Module 3 –
Green Chemistry

Global Greenchem
Innovation & Network Program

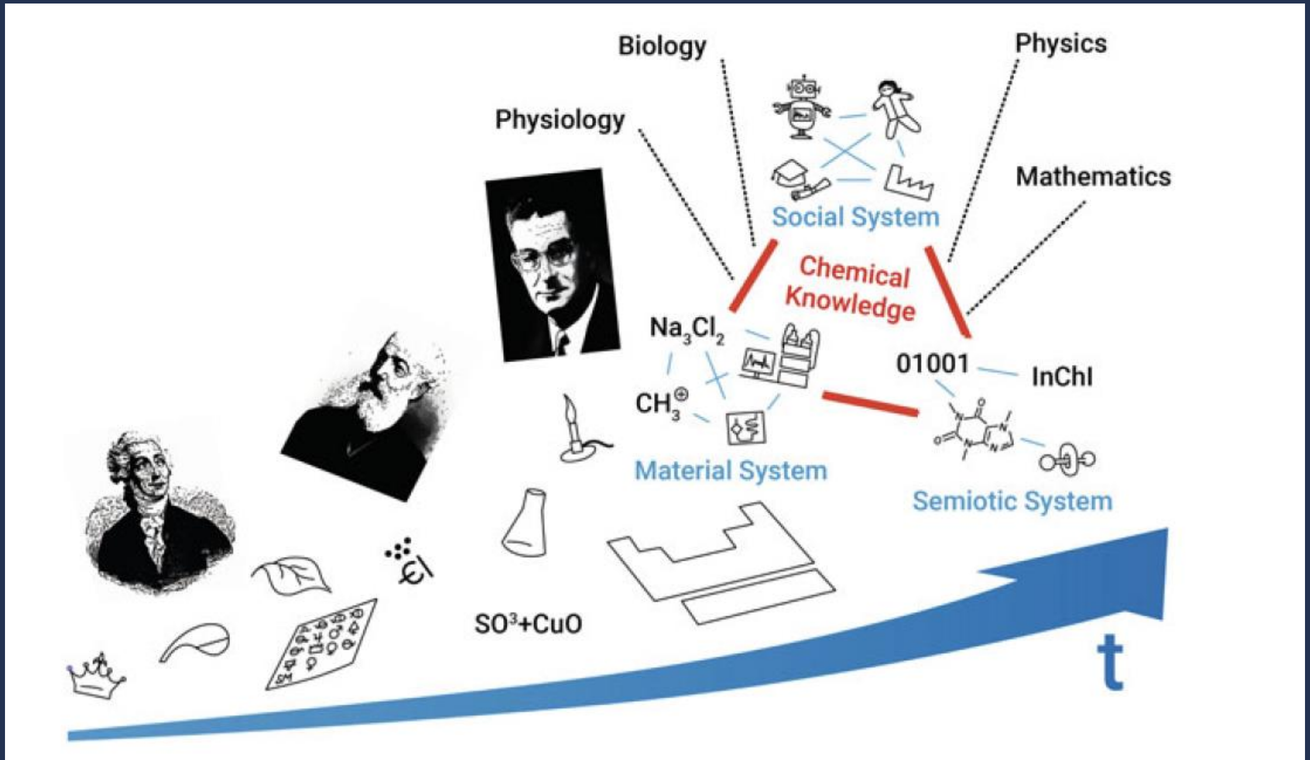
UNIDO

Green Chemistry Toolkit

gef

Center for Green Chemistry &
Green Engineering at Yale

The advent of Green Chemistry



Jost, J., Restrepo, G. (2022). Modelling the Evolution of Chemical Knowledge. In: The Evolution of Chemical Knowledge. Wissenschaft und Philosophie – Science and Philosophy – Sciences et Philosophie. Springer, Cham.

What we “knew for sure” in 1991

- Hazard should be managed.
- Pollution can be controlled through engineering.
- High reactivity of reagents/substrates lowers reaction time and energy costs.
- Long-term durability of molecules and materials are good thing.

