The Twelve Principles of Green Chemistry

Goals for this class:

• Become familiar with the 12 Principles
• Discuss specific examples of practical value
• See the principles from a chemist's perspective
• Analyze the case of ibuprofen as an example of a green approach

Source material reproduced with modifications from:

www.beyondbenign.org/professional/community_college/12_principles_Cannon.ppt

Imperial College, London

What is Green Chemistry?

- Green Chemistry is a revolutionary approach to the way that products are made; it is a science that aims to reduce or eliminate the use and/or generation of hazardous substances in the design phase of materials development.
- It requires an inventive and interdisciplinary view of material and product design. Green Chemistry follows the principle that it is better to consider waste prevention options during the design and development phase than to dispose or treat waste after a process or material has been developed.

www.warnerbabcock.com/green_chemistry/about_green_chemistry.asp

What is Green Chemistry?

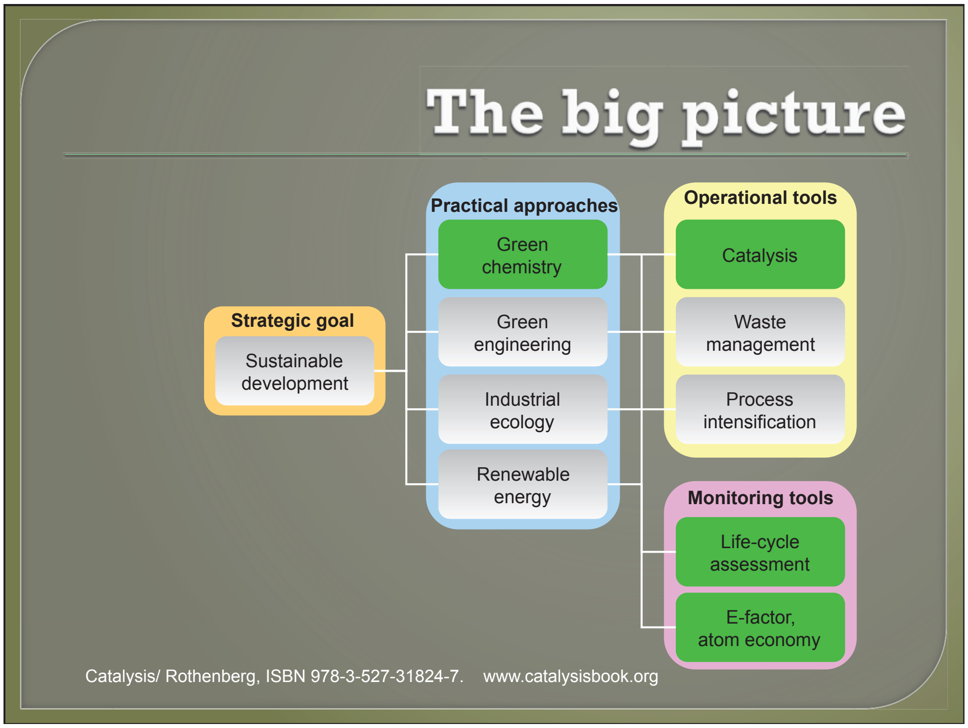
- Green Chemistry presents industries with an opportunity for growth and competitive advantage. This is because there is currently a significant shortage of green technologies: we estimate that only 10% of current technologies are environmentally benign; another 35% could be made benign relatively easily. The remaining 65% have yet to be invented!
- Green Chemistry also creates cost savings: when hazardous materials are removed from materials and processes, all hazard-related costs are also removed, such as those associated with handling, transportation, disposal, and compliance

