Principles of Chemistry

CHEM 118

Lec.
Green Chemistry

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25/12/2023

Lecture's outline

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2	Green chemistry	
3	Climate changes	
4	Environment vs Economy	
5	12 principles of Green Chemistry	

Introduction

- Any thing around us is matter thus, chemistry study its composition or changes.
- Green chemistry is alternating approach for **future study of matter and its affect on human health and environmental** issues based on designing safer **products** and industrial **processes** and systems in an efficient and economical way associated with materials and energy benefits.
- It is useful to understand of **chemicals, their transformation and their role in society** and economy moreover, to distinguish if chemical product is green and sustainable or not.

Chemicals related accidents

Although chemicals have many benefits but they are the main cause of accidents in particular:

CO **1-CO:** it is colorless and odorless , can cause headache, sudden death and high rate of fatalities.

NH_3 **2-Ammounia:** colorless with strong smell, can cause sudden death and it used as fertilizer and refrigerant.

Cl **3-Chlorine:** colorless gas with strong smell, used in many industries, PVC, foam, paper industries and swimming pools.

4- HCl: highly corrosive to human skin, used in dyes, plastic and fertilizers most problem during transportation.

H_2SO_4 **5-Sulfuric acid:** highly corrosive, used in explosives, purify petroleum and metal processing, most accidents due to equipment failure.

- some of latest accidents were in the Tianjin (2015) and Beirut (2020) ports that causes series of explosive due to improper storage conditions for hazardous materials (Ammonium nitrate, Sod. Cyanide and Cal. Carbide)

Harmful consumer's products

Some examples of **harmful product for our daily use** such as:

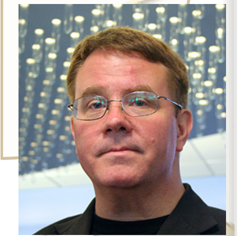
- **Bisphenol A & S (BPA)/ (BPS):** it is widely used as cross-linker in packaging industry and it is hormone disrupter.
- **NPEs:** found in cleaner and paints.
- **Triclosan:** used as pesticide.
- **PFCs:** found in stain and water resistant fabrics.
- **Phthalates:** found in plastic and floor resisting materials.
- **Parabens:** found in preservatives in pharmaceuticals and cosmetics.
- **Organotins:** found in biocide and pesticides.
- **PCBs:** no longer manufactured.

N.B. Most of people have synthetic chemical in our blood.

Fixing the problems

It is not easy to find a way to solve immediately the problems as sometimes it ended up by unintended consequences.

- Some factors may affect our solutions such as in the industrial era the rapid increase in population that increase the need for many resources like increase in water use, primary energy use, water use, transportation, paper production, (CO_2 &CH_4) emissions and tropical forest loss.
- Replacing of ammonia with non toxic and non-flammable CFCs as refrigerant but later, it CFCs causing ozone layer depletion.
- Photovoltaic cell is an excellent source of energy but it made from rare, precious and toxic metals.



Green chemistry

It defined by its the Co-founder **John Warner** as "*It is revolutionary approach to the way that products are made, in which it aims to reduce or eliminate the use and /or generation of hazardous substances in the design phase of materials development*".

12 principles of Green Chemistry	
1- Waste prevention.	7- Use of renewable feedstock.
2- Atom economy.	8- Reduce derivatives.
3- Less hazardous chemical synthesis.	9- Catalysis.
4- Design safer chemical.	10- Design for degradation.
5- Safer solvents and auxiliaries.	11- Real-time analysis for pollution prevention.
6-Design for energy efficiency.	12- Inherently safer chemistry for accident prevention.

The 12 principles address the following benefits:

- **Toxicity:** reducing the hazard in particular to humans,
- **Feedstock (Raw material):** use of renewable resources,
- **Designing safer products:** non-toxic products by design,
- **Scientific innovation**: fundamental new understanding (it means to think that hazard is a flaw of the design process).
- **Energy:** reducing the energy needs,
- **Accidents:** eliminating accidents,
- **Efficiency:** shorter processes (synthesis) thus could boost economy.
- **Sustainability**: products made from renewable resources,

生物可降解性

- **Biodegradability:** enhancing breaking down at the end of life and won't be persistent in environment,