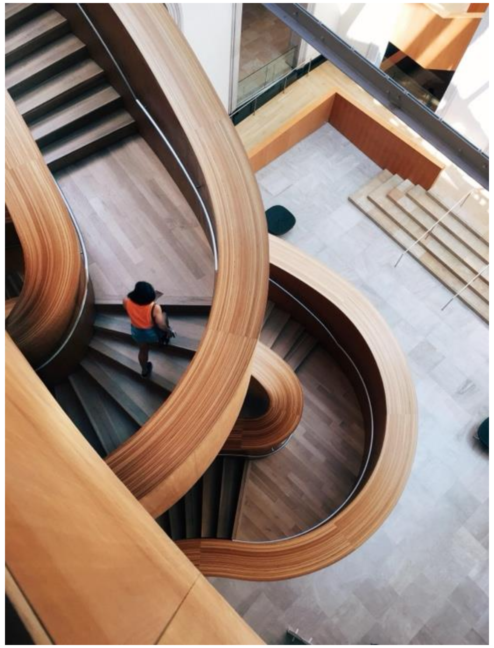
Image by OpenClipart-Vectors from Pixabay
Image by Jürgen from Pixabay

What we “knew for sure” in 1991

- Organic solvents are required for chemical transformations.
- Toxicity and function are inextricably linked.
- Environmental issues simply cost money.
- Our responsibility as chemists is to comply with the law.

Image by herbinisaac from Pixabay
Image by Sebastian Ganso from Pixabay

What we realized since 1991



- Hazard is a design flaw and can be addressed by conscious design.
- Pollution can be avoided, and "waste" are resources that haven't been put to use.
- Nature does chemistry at the time and place it needs it, using benign materials.
- Persistence of a material beyond its useful life is bad and should be avoided.

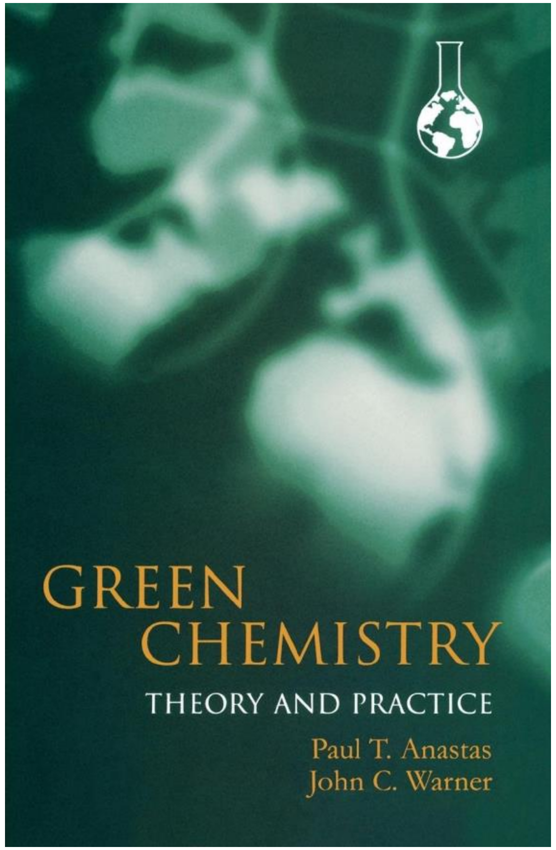
Image by Pexels from Pixabay
Image by DerWeg from Pixabay

What we realized since 1991

- Benign solvents and solventless systems should be the rule.
- Toxicity can be minimal while function is enhanced.
- Green Chemistry can solve environmental & health issues while being profitable.
- Chemists or engineers can use their abilities for global sustainability.

Image by Alexa from Pixabay

Green Chemistry – How did it start?



Definition of Green Chemistry:

Green chemistry is the design of chemical products or processes that reduce or eliminate the use or generation of harmful and dangerous substances.

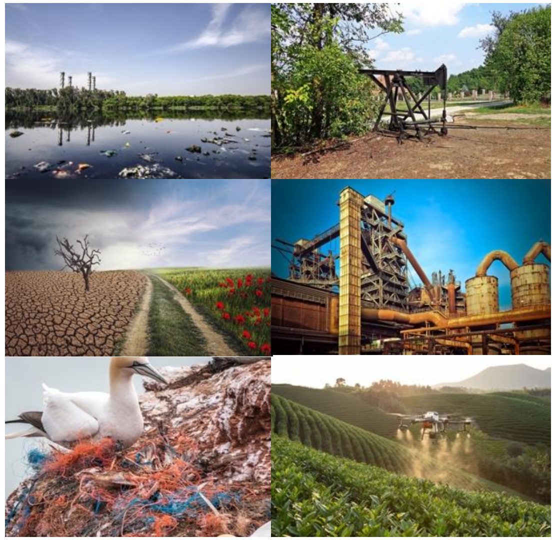
Paul Anastas and John Warner (1998)

