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ASSIGNMENT – II

Q:① Discuss the Mechanism of anionic Polymerization using a Suitable monomer.

Ans: Anionic Polymerization mechanism involves the following step. → As in free radical Polymerization, there are initiation and Propagation steps.

$$NaNH_2 \rightleftharpoons Na^+ + NH_2^-$$

$$NH_2^- + CH_2=CH \longrightarrow H_2N-CH_2-CH:^{\ominus}$$

Propagation Proceeds in the usual manner, but there is no termination of the type that occurs when free radicals Collide.

$$\text{—}CH_2-C:^{\ominus} + CH_2=CH \longrightarrow \text{—}CH_2-CH-CH_2-CH:^{\ominus}$$

If a Solvent that is able to release a Proton is used it can react with the active site. Ammonia is an example of such a Protic Solvent and the reaction results in the formation of a negatively charged NH_2 ion. which can initiate the Polymerization of a new chain. In other words, we have chain transfer to Solvent.

$$\text{—}CH_2-C:^{\ominus} + NH_3 \Longrightarrow \text{—}CH_2-CH + NH_2^-$$

Anionic Living Polymerization

Let's Consider the Polymerization of styrene initiated by metallic Sodium in an "inert" solvent in which there are no Contaminants (i.e. there are no molecules with active hydrogens around).

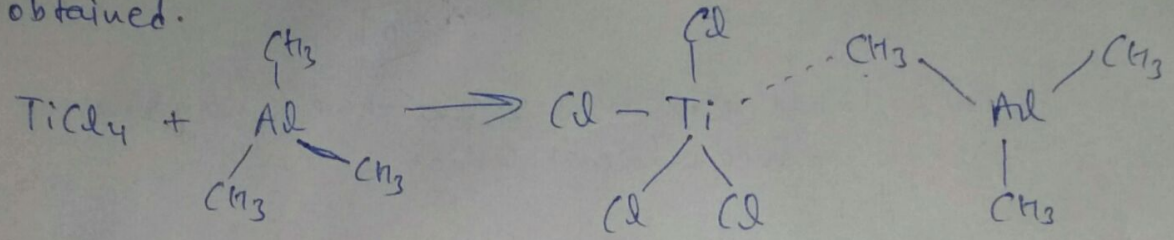
$$Na + CH_2=CH \longrightarrow CH_2-CH:^{\ominus} + Na^+$$

$$2\ CH_2-CH:^{\ominus} \longrightarrow {}^{\ominus}:CH-CH_2-CH_2-CH:^{\ominus}$$

There are a lot more interesting things about anionic Polymerization — ... effect of Polar groups, the fact that not all monomers can be used to make block Copolymers, the ability to make Certain Polymers with very narrow molecular weight distributors. and so on — [redacted]

Q:(2) Write a short note on Coordination Polymerization.

Ans: In Coordination Polymerization the Counter ion Controls the Propagation reaction by Coordinating and by orienting the monomer Propagation before ionic reaction ~~before~~ 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.



[Ziegler Natta Catalyst]

Mechanism of Coordination Polymerisation

(i) **Initiation**

$$Cat-R^1 + CH_2=CH_2 \longrightarrow Cat\cdot-CH_2-CH_2-R^1$$

(Catalyst) (Monomer)

(ii) **Propagation**

$$Cat\cdot-CH_2-CH_2-R^1 + n\,CH_2=CH_2 \rightarrow Cat\cdot-CH_2-CH_2-(CH_2-CH_2)_n-R^1$$

(iii) **Termination**

$$Cat\cdot-CH_2-CH_2-(CH_2-CH_2)_n-R^1 + HX \longrightarrow Cat\cdot-X + CH_3-CH_2-(CH_2-CH_2)_n-R^1$$

Q:(3) A Polymer has been found to Possesses the Population of various molecules, as follows:
Calculate its Number Average Molecular weight. Average Molecular weight and P.D.I. and explain the Significance of P.D.I.