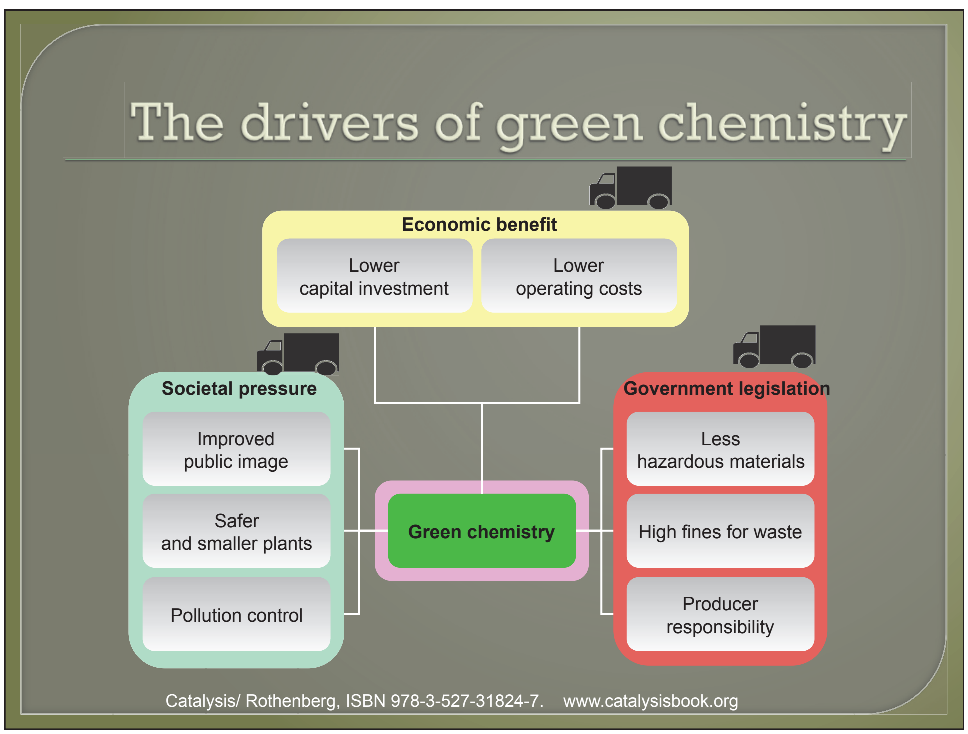
www.warnerbabcock.com/green_chemistry/about_green_chemistry.asp

What is Green Chemistry?

- For a technology to be considered Green Chemistry, it must accomplish three things:
- Through Green Chemistry, environmentally benign alternatives to current materials and technologies can be systematically introduced across all types of manufacturing to promote a more environmentally and economically sustainable future.

www.warnerbabcock.com/green_chemistry/about_green_chemistry.asp


The big picture
Strategic goal
Sustainable development
Practical approaches
Green chemistry
Green engineering
Industrial ecology
Renewable energy
Operational tools
Catalysis
Waste management
Process intensification
Monitoring tools
Life-cycle assessment
E-factor, atom economy
Catalysis/ Rothenberg, ISBN 978-3-527-31824-7. www.catalysisbook.org


The drivers of green chemistry
Economic benefit
Lower capital investment
Lower operating costs
Societal pressure
Improved public image
Safer and smaller plants
Pollution control
Green chemistry
Government legislation
Less hazardous materials
High fines for waste
Producer responsibility
Catalysis/ Rothenberg, ISBN 978-3-527-31824-7. www.catalysisbook.org

12 Principles of Green Chemistry

1. **Prevention**. It is better to prevent waste than to treat or clean up waste after it is formed.
2. **Atom Economy**. Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product.
3. **Less Hazardous Chemical Synthesis.** Whenever practicable, synthetic methodologies should be designed to use and generate substances that possess little or no toxicity to human health and the environment.
4. **Designing Safer Chemicals.** Chemical products should be designed to preserve efficacy of the function while reducing toxicity.
5. **Safer Solvents and Auxiliaries.** The use of auxiliary substances (solvents, separation agents, etc.) should be made unnecessary whenever possible and, when used, innocuous.
6. **Design for Energy Efficiency**. Energy requirements should be recognized for their environmental and economic impacts and should be minimized. Synthetic methods should be conducted at ambient temperature and pressure.
7. **Use of Renewable Feedstocks.** A raw material or feedstock should be renewable rather than depleting whenever technically and economically practical.
8. **Reduce Derivatives.** Unnecessary derivatization (blocking group, protection/deprotection, temporary modification of physical/chemical processes) should be avoided whenever possible .
9. **Catalysis.** Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.
10. **Design for Degradation**. Chemical products should be designed so that at the end of their function they do not persist in the environment and instead break down into innocuous degradation products.
11. **Real-time Analysis for Pollution Prevention.** Analytical methodologies need to be further developed to allow for real-time in-process monitoring and control prior to the formation of hazardous substances.
12. **Inherently Safer Chemistry for Accident Prevention**. Substance and the form of a substance used in a chemical process should be chosen so as to minimize the potential for chemical accidents, including releases, explosions, and fires.