Status Quo

Fulfilling a function…

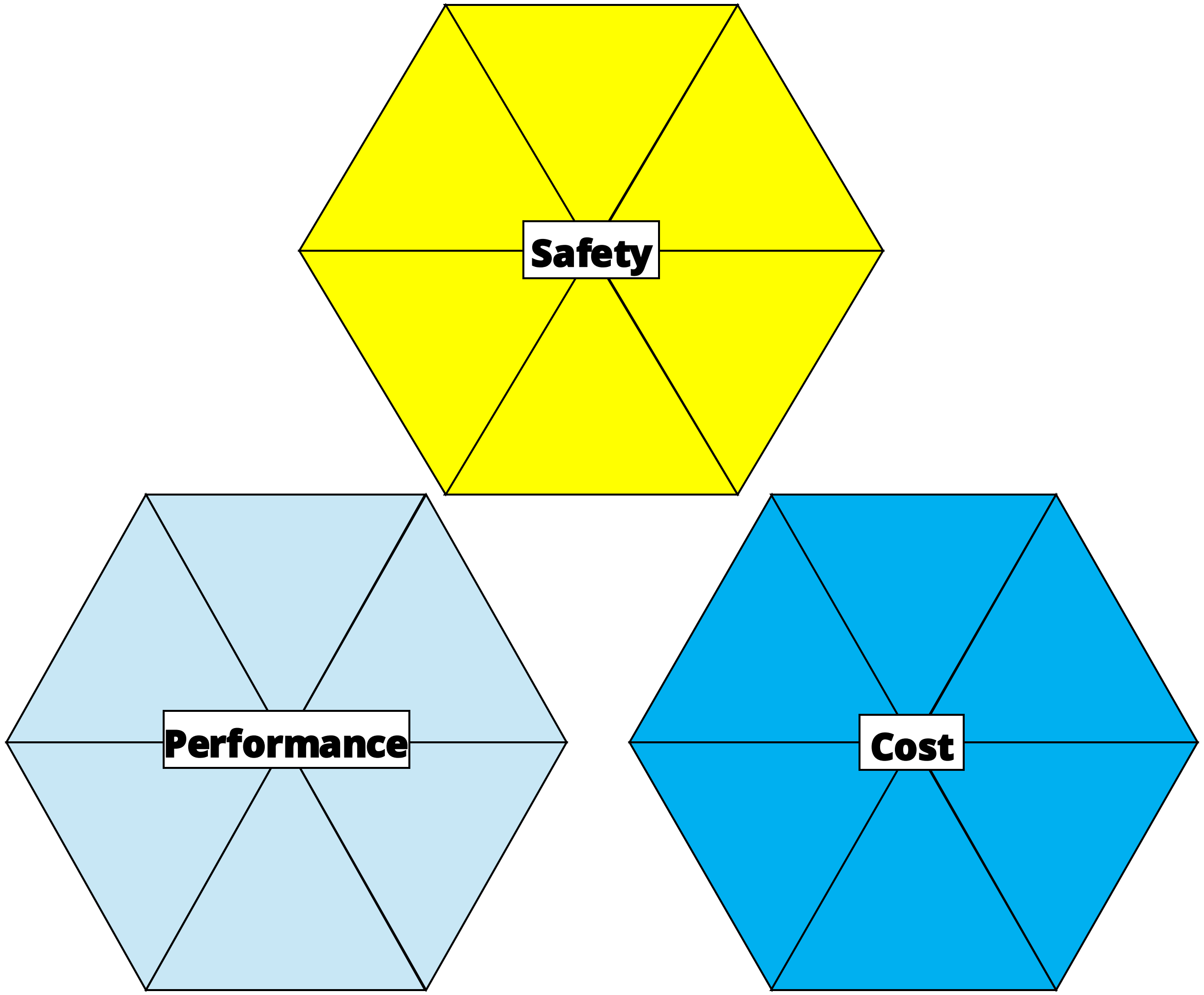
~~Fulfill the function, negotiate the risk!~~

