Green chemistry

- volatile organic solvents, polymers, dry cleaning, agriculture, use of detergents, and so on, which creates different kind of pollutions.
- Mankind cannot survive without using many of these toxic chemicals to make their life more comfortable even at the cost of their health.
- Therefore, there is a pressing demand all over the world to either reduce the use of more toxic materials or to replace them with less toxic or less harmful alternates.
- This can be achieved by transforming from gray chemistry to green chemistry.

Green chemistry

- The term green chemistry was used first by Paul T. Anastas in the beginning of last decade of 20th century.
- The green chemistry is in no way different from gray chemistry except that the approach toward a chemical process, may be manufacture design, and applications.
- Green chemistry is totally different from environmental chemistry.
- In environmental chemistry, one takes care of the kind of pollution, extent of pollution, and methods to combat against this pollution,

Green chemistry

- Whereas, green chemistry takes care of all these factors in advance (beforehand).
- It is something like (diagnosis of any disease and its treatment = environmental chemistry),
- while,
- (prevention from that disease = green chemistry).
- There is a well-known proverb that "Precaution is better than Cure".
- Prevention is a green chemical pathway while cure is an environmental pathway.

Green chemistry

- Green chemistry utilizes a set of 12 principles (mentioned before) that either reduces or eliminates the use or generation of any hazardous substance in designing, manufacture and application of chemicals.
- This is as approach, which is based on reducing the amount of waste generated at source rather than treating this waste after it has been formed.
- Chemists are normally blamed for creating pollution, but the green chemical approach not only solve the problem of pollution but it will also provide the methods to synthesize or utilize substances in an eco-friendly manner.

Green chemistry

- Green chemical approach is holistic (all-inclusive) in nature and encompasses almost all the major branches of chemical science, such as organic or inorganic synthesis, catalysis, drug discovery, material science, polymer, nanochemistry, supramolecular chemistry, treatment of waste water, and so on. Green chemistry has synonyms such as:

1. Clean chemistry
2. Atom economy
3. Benign by design chemistry
4. Eco-friendly chemistry
5. Environmentally benign chemistry
6. Sustainable Chemistry and also 7. E-Chemistry.

- Benefits of green chemistry:
- Improved health: Reducing exposure to hazardous chemicals can protect human health and prevent diseases.
- Environmental protection: Minimizing pollution and preserving ecosystems for future generations.
- Economic sustainability: Creating more efficient and sustainable processes can lead to long-term economic benefits.

Green chemistry

- Atom economy is an important concept in philosophy of green chemistry.
- It is important to utilize maximum number of atoms of the reactant to minimize the generation of waste products.
- It is defined as atom economy in green chemistry, meaning by one has to be economic in use of atoms.
- The atom economy is defined as:

$$\%\,\text{Atom Economy} = \frac{\text{Molecular weight of desired product}}{\text{Molecular weight of all reactants}} \times 100\%$$

Green chemistry

- Addition reactions and rearrangements are normally follow atom economy but the chemistry is not complete with only these reactions, hence, some substitution and elimination reactions are also required; thus, generation of wastes is bound to be there but the efforts of the chemists should be to produce minimum byproducts.
- "Gray" process can be made "Green" by making a judicious selection of green substrate, ***green solvents***, green reagents, green catalysts, green conditions, and so on, to synthesize a green product.

Green chemistry

Some examples of atom economy are;

A. Addition Reactions:

- Hydrogenation of alkenes: Adding hydrogen to an alkene to form an alkane. For example, the hydrogenation of ethylene to form ethane has a 100% atom economy.

$$CH_2{=}CH_2 + H_2 \rightarrow CH_3\text{-}CH_3$$

- Hydrohalogenation of alkenes: Adding a hydrogen halide (e.g., HCl, HBr) to an alkene. This reaction also has a 100% atom economy.

$$CH_2{=}CH_2 + HCl \rightarrow CH_3\text{-}CH_2Cl$$

Green chemistry

B. Green Chemistry Processes:

- Catalytic processes:
- Using catalysts to accelerate reactions and minimize byproducts. For example, the use of enzymes in biocatalysis can often lead to high atom economies.
- Solvent-free reactions:
- Conducting reactions without solvents to reduce waste.
- Renewable feedstocks:
- Using renewable resources instead of fossil fuels as starting materials.