Ans:

	M_i (Molecular mass)	N_i (No. of molecules)	M_i^2	$M_i \cdot N_i$	$M_i^2 \cdot N_i$
(i)	25000	12	6.25×10^8	3×10^5	7.5×10^9
(ii)	30000	10	9×10^8	3×10^5	9×10^9
(iii)	45000	30	2.025×10^9	13.5×10^5	60.7×10^9
(iv)	62000	30	3.84×10^9	18.6×10^5	115.3×10^9
(v)	100000	30	1×10^{10}	30×10^5	300×10^9
		112		68.1×10^5	492.5×10^9

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

$$M_n = \frac{68.1 \times 10^5}{112}$$

$$\boxed{M_n = 6.080 \times 10^4}$$

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

$$M_w = \frac{492.5 \times 10^9}{68.1 \times 105}$$

$$\boxed{M_w = 7.232 \times 10^4}$$

∴ Poly DisPersive Index (PDI) $= \frac{M_w}{M_n}$

$$PDI = \frac{7.232 \times 10^4}{6.080 \times 10^4}$$

$$\boxed{PDI = 1.1894}$$

Q:④ List and explain important Properties of batteries.

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 delives 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 time 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.

Q.5 Write detailed notes on:

Ans: (a) Fuel Cells

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

Fuel + oxygen ⟶ oxidation Products + electricity

One of the most successful fuels is hydrogen–oxygen fuel cell. It consist 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.

Anode: $2H_2 + 4OH^- \longrightarrow 4H_2O + 4e^-$

Cathode: $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

Net: $2H_2 + O_2 \longrightarrow 2H_2O$

The standard emf of cell

$$E^\circ = E^\circ_{oxid.} + E^\circ_{reduct.} = 0.83 + 0.40$$

$$\boxed{E^\circ = 1.23\ V}$$

Application – Hydrogen–oxygen fuel cell are used as auxilliary energy source in space vehicles (e.g. Apollo Spacecraft), sub–marines or other military vehicles.

(b) Lithium Batteries

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 cells 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 larger energy density is lithium – thionyl chloride cell. It is not sold to the consumer market. It is not rechargable. The cell contains a liquid mixture of $SOCl_2$ and $LiAlCl_4$ which acts 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

Anode: $Li \longrightarrow Li^+ + e^-$

Cathode: $MnO_2 + Li^+ + e^- \longrightarrow MnOOLi$

Net : $MnO_2 + Li \rightarrow MnOOLi$

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 alkali cells in many devices Such as clocks & Cameras. They also Prove valuable in oceanographic.