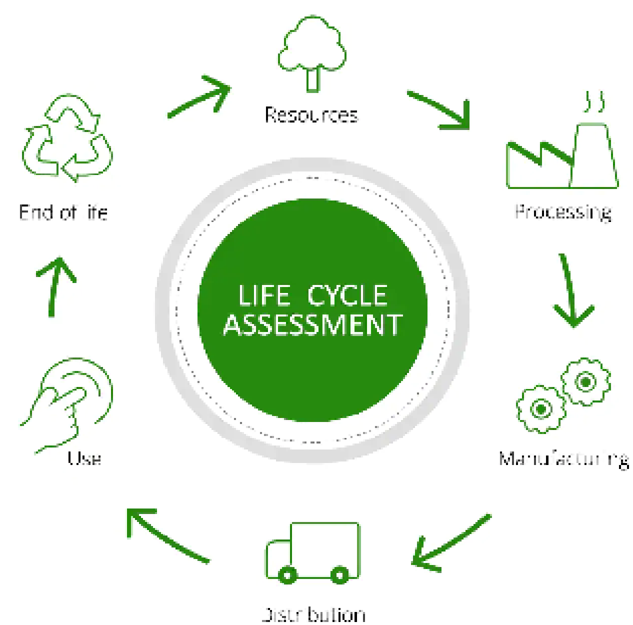
Hence, green chemistry is focusing on **design feature for more sustainable chemistry** includes (safer design, waste & accidents prevention, reducing cost & energy, enhancing performance, innovative and atom economy) moreover, to enhance the avoidance of unintended consequences, limit the effects of climate changes

- The traditional approach to hazards on **reducing risk by minimizing exposure** for example wearing PPEs or ventilation for volatile hazard. While, green chemistry focuses on no hazard so exposure becomes irrelevant.

$$Risk = \boldsymbol{Hazard} \times \boldsymbol{Exposure}$$

time and concentration

- **The final product** of any chemical process in the green approach is **not** our sole target we look for every step even after it consumed "*The cradle to grave approach*" by considering all the factors in the processing and usage or disposal of the product.



Climate changes

- **The main cause of it** is the generation of greenhouse gas (GHG) emissions.
- GHS **sources**: are electricity, transportation, industry, commercial, residential and agriculture activities.
- **Climates change causes:**

Temperature change, raising CO_2 levels and depleting natural source (fossil fuel).

- **Contribution to cumulative emission reduction:**

Avoid deforestation, reduce other GHG, reduce other energy-related emissions, increase bio-energy, increase solar and wind power, increase CO_2 capture and storage and improve energy efficiency

Environment vs Economy

- Economical growth and environmental protection are often seen to be on two different roads.
- Green chemistry seeks to merge them in order to be as two crossing paths.
- Green chemistry is used in many industries: automobile, agriculture, cosmetics, electronics etc. It is predicted that its market size will be increased for it.

The cost of using hazardous materials:

it costs a lot such as:

- Storage,
- Transportation,
- Treatment,
- Disposal,
- Regulatory costs,
- Liability,
- Worker health and safety,
- Corporate reputation,
- Community relations,
- New employee recruitment.

1-Waste prevention

- **Dealing with** wastes can be (treatment, control and disposal).
- It is highly recommended to **avoid the production of waste** in the first place than to treat it, by creating new design of the process or to find alternatives of reactants, use catalysis to ensure almost a complete reaction.
- Other mechanisms to deal with end-of-pipe problems:
- Continuous pollutant monitoring,
- Hazardous waste clean up,
- Developing of **standard and regulation for waste management** including:
  - Air emission,
  - Releasing pollutant to water sources,
  - Land disposal.

Suggestions for waste prevention

- Currently, Industries produce/synthesize chemical then creates waste after that, clean up hence, a better design in term of green chemistry is needed.
- Material selection must be based on their hazardous such as solvent/reagent,
- Stop searching for the cost (performance measure) not the hazard,
- Persistence of chemicals is a major concern in order to avoid using them.

$$A + B \rightarrow C + Waste$$

- **E-factor:** a simple calculation for **how much waste in chemical industries** divided over the final products (small number will be good but keep in mind the annual production of the industry).

$$E - factor = \frac{mass\ of\ waste}{mass\ of\ products}$$

- **Revalorization (adding value)** is defined as make useful of wastes into energy and other materials.

