carbon material serve as a cathode current collector which receives electrons from external circuit.

### Lithium-Manganese Dioxide Cell



Application: Lithium batteries find application in many long life, critical devices, such as pacemakers and other implantable electronic devices. They can be used in place of ordinary alkaline cells in many devices such as clocks & cameras. They also prove valuable in oceanographic.

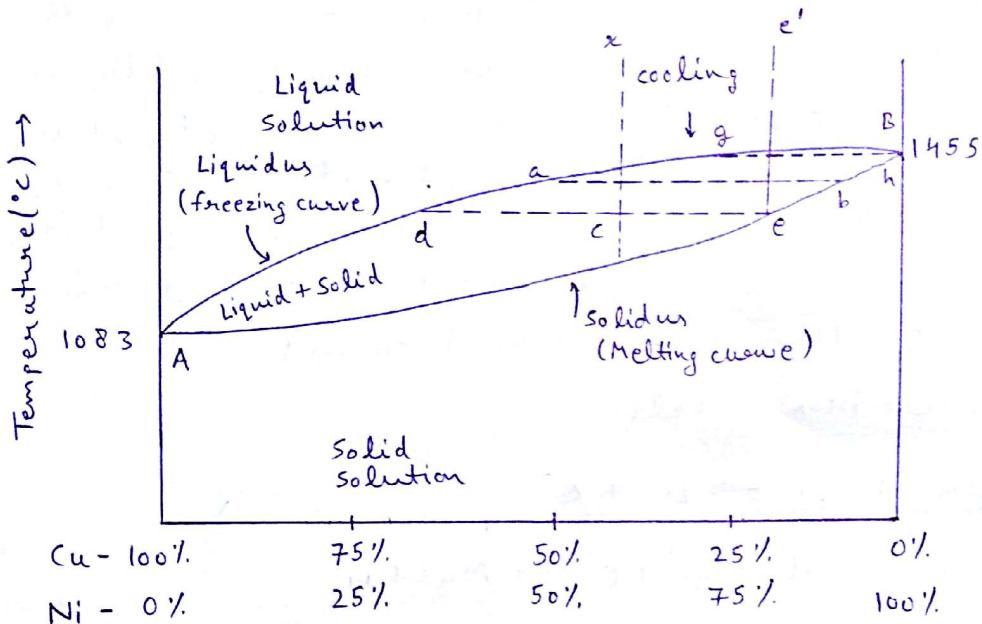
### (c) Electroplating.

Any - Electroplating is a process that uses electric current to reduce dissolved metal cations so that they form a thin metal coating coating on an electrode. The process used in electro-plating is called electrodeposition. It is analogous to a galvanic cell acting in reverse. The part to be plated is the cathode of the circuit. In one technique, the anode is made of the metal to be plated on the part. Both components are immersed in a solution called an electrolyte containing one or more dissolved metal salts, that permit the flow of electricity.

Electroplating is primarily used to change the surface properties of an object (e.g. abrasion and wear resistance, corrosion protection, lubricity, aesthetic qualities etc.) but also may be used to build up thickness on undersized parts or to form objects by electroforming.

Q6.

Ans -



T-C Phase Diagram Of Cu-Ni System

→ Copper and nickel are soluble in each other in all proportions in solid state. The phase diagram of the system is shown in temperature composition diagram. The freezing points of copper and nickel are respectively  $1083^{\circ}\text{C}$  and  $1455^{\circ}\text{C}$ . The addition of nickel to copper raises the freezing point, whereas addition of copper to nickel depresses the freezing point. Consequently, the freezing point of a mixture of Cu and Ni of any composition lies between the individual freezing point of copper and nickel.

The upper curve represent the liquidus or freezing curve, since above this, the system is completely liquid only. On the other end the lower curve represents the solidus or melting curve since, below it only solid phase exists. In between the solidus and liquidus, both solid and liquid phase co-exist. The two components form continuous series of solutions, without any minimum or maximum congruence point of two curves.

The composition of a liquid solution in equilibrium with solution is given by a tie line. Thus, a liquid solution of composition a is in equilibrium with solid solution of composition b. This state of affair happens along the curve between the melting points of Cu & Ni i.e. between  $1083^{\circ}\text{C}$  and  $1455^{\circ}\text{C}$ .

Any mixture of Cu & Ni in molten state represented by point 'x' has two degrees of freedom, since it is a 2 component system in one phase :  $F = C - P + 1 = 2 - 1 + 1 = 2$ . This system now has two phases and hence it's degree of freedom,  $F = C - P + 1 = 2 - 2 + 1 = 1$ , i.e. univariant therefore system can not be cooled without affecting conc.

Q7.

Ans - Green Chemistry or sustainable chemistry is a philosophy of chemical research and engineering that encourages the design of products & processes that minimize the use and generation of hazardous substance. It applies to organic, inorganic, bio, analytical and even physical chemistry.

The 12 green chemistry principles are →

- ① It is better to prevent waste than to treat or clean up waste after it is formed.

The ability of chemists to redesign chemical transformations to minimize the generation of hazardous waste is an important first step in pollution prevention. The first principle says that prevention is better than cure. The process design should be such that waste by-products can be minimized.

- ② Synthetic Method should be designed to ~~minimize~~ maximize the incorporation of all materials used in the process into the final product.

