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CHEMISTRY VT-1

(1) Give any 6 principles of green chemistry.

(Ans) 6 principles of green chemistry are :

(a) 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 imp. first step in pollution prevention. It suggests that prevention is better than cure. Eg. Metathesis is a reaction in which double bonds are broken and made between C-atoms in ways that causes atom groups to change places with help of special catalyst. It is used in development of pharmaceuticals and advanced plastic materials.

(b) Chemical products should be designed to preserve efficacy of function while reducing toxicity : Such products should be explored which retain their effective functions with simul. reduction of toxicity. (Design of safer chemical). Eg. Properties of super critical CO_2 make it possible to be used as good solvent.

(c) Use of auxilliary subs. (eg. solvents, separation agents etc.) should be made unecessary wherever possible and innocuous when used : Development of dry rxn. techniques follows this, making application of solvent redundant.

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(d) Wherever possible, synthetic methodologies should be designed to use and generate substances that possess no toxicity to humans and environment: Some toxic chemicals are replaced by safer ones, when choice exists for particular transformation. Eg. In manufacture of polystyrene foam sheet packing material, CFC's which contribute to O_3 depletion and global warming and smog, have been replaced by CO_2 as blooming agent.

(e) Energy requirements should be recognised for environmental and economic impact and should be minimised. Synthetic processes should be conducted at ambient temp. and pressure. Eg. Ionic liquids work as an excellent solvent under ambient conditions.

(f) A raw material or feedstock should be renewable rather than depleting wherever technically or economically practicable: Eg. Preparation of adipic acid has been replacement of benzene by glucose with reaction carried out in water. (Adipic acid used for production of nylon and plasticizers etc)

(2) What are green solvents? Give some examples.

Ans) • A principle of green chemistry holds that use of auxiliary substances such as solvents should be made

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unecessary wherever possible and innocuous when used. Solvents are a key priority when greening chemistry, because they are used in high volumes and are typically volatile organic compounds (VOC's) leading to high risks for large amount of waste air pollution and other health concerns.

- Finding safer alternatives is one of most effective ways to impact safety and eff. of a process. ∴ Green Solvents are environment friendly solvents or biosolvents which are derived from the processing of agricultural crops. Green solvents were developed as more friendly alternative to petrochemical solvents.
- Eg. (i) Supercritical Carbon dioxide which functions like a liquid when under pressure and at slightly elevated temp. It is used by manufacturers of laundary detergents, spray cleaners etc.

(ii) Cellulosic ethanol B. which is produced by a plant will replace ethanol derived from corn Kernels.

(iii) 1,3 - Propanediol, - used as solvent, stabilizer and enzyme carriers. It is found in environmentally friendly method brand cleaning products, including a spray cleaner and concentrated laundary detergent.

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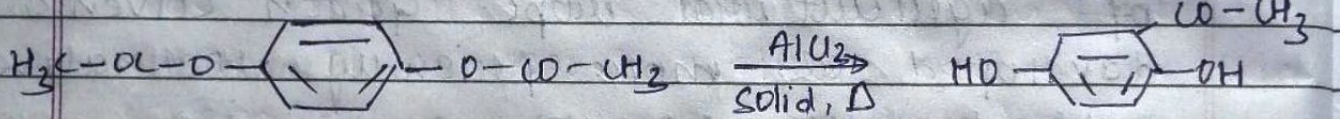
(3) Define solvent free reactions, microwave aLLicted reactions and ultrasound aLLicted reactions with suitaLLe examples.

Ans.) • Solvent Free Reactions : A solvent free or solid State rxn. is carried out in aBcence of solvent. It can be carried out using solvents alone or incorporating them in clays, zeolites, silica, alumina or other matrices.

Eg. → $NH_4NCO \xrightarrow[\Delta]{Solid} NH_2-CO-NH_2$

→ certain Friedel-crafts rxn or Fries rxn are carried out in absence of aLolvent.