Useful examples:

- ✓ In pharmaceutical is the selection of new solvent, recovery of solvents and redesign the process to minimize the quantity of solvent.
- ✓ Producing chemicals from petroleum like phenol as it depleting resources so from biomass (wooden materials) like lignin as starting material and adding hydrogen gas.
- ✓ Ethylene oxide used to produce ethylene glycol, fumigant (kill insects) also sterilize medical equipment but it uses chlorine which produces $CaCl_2$ as by product e-factor 5 kg so new route is to use molecular oxygen instead of chlorine.

- Designing of new processes or products with reduced hazards at the discovery phase of them.

For example: dyeing industry consumes massive amount of water and chemicals and it was naturally produced from plants and animals until **Perkin** discovered a synthetic dye Mauve named by purple plant then the market now is no longer for any natural dyes.

- Much of wastewater from industry is dumbed untreated into water bodies contains a lot of pollutants and then it spreads out around the globe.
- Nowadays, structural colors are innovated that inspired by a butterfly and based on varying thickness and structure of fibers.

2-Atom economy

- Synthetic methods (processes) should be designed to be incorporate all the raw materials to be in the final product.
- In this way; **less wastes** will be generated and It is a way of calculation to the efficiency of the chemical reaction.
- For example: expoidtion of styrene and synthesis of ibuprofen as pain killer.

3- less hazardous chemical synthesis

- Chemical process should be designed to produce new substance with less or no toxicity to human health and the environment.
- Starting from non-toxic substance or less hazardous substances.
- Cascade, tandem, metathesis and enzymatic reactions are examples of cleaner routes.
- Ex; prepare adipic acid using bio-catalytic reaction.
- Bleaching of paper (lignin is brown) by using **chlorine dioxide (ClO_2)** it produced a lot of chlorinated pollutants which discharge into water. **But**, using **hydrogen peroxide** (the by-product is water and process can be operated at low time and low heat).

4-Design safer chemicals

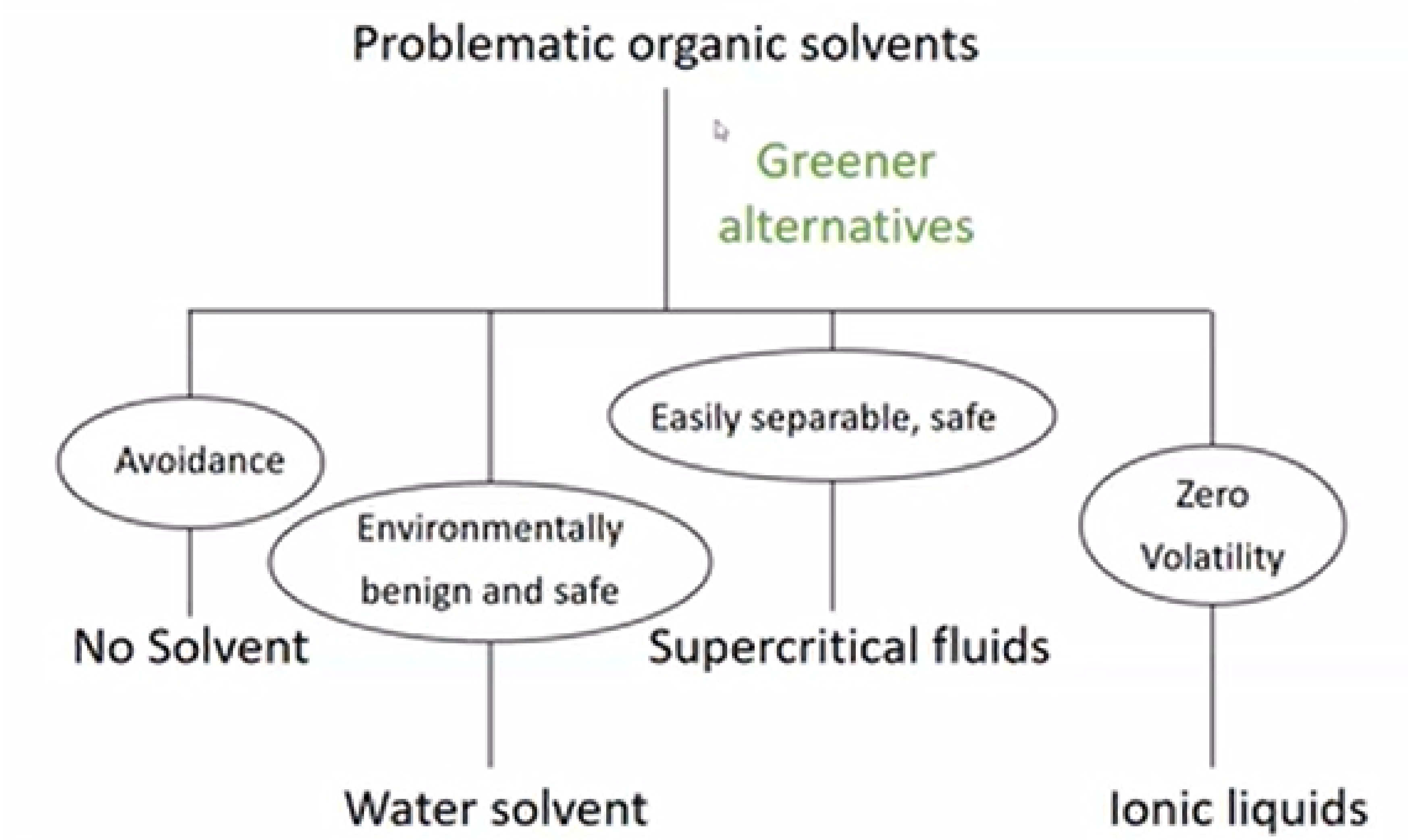
- Chemicals should be produced to provide efficacy of the function with less toxicity.
- In the beginning people interested in the function not on the hazardous but later think about molecule and assessed if it is toxic or not based on the dose so reducing toxicity mean reduce the risk.