Green chemistry

C. The Diels-Alder reaction, a [4+2] cycloaddition reaction. It has gained significant attention in green chemistry due to its atom economy, high selectivity, and mild reaction conditions.

Examples of Diels-Alder Reactions in Green Chemistry

Water as a Solvent:

1. Advantages: Water is abundant, non-toxic, and environmentally friendly.
2. Example: The reaction between cyclopentadiene and maleic anhydride in water to form the Diels-Alder adduct.

Green chemistry

- Ionic Liquids as Solvents:
- Advantages: Ionic liquids are often recyclable, non-volatile, and can be designed to be more environmentally friendly than traditional organic solvents.
- Example: Using imidazolium-based ionic liquids as solvents for Diels-Alder reactions between dienes and dienophiles.
- Solvent-Free Conditions:
- Advantages: Eliminates the need for solvents, reducing waste and environmental impact.

Green chemistry

- Example: Grinding reactants together in a ball mill to promote the Diels-Alder reaction without solvent.
- Microwave-Assisted Diels-Alder Reactions:
- Advantages: Can significantly reduce reaction times, improve yields, and minimize energy consumption.
- Example: Using microwave irradiation to accelerate Diels-Alder reactions between dienes and dienophiles.

Green chemistry

- Biocatalyzed Diels-Alder Reactions:
- Advantages: Enzymes can provide high selectivity and stereoselectivity, reducing waste and improving efficiency.
- Example: Using enzymes to catalyze Diels-Alder reactions between dienes and dienophiles.
- Flow Chemistry:
- Advantages: Enables precise control over reaction conditions, minimizes waste, and can be easily scaled up or down.
- Example: Conducting Diels-Alder reactions in a continuous flow reactor using a microfluidic device.

Green chemistry

- E-factor is a metric used in green chemistry and process engineering to assess the environmental impact of a chemical manufacturing process.
- It's calculated the actual amount of waste, defined as "everything but the desired product" produced per kg of product, including
- Byproducts
- Leftover reactants
- Solvent losses
- Spent catalysts and catalyst supports
- Other materials considered waste

Green chemistry

- The E-factor has been applied to different industrial sectors and it was shown that the proportion of waste generated by pharmaceuticals production was much greater than fine or bulk chemicals production.
- GlaxoSmithKline plc (GSK) has estimated that more than 70% of the waste associated with pharmaceutical production is solvents.
- This can be attributed to the greater number of steps in the synthesis of a complex pharmaceutical.
- Process mass intensity (PMI) also shown that the number of isolations of intermediate products that leads to large amounts of solvent waste

Green chemistry

- Significance of E-factor

Lower E-factor: Indicates a more environmentally friendly process, as less waste is generated per unit of product.

- Higher E-factor: Suggests a less sustainable process, with more waste produced.
- Factors Influencing E-Factor
- Reaction efficiency: Higher yields reduce waste.
- Solvent choice: Less volatile or less toxic solvents can minimize waste.
- Process design: Optimized processes can reduce byproducts and energy consumption.
- Waste management: Efficient waste treatment and recycling can reduce overall impact.