… without the imminent risk

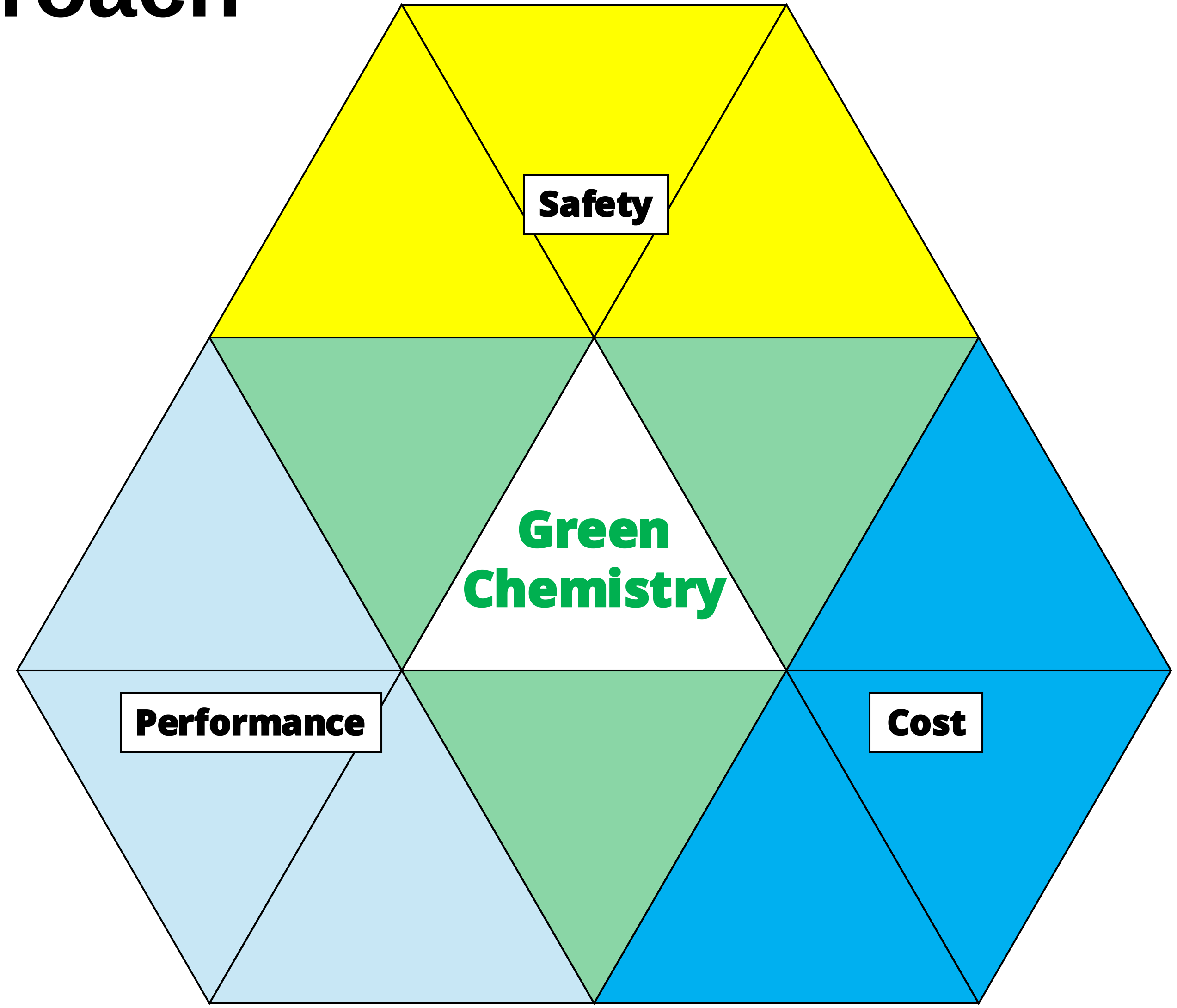


Green Chemistry arises from the necessity to change the status quo!

Reductionist approach



Holistic approach



Benign by Design!