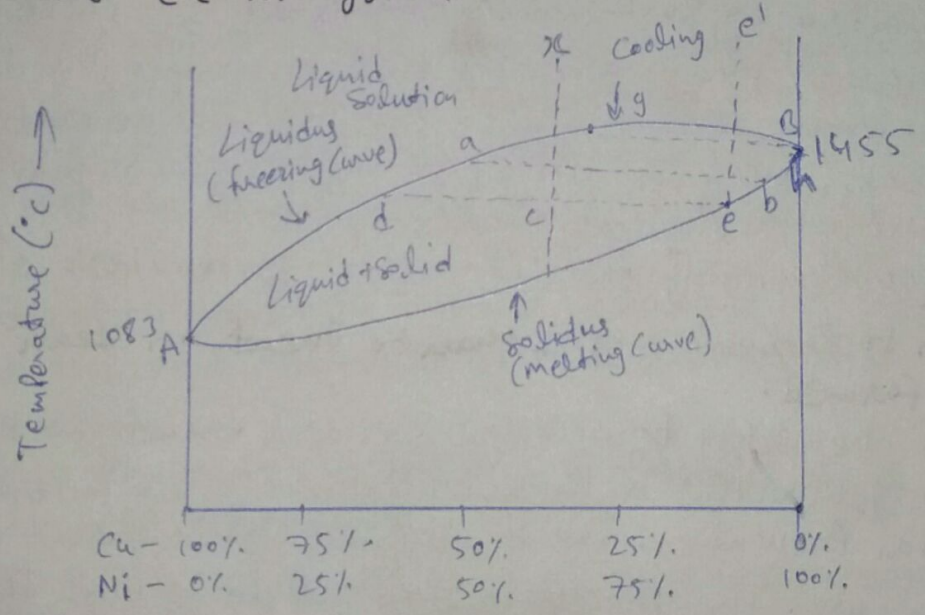
© **Electroplating** –

Electroplating is a Process that uses electric Current to reduce dissolved metal Cations so that they form a thin metal Coating on an electrode. The Process used in electroplating is Called electrode– -Position. It is analogous to a galvanic Cell acting in reverse. The Part to be Plated is the Cathode of the Circuit. In one techniques, 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. abbreviation and wear resistance, Corrosion Protection, lubricity, anesthetic qualities etc.) but also may be used to build up thickness on undersized Parts or to form objects by electroforming.

Q:⑥ What is Solid Solution? Explain the Phase diagram of a two Component Cu–Ni System.

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 ~~is~~ are respectively 1083°C & 1455°C. The addition of nickel to Copper raises the freezing Point, whereas addition of Copper to nickel depress 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 ~~the~~ form Continuous Series of Solutions, without any minimum or maximum Convergence 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 a Composition a is in equilibrium with Solid Solution of Composition b. This state of affairs happens along the Curve between the melting Points of Cu & Ni. ie. between 1083°C and 1455°C.

Any mixture of Cu & Ni in ~~molten~~ molten state represented by Point 'x' has two degrees of freedom, Since it is a 2 Component System in ~~two~~ one Phase: $F = C - P + 1 = 2 - 1 + 1 = 2$. This System ~~is~~ also 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 Concentration.

8: (7) what is Green chemistry? Discuss the Principles of green chemistry with Suitable examples.

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 chemistry 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 maximize the incorporation of all materials used in the Process into the final Product.

The Process should be so ~~redes~~ 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 Substance that Possess little or no toxicity to human ~~beings~~ 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 efficiency of function while reducing toxicity.
This Principle emphasizes designing of safer chemical. for example, Properties of Super Critical CO_2 makes it Possible to be used as a good effective Solvent.

(5) The use of auxiliary Substance should be made unnecessary wherever Possible and innocuous when used.
Developement 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 ~~non~~ 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 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 ~~so~~ some accident takes Place there should not be any damage to the environment.

Q: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.

Ans:

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

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

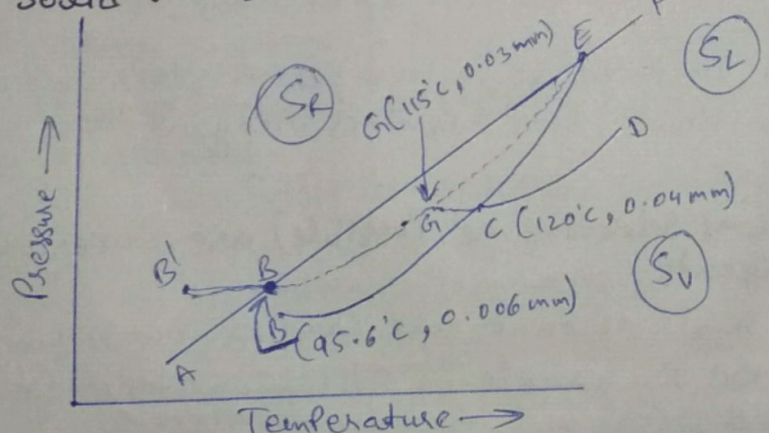
$= \frac{120.5}{102+119} \times 100$

$= 54.52\ \%$

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

Q:10 Draw the Phase diagram of Sulphur and mark the Curve showing Solid - Solid transformation.

Ans:



→ There are six stable Curves AB, BC, CD, BE, CE and EF respectively representing equilibria of two Phases 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 rhombic Sulphur ($S_R \rightleftharpoons S_v$). Curve BA ends at 50°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 Point 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.