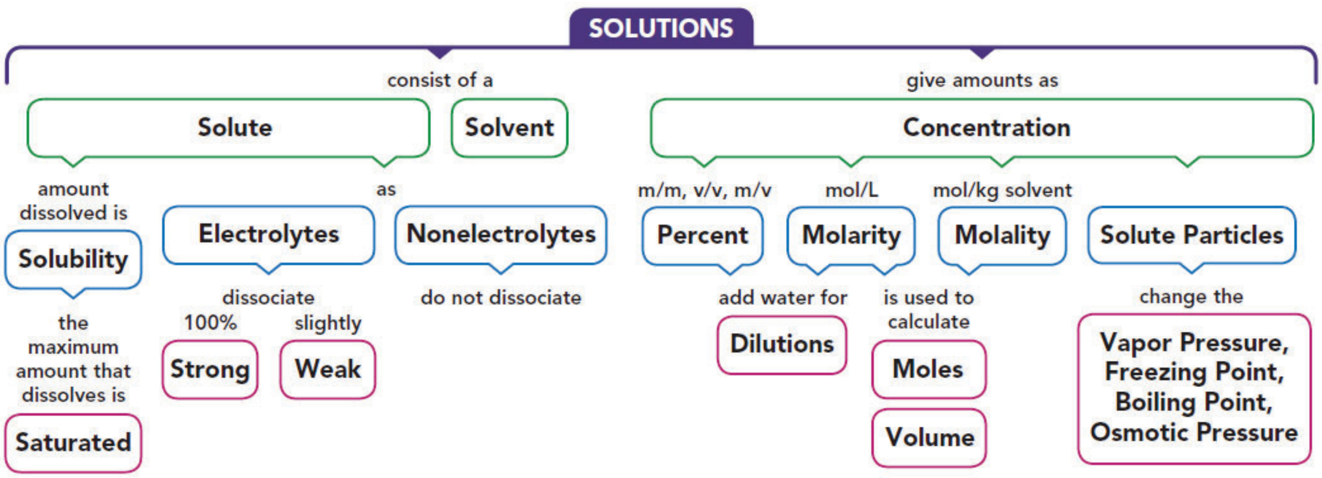
- Principles of green chemistry are beautifully condensed as PRODUCTIVELY:

Principles of Green Chemistry:

P – Prevent wastes
R – Renewable materials
O – Omit derivatization steps
D – Degradable chemical products
U – Use safe synthesis methods
C – Catalytic reagents
T – Température and pressure ambient
I – In-process monitoring
V – Very few auxiliary substances
E – E-factor, maximize feed in product
L – Low toxicity of chemical products
Y – Yes, it's safe

Solutions

Whenever a homogeneous liquid mixture is present, there is a solvent. The solvent is the major component of the liquid mixture (solution) and it is usually a liquid under the conditions described when pure. The minor components of the solution are the solutes.



Predicting Solubility

- The dividing line between soluble and insoluble is arbitrary, but the following are common criteria for describing substances as insoluble, soluble, or moderately soluble.

1. If less than 1 gram of the substance will dissolve in 100 milliliters (or 100 g) of solvent, the substance is considered insoluble
2. If more than 10 grams of substance will dissolve in 100 milliliters (or 100 g) of solvent, the substance is considered soluble
3. If between 1 and 10 grams of a substance will

Predicting Solubility

- dissolve in 100 millilitres (or 100 g) of solvent, the substance is considered moderately soluble.
- Although it is difficult to determine specific solubilities without either finding them by experiment or referring to a table of solubilities, we do have guidelines that allow us to predict relative solubilities

Predicting Solubility

1. Polar substances are likely to dissolve in polar solvents. For example, ionic compounds, which are very polar, are often soluble in the polar solvent water
2. Nonpolar substances are likely to dissolve in nonpolar solvents. For example, nonpolar molecular substances are likely to dissolve in hexane, a common nonpolar solvent.

- Two additional guidelines are derived from these:

1. Nonpolar substances are not likely to dissolve to a significant degree in polar solvents. For example, nonpolar molecular substances, such as hydrocarbons, are likely to be insoluble in water.