$$Risk = Hazard \times Exposure$$

- Hazardous can be toxicological (carcinogenic chemicals) or physical property (flammable) or chemical property (solubility in organic solvents).
- As a chemist features we can tailor to achieve the goal like log Kow means (octane – water) portioning coefficient to measure where the substance is hydrophilic or hydrophobic, volatility, aspect ratio, reductant or oxidant, nucleophile or electrophile.
- Also minimize or eliminate hazards functional groups.
- Minimize or eliminate bioavailability of chemical hence, the body will not absorb it.

5- Safer solvent and auxiliaries

- Thinks about other stuff than reactant and products for the devices, extra-substance for extraction etc.
- Should be innocuous (not harmful) as they are organic volatile, flammable, toxic and pollute air, land and water.
- Recovery and reuse of them are associated with energy (consume energy), intensive distillation and cross contamination.
- Use environmental solvent like water or super critical fluid as CO_2 which is easily to be separated, and may be ionic liquid which have zero volatility.


Problematic organic solvents
Greener alternatives
Avoidance
No Solvent
Environmentally benign and safe
Water solvent
Easily separable, safe
Supercritical fluids
Zero Volatility
Ionic liquids

6- Design for energy efficiency

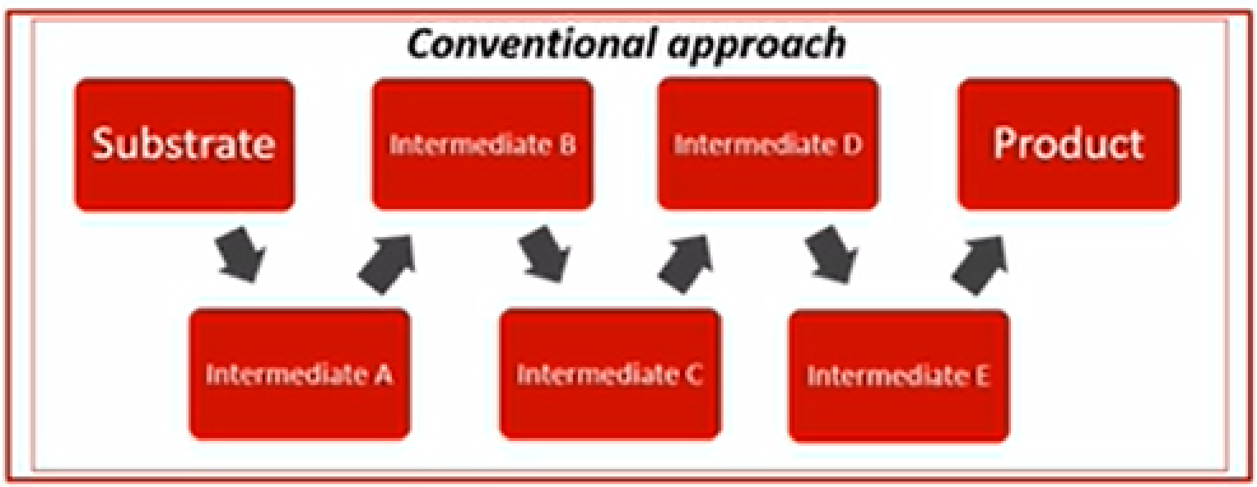
- The environmental and economical impact of energy requirements **should be considered** while method design and working at ambient temperature and atmospheric pressure.
- **To minimize energy** for heating, cooling, separation or pumping.