Anastas, P. T.; Warner, J.C. Green Chemistry: Theory and Practice, Oxford University Press,1998.

1. Prevention

Environmental Disasters

- Love Canal
  - in Niagara Falls, NY a chemical and plastics company had used an old canal bed as a chemical dump from 1930s to 1950s. The land was then used for a new school and housing track. The chemicals leaked through a clay cap that sealed the dump. It was contaminated with at least 82 chemicals (benzene, chlorinated hydrocarbons, dioxin). Health effects of the people living there included: high birth defect incidence and seizure-inducing nervous disease among the children.

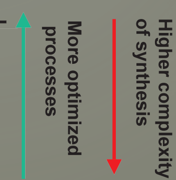
2. Atom Economy

Definition of Sheldon environmental acceptability

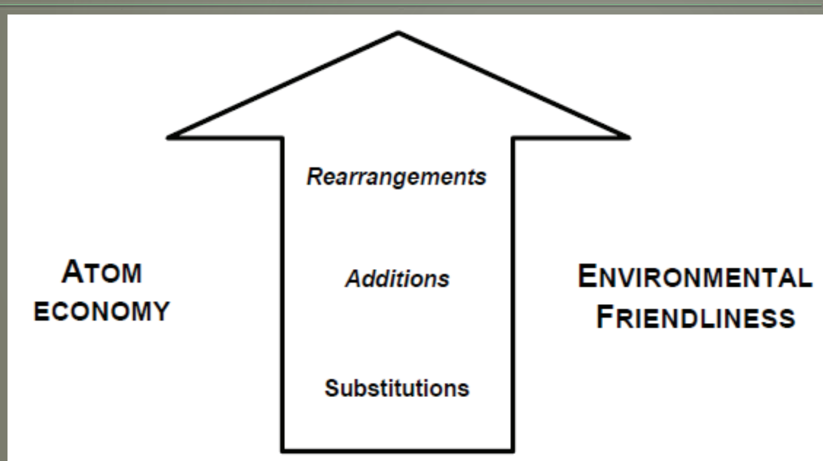
Environmental acceptability (E)

$$E = \frac{\text{Kg waste + unwanted byproducts}}{\text{Kg desired product(s)}}$$

	Volume of production in tons per Year	E value
Oil refining	10^6 - 10^8	0.1
commodity chemicals	10^4 - 10^6	< 1.5
special chemicals	10^2 - 10^4	5 - 50
drugs	10^1 - 10^4	25 - >100



General classification of atom economic reactions



3. Less Hazardous Chemical Synthesis

Less Hazardous Chemical Synthesis

Polycarbonate Synthesis: Phosgene Process

- Disadvantages
  - phosgene is highly toxic, corrosive
  - requires large amount of CH_2Cl_2
  - polycarbonate contaminated with Cl impurities

Less Hazardous Chemical Synthesis

Polycarbonate Synthesis: Solid-State Process

- Advantages
  - diphenylcarbonate synthesized without phosgene
  - eliminates use of CH_2Cl_2
  - higher-quality polycarbonates

Komiya *et al.,* Asahi Chemical Industry Co.

4. Designing Safer Chemicals

Designing Safer Chemicals
Case Study: Antifoulants (Marine Pesticides)

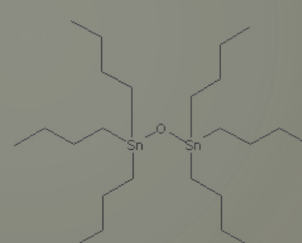
http://academic.scranton.edu/faculty/CANNM1/environmentalmodule.html

Designing Safer Chemicals:
Case Study: Antifoulants

Antifoulants are generally dispersed in the paint as it is applied to the hull. Organotin compounds have traditionally been used, particularly tributyltin oxide (TBTO). TBTO works by gradually leaching from the hull killing the fouling organisms in the surrounding area

TBTO and other organotin antifoulants have long half-lives in the environment (half-life of TBTO in seawater is > 6 months). They also bioconcentrate in marine organisms (the concentration of TBTO in marine organisms to be 104 times greater than in the surrounding water).