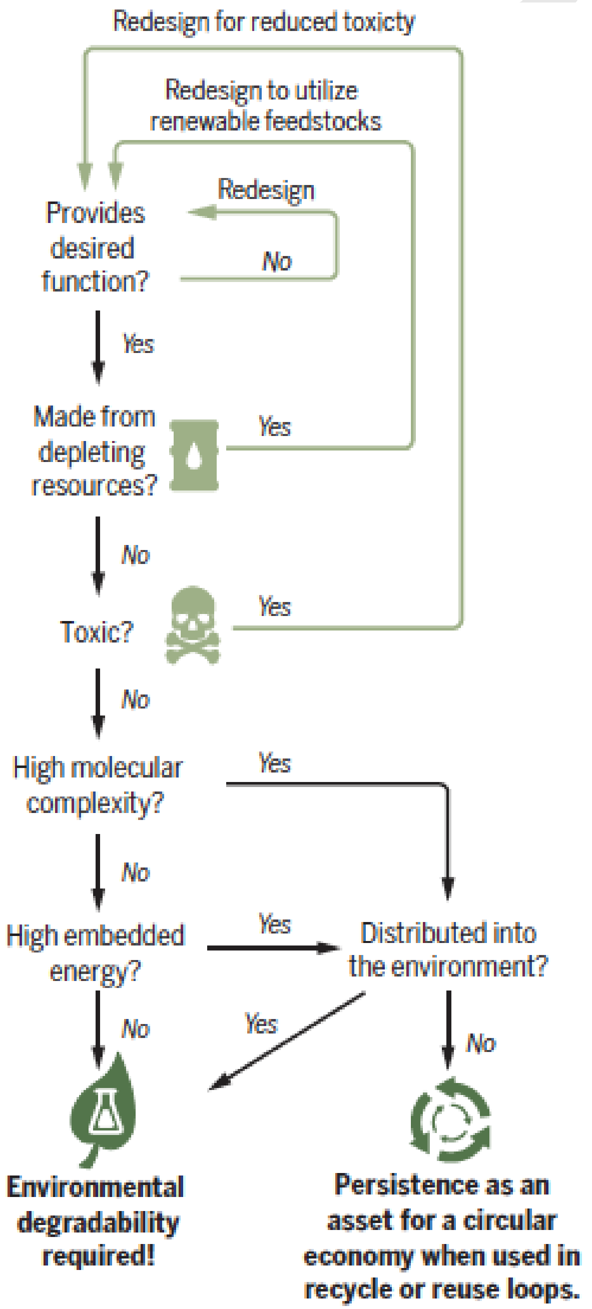
Green chemistry is the design of chemical products or processes that reduce or eliminate the use, or generation of, harmful and dangerous substances.

Design is intentional!
Being benign is intentional!

Depleting chemicals are based on finite fossil resources and contribute to greenhouse gas emissions

Chemical toxicity can result in adverse outcomes, including immediate (acute effects) and long-term (chronic) effects, including across generations.

Persistence of chemicals in the environment may be a concern for human and environmental health, particularly in combination with high environmental mobility. Challenges include bioaccumulation, unknown effects of low-dose and long-term exposure, and the opportunity to react with other chemicals in the environment.



Zimmerman, J. B., Anastas, P. T.; Erythropel, H.; Leitner, W. "Designing a for a green chemistry future," Science, 367, 397-400, 2020

The 12 Principles

A powerful toolbox!

It is important to consider, that the improvement concerning one or several principles is only an improvement, if none of the others is affected negatively.

A quick overview

The 12 Principles of Green Chemistry

1. Get rid of waste and pollution!

Principle 1: It is better to prevent waste than to treat or clean up waste after it has been created.

Get rid of waste and pollution!

The concept of waste is entirely human one, nature knows no waste. Preventing residues in chemistry can be approached from several perspectives:

Most waste is produced when a reaction is inefficient, or after the reaction occurs.