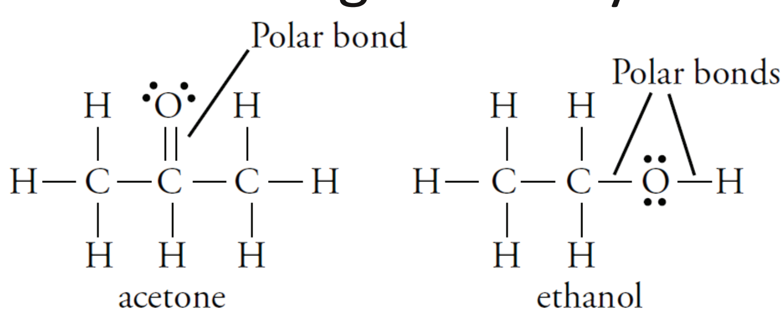
Predicting Solubility

1. Polar substances are not likely to dissolve to a significant degree in nonpolar solvents. For example, ionic compounds are insoluble in hexane

- It is more difficult to predict the solubility of polar molecular substances than to predict the solubility of ionic compounds and nonpolar molecular substances.
- Many polar molecular substances are soluble in both water and hexane. For example, ethanol is miscible with both water and hexane.
- The following generalization is helpful:

1. Substances composed of small polar molecules, such as acetone and ethanol, are usually soluble in water. (They are also often soluble in hexane.)

Predicting Solubility



- The guidelines we have discussed are summarized in this Table;