Organotin compounds are chronically toxic to marine life and can enter food chain. They are bioaccumulative.



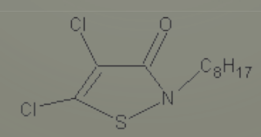
Tributyltin Oxide

http://academic.scranton.edu/faculty/CANNM1/environmentalmodule.html

Designing Safer Chemicals: Case Study: Antifoulants

Rohm and Haas
Presidential Green Chemistry Challenge Award, 1996

The active ingredient in Sea-Nine® 211, 4,5-dichloro-2-*n*-octyl-4-isothiazolin-3-one (DCOI), is a member of the isothiazolone family of antifoulants.



4,5-dichloro-2-n-octyl-4-isothiazolin-3-one

DCOI

http://academic.scranton.edu/faculty/CANNM1/environmentalmodule.html

Designing Safer Chemicals: Case Study: Antifoulants

Sea-Nine® 211 works by maintaining a hostile growing environment for marine organisms. When organisms attach to the hull (treated with DCOI), proteins at the point of attachment with the hull react with the DCOI. This reaction with the DCOI prevents the use of these proteins for other metabolic processes. The organism thus detaches itself and searches for a more hospitable surface on which to grow.

Only organisms attached to hull of ship are exposed to toxic levels of DCOI.

Readily biodegrades once leached from ship (half-life is less than one hour in sea water).

http://academic.scranton.edu/faculty/CANNM1/environmentalmodule.html

5. Safer Solvents and Auxiliaries

Safer Solvents

- Solvent Substitution
- Water as a solvent(?)
- New solvents
  - Ionic liquids
  - Supercritical fluids

Solvent Selection

Preferred	Useable	Undesirable
Water	Cyclohexane	Pentane
Acetone	Heptane	Hexane(s)
Ethanol	Toluene	Di-isopropyl ether
2-Propanol	Methylcyclohexane	Diethyl ether
1-Propanol	Methyl t-butyl ether	Dichloromethane
Ethyl acetate	Isooctane	Dichloroethane
Isopropyl acetate	Acetonitrile	Chloroform
Methanol	2-MethylTHF	Dimethyl formamide
Methyl ethyl ketone	Tetrahydrofuran	N-Methylpyrrolidinone
1-Butanol	Xylenes	Pyridine
t-Butanol	Dimethyl sulfoxide	Dimethyl acetate
	Acetic acid	Dioxane
	Ethylene glycol	Dimethoxyethane
		Benzene
		Carbon tetrachloride

"Green chemistry tools to influence a medicinal chemistry and research chemistry based organization"
Dunn and Perry, et. al., Green Chem., 2008, 10, 31-36

Solvent replacement table

Undesirable Solvent	Alternative
Pentane	Heptane
Hexane(s)	Heptane
Di-isopropyl ether or diethyl ether	2-MeTHF or *tert*-butyl methyl ether
Dioxane or dimethoxyethane	2-MeTHF or *tert*-butyl methyl ether
Chloroform, dichloroethane or carbon tetrachloride	Dichloromethane
Dimethyl formamide, dimethyl acetamide or N-methylpyrrolidinone	Acetonitrile
Pyridine	Et_3N (if pyridine is used as a base)
Dichloromethane (extractions)	EtOAc, MTBE, toluene, 2-MeTHF
Dichloromethane (chromatography)	EtOAc/heptane
Benzene	Toluene

"Green chemistry tools to influence a medicinal chemistry and research chemistry based organization"
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Pfizer's results

Use of Solvent Replacement Guide resulted in:

- 50% reduction in chlorinated solvent use across the whole of their research division (more than 1600 lab based synthetic organic chemists, and four scale-up facilities) during 2004-2006.
- Reduction in the use of an undesirable ether by 97% over the same two year period
- Heptane used over hexane (more toxic) and pentane (much more flammable)

"Green chemistry tools to influence a medicinal chemistry and research chemistry based organization"
Dunn and Perry, et. al., Green Chem., 2008, 10, 31-36

6. Design for Energy Efficiency

Energy in a chemical process

- Thermal (electric)
- Cooling (water condensers, water circulators)
- Distillation
- Equipment (lab hood)
- Photo
- Microwave

Source of energy:

- Power plant – coal, oil, natural gas

Laboratory scale energy use


microwave


oil bath


heating mantle