• Microwave Assisted Reactions : Microwaves have wavelength of 1mm to 1m corresponding to frequencies b/w 0.3 and 300 GHz. Microwave di-electric heating uses the ability of some liquids to transform electromagnetic radiation into heat to drive chemical rxn. Such rxns are known as microwave assisted rxn.

Eg. Hydrolysis of Benzyl Chloride -

$C_6H_5CH_2Cl + H_2O \xrightarrow[3\ min]{MW} C_6H_5CH_2OH$

(Benzyl Chloride) (Benzyl Alcohol) 97%

• Ultrasound Assisted Reactions : The reactions which are carried out with the help

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of ultrasound are called ultrasound assisted reactions. The ultrasound frequencies of interest for chemical rxn are in range of about 20 – 100 KHz. The term 'sonochemistry' is used to describe the effect of ultrasound waves on chemical reactivity.

Eg. → Esterification:

$$RCOOH + R'OH \xrightarrow[\text{)))}]{H_2SO_4,\ \Delta} RCOOR'$$

→ Nitriles can be hydrolysed to carboxylic acids under basic condition on sonication.

$$ArCN \xrightarrow[\text{)))}]{OH^-,\ H_2O} ArCOOH.$$

(4) Define total hardness, temporary hardness, and permanent hardness of water. What are the units used for indicating hardness of water?

ding Ans.) • Hardness: It is the characteristic of preventing lather formation of water with soap. Generally salts like chlorides, bicarbonates and sulphates of Ca^{2+}, Mg^{2+}, and Fe^{2+} make water hard. This hard water of treatment with soap causes white ppt formation.

$$2\,C_{17}H_{35}COONa + CaCl_2 \longrightarrow (C_{17}H_{35}COO)_2Ca + 2NaCl$$

(soap) → calcium stearate (insoluble)

• Temporary hardness: It is the hardness due to bicarbonates of Ca^{2+} and Mg^{2+}

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and carbonate of Fe^{2+}. Since bicarbonates readily get precipitated on boiling the water temp. hardness can be easily removed.

$$Ca(HCO_3)_2 \xrightarrow{heat} CaCO_3 \downarrow + H_2O + CO_2$$

insoluble

- Permanent Hardness : It is due to presence of chlorides and sulphates of Ca, Mg, Fe etc. Permanent hardness can't be removed easily on boiling.
- Both temporary and permanent hardness are expressed in "ppm as $CaCO_3$. The" choice of $CaCO_3$ is due to the fact that its mol. wt. is 100 and eq. wt. is 50 and it is most insoluble salt.
(ppm ≡ parts per million).

(5) Discuss TGA with principle, instrument and its applications.

- Thermal analysis is the analysis of change in property of a sample, which is related to imposed change in the temperature. The analysis of change in the mass of a sample on heating is known as Thermogravimetric analysis (TG).
- In TGA mass of substance is measured as function of temperature while it is subjected to a controlled temp. program. The resultant is the TG curve or thermogravimetric ; time (t) or Temp. (T) is plotted on X-axis which ↑ from

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left - right whereas mass is plotted on y- axis which ↓ downwards.

- **PRINCIPLE**: The basic principle underlined here is that as a sample is heated, its mass changes. This change can be utilised to determine the foremost the composition of a material or its thermal stability upto 1000°C. The sample which is analyzed loses wt as it is heated up which may be due to chemical phenomena like decomposition, reduction etc. In some cases sample would also gain wt due to oxidation or absorption from atmosphere.

- **WORKING / INSTRUMENTATION**: → Samples are placed in crucibles / shallow dish / basket which is positioned in furnace on a quartz beam attached to recording balance.
  → Quartz beam is maintained at NULL pos. by current flowing through the transducer of electromagnetic balance.
  → Movement of beam is maintained through photosencitive diodes. Any change in wt is detected through deflection in beam sensed by photodiodes. The current is proportional to the change in wt of sample. Heating rates are usually 5-10°C/min. Amt of sample ranges from 1-200 mg.

- **Applications**: → Thermal stability of substance
  → Decomposition mechanism of inorganic salts.