7- Using of renewable raw materials

- Whenever it possible **the usage of renewable materials instead of depleting source** as technically and economically practical.
- **Biomaterial** which is already functionalized materials.
- **Petroleum** is deposit of dead biomass.
- **Biomass** is enormous production per year.
- **Carbohydrates** a lot of sugar in form of starch non aromatic.
- **Lignin** from trees is more aromatic carbon and the rest for functionalized compounds.

8- Reduced derivatives

- Unnecessary derivatization should be avoided to reduce the intermediates compounds (less steps in the path way for producing the product).



9- catalysis

- Catalytic reagent is superior and selective to stoichiometric reactions.
- It facilitates the reaction by lowering the activation energy (energy barrier get lower) chemical reactions goes at lower temperature.
- Controlling the site of the reaction.
- They are two kind: heterogeneous 多相 and 单相 homogenous catalyst in which can be in same phase or different phase of reactant based in the state of matters.
- Green chemistry think to **combine best property of homogenous and heterogeneous to design green catalyst**.

Comparison between types of catalyst

Heterogeneous catalysts	Homogenous catalyst
Distinct solid phase.	Same phases as reactant.
Readily regenerated & recycled.	Expensive to and difficult to be separated.
Readily separated.	
Rates not as fast.	Very high rate.
Diffusion limited.	Not diffusion controlled.
Sensitive to poisons.	Robust to poisons.
Long service life.	Short service life.
High energy process.	Mild conditions.
Poor mechanistic understanding.	Mechanism well-understood.

10- Design for degradation

- Many chemicals **don't degraded** in the environment such as CFCs, DDT etc.
- It should not be persist in the environment hence, breakdown into innocuous degradation products.
- Plasticizer and PET persist in environment and deplete the resource of petroleum so now the usage of PLA from bio-based source (starch) which is compostable, recyclable and cost effective.
- PYROOCOOL for fire distinguisher rather than Halon gas.

11- Real time analysis for pollution prevention

- Analytical methods should be developed to allow real time in process monitoring and control prior to the formation of hazardous substance.
- Following up the progress of chemical reaction immediately to save time, energy and no waste generation.
- Determination of how greener our reaction is using the tools of analytical chemistry (identification, monitoring, quantity, characterization (the right compound or not) so the green analytical chemistry (include process, method, and protocols).
- Monitor waste generation.

Example:

While, using **water** for cooling there is a possibility for microbial growth and scaling (deposit of minerals) so it will decrease efficiency and increase energy consumption also the need of biocide so what to do.?

Real time system will monitor the scaling of the minerals

and bio-control system to check the amount of bacteria hence, adding specific amount of biocide to avoid over-treated of the water.

12- Inherently safe chemistry for accident prevention

A
E
B F
CD . I

- **Accidents** can be avoided if we minimized hazardous.
- **Substance** should be chosen to avoid releasing, explosive and fire. Hence, Staying away from volatile hazardous using solids or lower vapor pressure solution, and avoid use molecular halogen in large quantity (powerful oxidant).
- **Continuous flow process** reduce the hazardous (flow reagent in the reaction as batch process.
- **Applying proper** occupational safety and health precautions and regulations.

Thank you for your attention