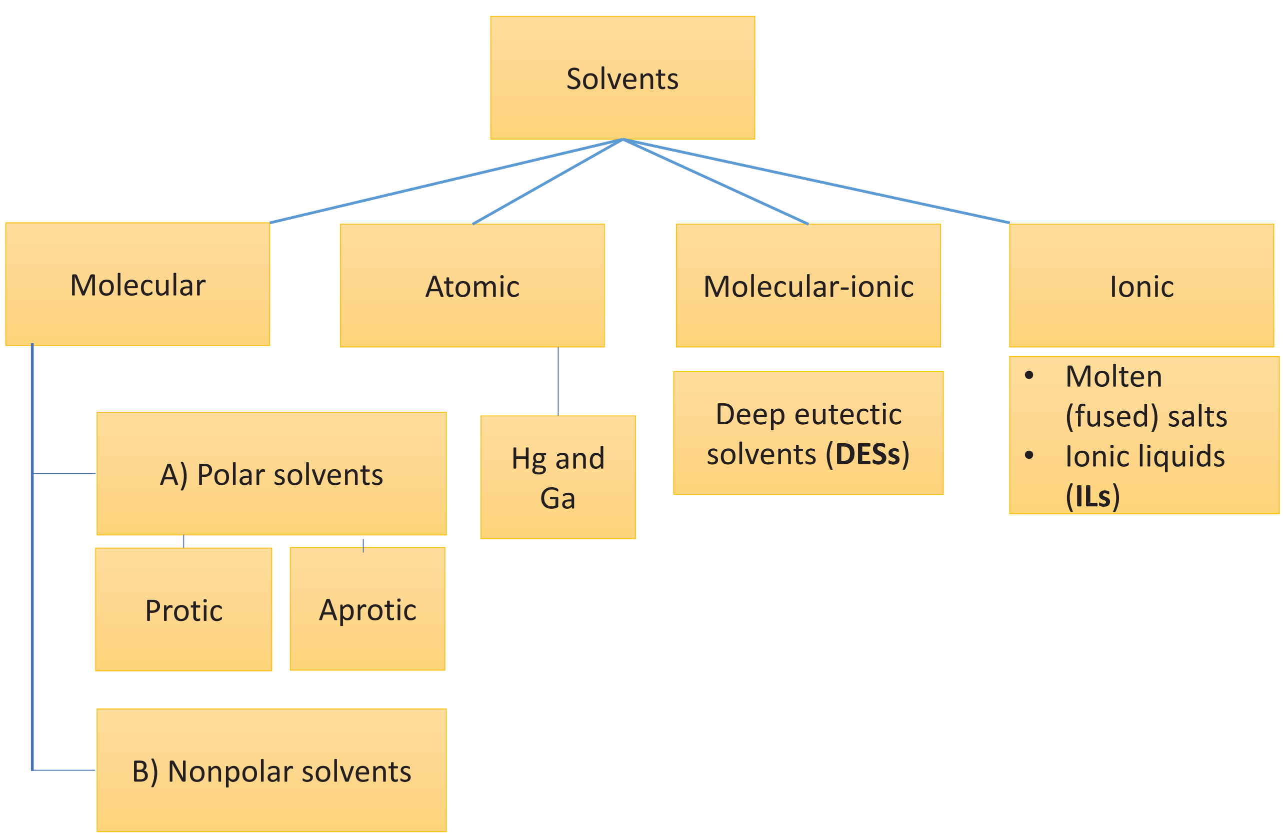
Summary of Solubility Guidelines

Type of substance	**Soluble in water?**	**Soluble in hexane?**
Ionic compounds	Often	No
Molecular compounds with nonpolar molecules	No	Yes
Molecular compounds with small polar molecules	Usually	Often

What are solvents?

- Solvents are substances that dissolve other material(s) to form a homogeneous solution.
- Common solvents are liquid at room temperature but can also be solid (e.g., molten salts) or gaseous (e.g., carbon dioxide).
- Solvents are either molecular (covalent bonds), ionic (ionic bonds), molecular-ionic (ionic and intermolecular forces) or atomic (metallic bonds) solvents.
- Next two Figures are showing simple classification of different solvents.

Types of solvents?