→ Composition, purity and moisture content can also be measured.
→ Estimated lifetime of product.

(6) Discuss IR spectroscopy with principle, instrumentation and its applications.

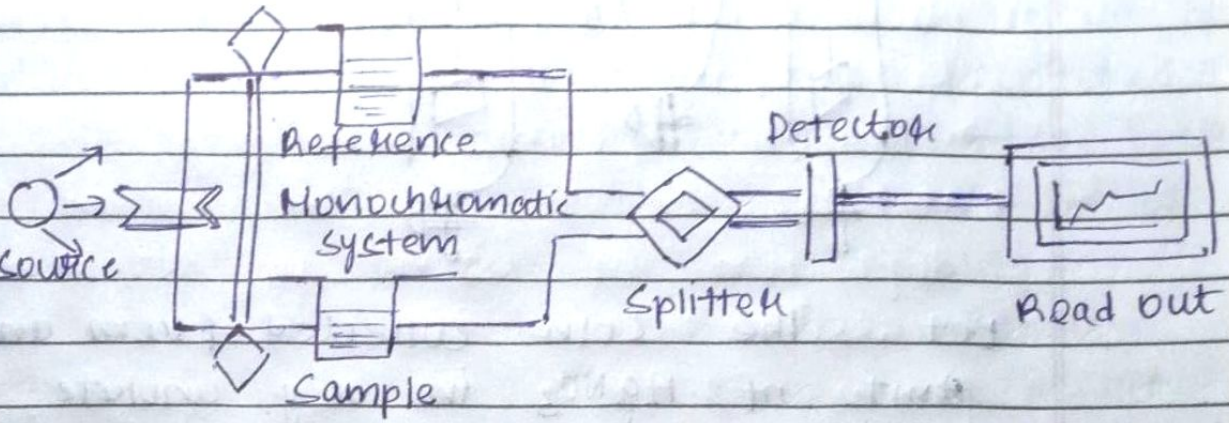
Ans) • IR spectroscopy deals with infra-red region of the electromagnetic spectrum. It generally refers to the analysis of the interaction of a molecule with IR light.

• An IR spectrum is generally a graph plotted with IR light absorbed on the Y-axis against frequency or wavelength on X-axis. It detects frequencies of ~~molecule~~ IR light that are absorbed by a molecule.

• PRINCIPLE : IR spectroscopy theory utilises the concept that molecules tend to absorb specific frequencies of light that are characteristic of corresponding structure of the molecules. The energies are reliant on the shape of the molecular surfaces, the associated vibronic coupling, and mass corresponding to the atoms. For instance, the molecule can absorb the energy contain in the incident light and the result in faster rotation.

• INSTRUMENTATION: First, a beam of IR light from source is split into two and pass through the reference and the sample resp. Now, both of these beams are reflected to pass through a detector. Finally the read. reading is printed out

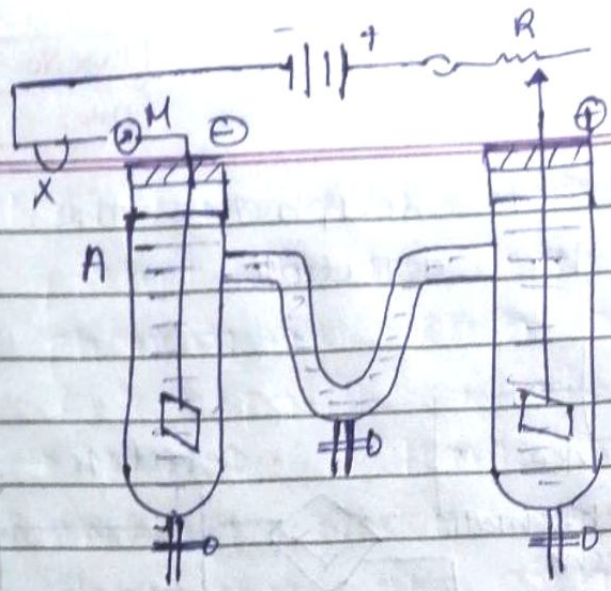
after the processor deciphers the data passed through the detector.