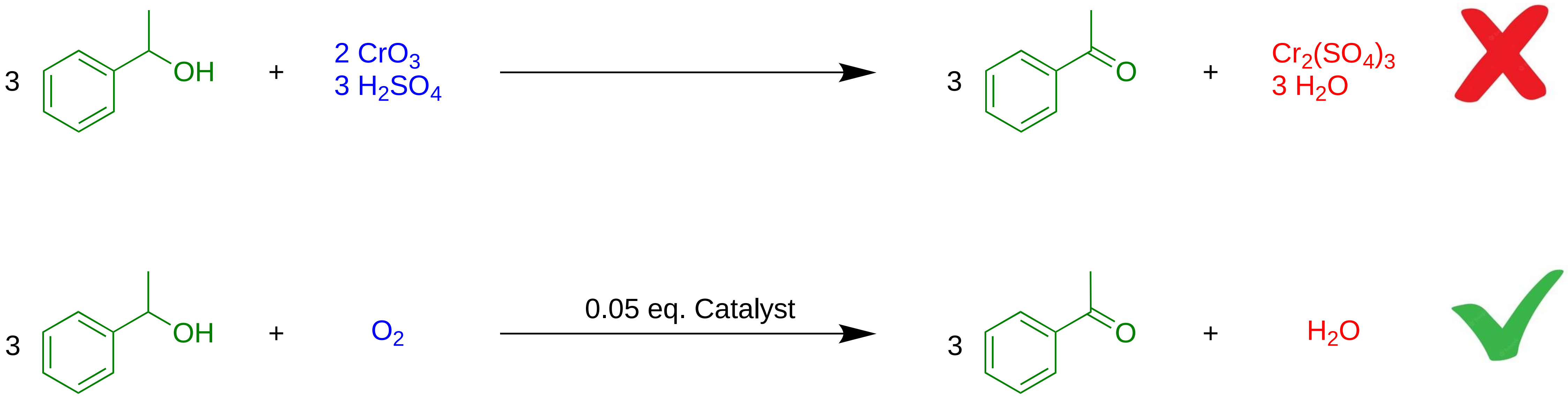
- Identify best reaction conditions
- Avoid Purification
- Apply the least wasteful starting materials

2. Incorporate all atoms!

Principle 2: Synthetic methods should be designed to maximize incorporation of atoms used in the process into the final product.

Incorporate all atoms!

Starting Material + Reagents → Products + Residues



For additional reading on atom economy:

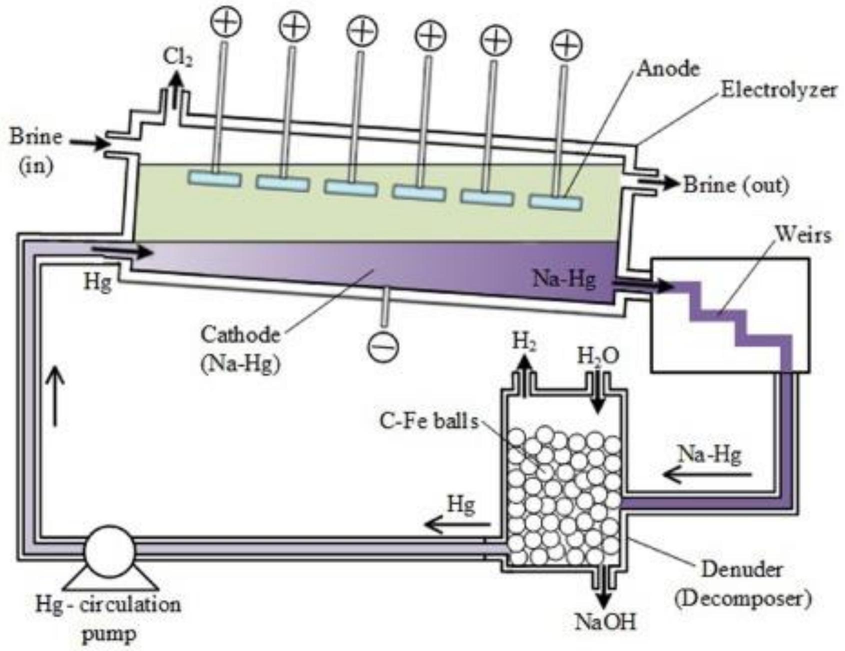
- https://www.scranton.edu/faculty/cannm/green-chemistry/english/or

3. If there is a safe alternative, use it!

Principle 3: Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment.