The process should be so redesigned to give maximum yield and maximum efficiency.

$$\% \text{ Atom Economy} = \frac{\text{Molecular Mass Of final Product}}{\text{Molecular Mass Of All Reactants}} \times 100$$

- ③ Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and environment.

Some toxic chemicals are replaced by safer ones for a green technology, when reagent choices exist for a particular transformation. This principle focuses on choosing reagents that pose the least risk and generate only benign by-products.

- ④ Chemical products should be designed to preserve efficacy of function while reducing toxicity.

This principle emphasizes designing of safer chemical. For example, properties of super critical  $\text{CO}_2$  makes it possible to be used as a good effective solvent.

- ⑤ The use of auxiliary substances should be made unnecessary whenever possible and innocuous when used.

Development of dry reaction techniques follows this principle of green chemistry, making the application of solvent redundant.

- ⑥ Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic processes should be conducted at ambient temperature and pressure.  
For example Ionic liquids, work as an excellent solvent under ambient conditions. Such methods can lead to reduction in energy requirements for creation of reaction conditions.
- ⑦ A raw material should be ~~renewable~~ renewable rather than depleting wherever technically and economically practicable.  
The raw material should be renewable for assured production. Thus techniques are being developed for such processes.
- ⑧ Reduce derivatives -  
Derivatization result in increase in number of steps required in the process and each additional step requires reagent and can generate more waste.
- ⑨ Catalytic Reagents (as selective as possible) are superior to stoichiometric reagents.  
Catalyst are used in small amounts and can carry out a single reaction many times and so are preferable to stoichiometric reagents, which are used in excess and work only once.
- ⑩ Chemical products should be designed so that at the end of their function they do not persist in the environment and break down into ~~innocous~~ innocuous degradation products. This principle suggest that the breakdown of chemical product should not be harmful even in long run.
- ⑪ Analytical methodologies need to be further developed to allow real-time, in-process monitoring and control prior to the formation of hazardous substances.  
The quick detection of harmful substance can help in quick curative action.
- ⑫ Substances and the form of a substance used in a chemical process should be chosen to minimize potential for chemical accidents, including releases, explosion and fires.  
The process and substances used should be safe even if some accident takes place there should not be any damage to the environment.

Q8.



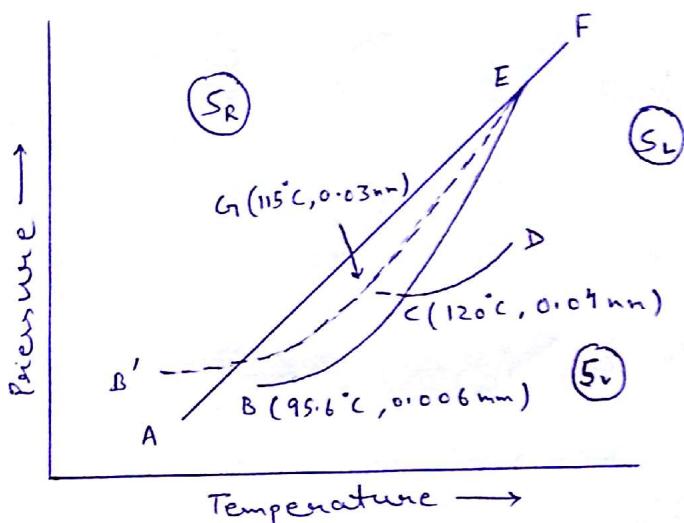
$$\therefore \% \text{ atom economy of } 1\text{-Chlorohexane} (\% \text{ AE}) = \frac{M(1\text{-Chlorohexane})}{M(\text{All reactants})} \times 100$$

$$= \frac{120.5 \times 100}{102 + 119} = 54.52\%$$

$\% \text{ AE} = 54.52\%$

Q10.

Ans-



→ There are six stable curves  $AB$ ,  $BC$ ,  $CD$ ,  $BE$ ,  $CF$  and  $EF$  respectively representing equilibria of two phase side by side. Beside these, there are four metastable curves depicted by dotted lines  $BG$ ,  $CG$ ,  $EG$  and  $BB'$ .

Curve AB is vapour pressure curve of solid ~~atomic~~ sulphur ( $S_R \rightleftharpoons S_v$ ). Curve BA ends at  $50^\circ\text{C}$  at A below which vapour pressure of  $S_R$  is not measurable. Point B is known as the transition temp. of  $S_R \rightleftharpoons S_m$ .

Curve BC represent the vapour pressure curve of monoclinic sulphur ( $S_m \rightleftharpoons S_v$ ).  $S_m$  is stable upto C, the melting pt. of monoclinic sulphur.

Curve CD is vapour pressure curve of liquid sulphur ( $S_L \rightleftharpoons S_v$ ). Curve CD can be prolonged beyond C in domain of  $S_m$  yielding the metastable vapour pressure curve of supercooled liquid sulphur.

Curve BE is transformation curve of rhombic-monoclinic sulphur ( $S_R \rightleftharpoons S_M$ ).

Curve CE represents the equilibrium between  $S_m$  and  $S_l$ . The density of liquid sulphur is less than that of monoclinic solid.

Curve EF represent melting curve of  $S_R$  ( $S_R \rightleftharpoons S_l$ ). The dotted curve EG is metastable curve of super cooled monoclinic sulphur.