- Applications: → Identification of functional group and structure elimination.
→ Identification of substances
→ Detection of impurities
→ Quantitative Analysis

(7) Give Hittorf's method for determination of Transport Numbers.

- Two broad vertical glass tubes A, B are connected in the middle by a 'U' tube 'C'. The three tubes are fitted with stopcocks.
- The tubes are fitted with silver plates which act as anode and cathode which are introduced into A and B. A dilute $AgNO_3$ soln ($N/20$) is taken for electrolysis. A current 0.01 to 0.02 A is passed for 2–3 hrs.
- A miliammeter M, voltmeter X are connected in series. After a definite time, the current is stopped. The soln from anode compartment is taken for analysis.



Let, The coln collected from anode (Anolyte) = x g
Amt. of $AgNO_3$ in x g anolyte = y g
Amt. of water containing y g $AgNO_3$ = (x − y) g
$AgNO_3$ present in (x − y) g of water before electrolysis = z g
Wt. of silver deposited on cathode in coulometer = W g
Increase in wt of $AgNO_3$ in anode comp. due to dissolution of silver from the anode = $\frac{W \times 170}{108} = W$ g

If no migration would have take place, total wt. of $AgNO_3$ should have been present (x − y) g of water in anode comp. = (W + z) g
Actual wt of $AgNO_3$ present = y g
Loss due to migration = (W + z) − y
= W − (y − z)

$$t_{Ag^+} = \frac{W - (y - z) \times 108}{170 \times W}$$

$$t_{NO_3^-} = 1 - t_{Ag^+}$$

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(8) Describe the causes and effects of Greenhouse effect and global warming.

- Greenhouse effect is the process by which radiations from the sun are absorbed by greenhouse gases and not reflected back into space. This insulates the surface of earth and prevents it from freezing.
- Greenhouse gases are gases that absorb IR radiations and create greenhouse effect. Eg. CO_2, CFC's
- CAUSES : → Burning of Fossil Fuels releases CO_2.
  → Deforestation : Due to cutting of trees there is considerable increase in greenhouse gases.
  → Nitrous oxide used in fertilizers is also one of the contributors.
  → Industrial waste and landfills
- EFFECTS : → Global Warming - It is the phenomena of gradual ↑ in avg. temp of Earth's atmosphere. The main causes for this environmental issue is increased volumes of greenhouse gases.
  → Depletion of ozone layer.
  → Smog and Air pollution
  → Acidification of water bodies.

(9) What are natural and man-made causes for destruction of ozone layer ?

- The chemicals responsible for ozone layer depletion are called ozone Depleting substances (ODS).

- NATURAL CAUSES: → Ozone layer has been found to be affected by certain natural phenomena such as sun-spots and stratospheric winds.
→ Major volcanic eruptions.
- MANMADE CAUSE: → The main cause for depletion of ozone is determined as excessive release of chlorine and bromine from CFC's. CFC's, halons, CH_3CCl_3, CCl are found to have direct impact on depletion of ozone layer.
→ CFC's are highly volatile and non combustible so they are very quickly evaporated and can easily reach in stratosphere where ozone is present here they start depleting ozone molecules.
→ Other causes are unregulated launches of rockets, global warming and nitrogenous compounds.

(10) What are new emerging trends in green chemistry ?

Ans:- • Oxidative chemical agents and catalysts: Many of catalysts and reagents are composed of metals. Since these substances are employed in massive volumes, metals are discharged in environment. These may be substituted by more eco-friendly substances.
- Computational chemistry: Branch of chem. that uses computers simulation to assist in solving chemical problems

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- Proliferation of solventless rxn: Eg. Microwave heating and ultrasonication techniques. This helps in dev. of product isolation, separation and purification that may be solventless.
- Use of green solvents and environmental conditions for carrying out rxns - Rxn. that take place at room temp. conditions or ambient condn. Such as presence of sunlight or UV rays are much preferred over those requiring lab set ups.