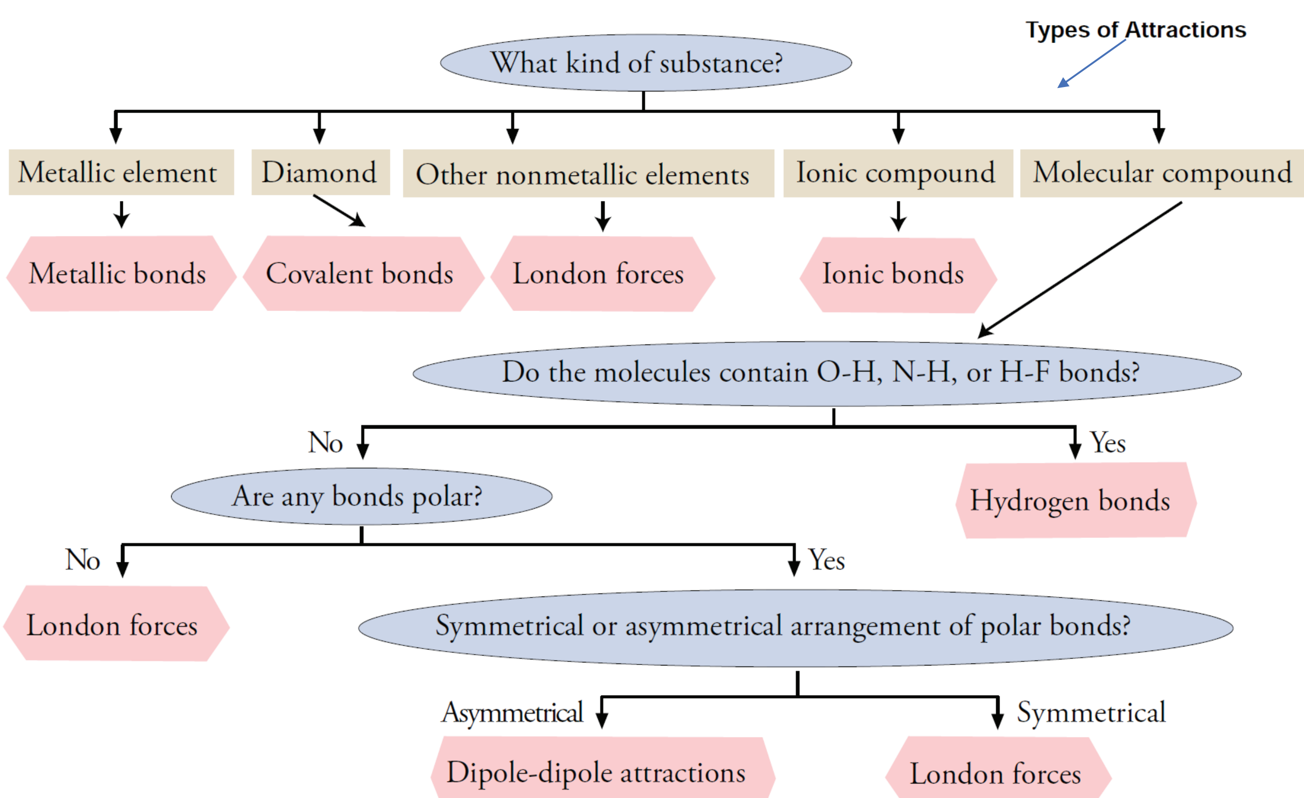


Types of solvents?

Molecular solvents

- A) Organic solvents
  - 1) Oxygenated solvents
  - 2) Halogenated solvents
  - 3) Hydrocarbon solvents
- B) Inorganic solvents
  - Aqueous solvent and other aqueous solvents containing additives

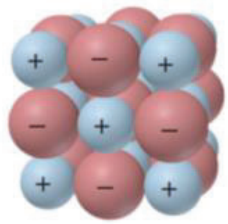
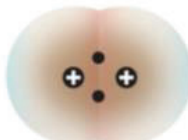
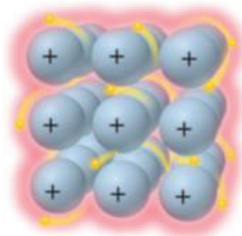
What are Intermolecular forces?



Scheme for predicting types of attractions.

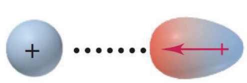
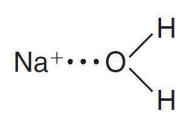
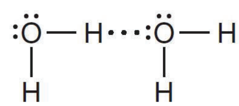
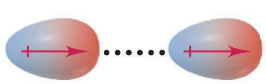
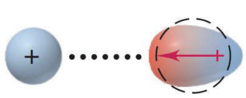
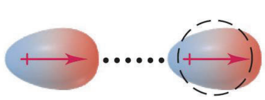
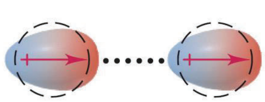
What are Intermolecular forces?

Comparison of bonding and nonbonding (intermolecular) forces

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Bonding				
Ionic		Cation–anion	400–4000	NaCl
Covalent		Nuclei–shared e^- pair	150–1100	H—H
Metallic		Cations–delocalized electrons	75–1000	Fe

What are Intermolecular forces?

Comparison of bonding and nonbonding (intermolecular) forces;

Force	Model	Basis of Attraction	Energy (kJ/mol)	Example
Nonbonding (Intermolecular)				
Ion-dipole		Ion charge–dipole charge	40–600	
H bond	δ– δ+ δ– —A—H·······:B—	Polar bond to H–dipole charge (high EN of N, O, F)	10–40	
Dipole-dipole		Dipole charges	5–25	I—Cl···I—Cl
Ion–induced dipole		Ion charge–polarizable e^- cloud	3–15	Fe^{2+}···O_2
Dipole–induced dipole		Dipole charge–polarizable e^- cloud	2–10	H—Cl···Cl—Cl
Dispersion (London)		Polarizable e^- cloud	0.05–40	F—F···F—F