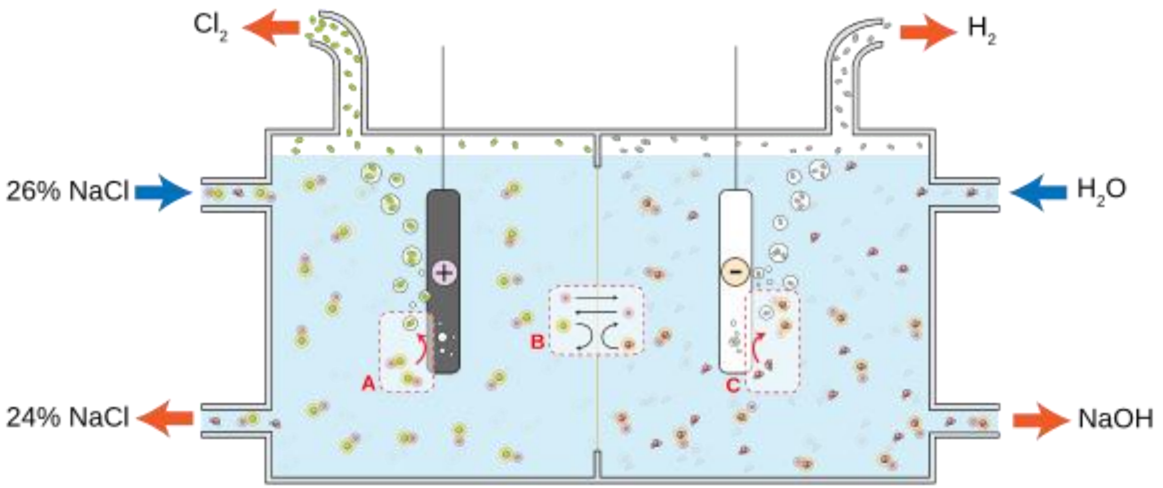
If there is a safe alternative, use it!

- Chlorine and sodium hydroxide are needed in the paper industry. Legacy processes use mercury electrodes, one of the key causes of the Minamata disease in many communities.



https://doi.org/10.1016/B978-0-12-819424-9.00011-2

- Process innovation and knowledge application changed this practice, and today there are only a few mercury reactors left.



https://en.wikipedia.org/wiki/Chloralkali_process

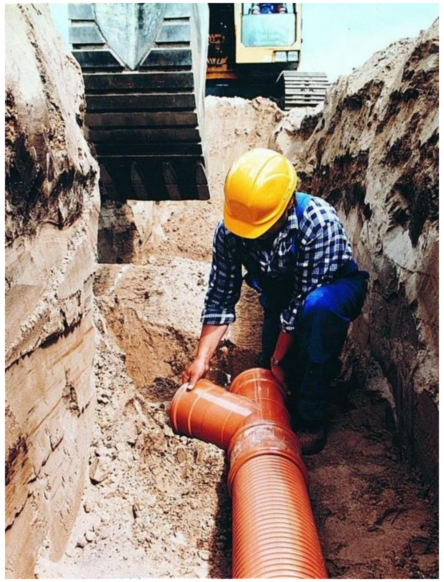
For additional reading :

- https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-1999-academic-award

4. Be benign by design!

Principle 4: Chemical products should be designed to preserve efficacy of function while reducing toxicity.

Be benign by design!

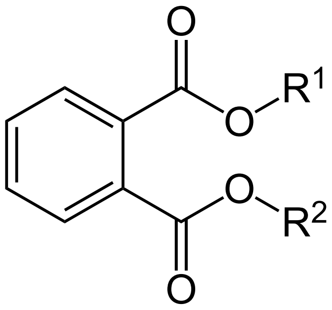


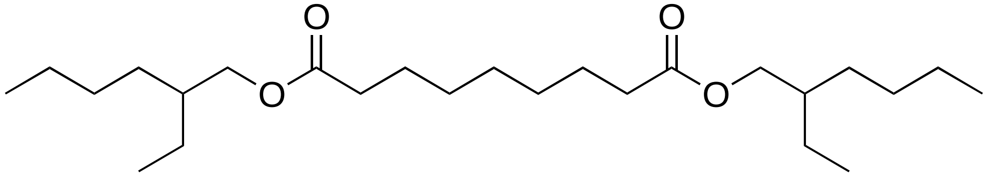
What do these materials have in common?

Both are plastics, both are PVC, and both contain platicizers!

Be benign by design!

Many roads lead to Rome!
But just because something works, does not mean that it was designed to be benign…





Phthalate-Plasticizers, Hormone Disruptor, persistent

Plasticizer from azelaic acid, biodegradable, biobased, designed to be more benign

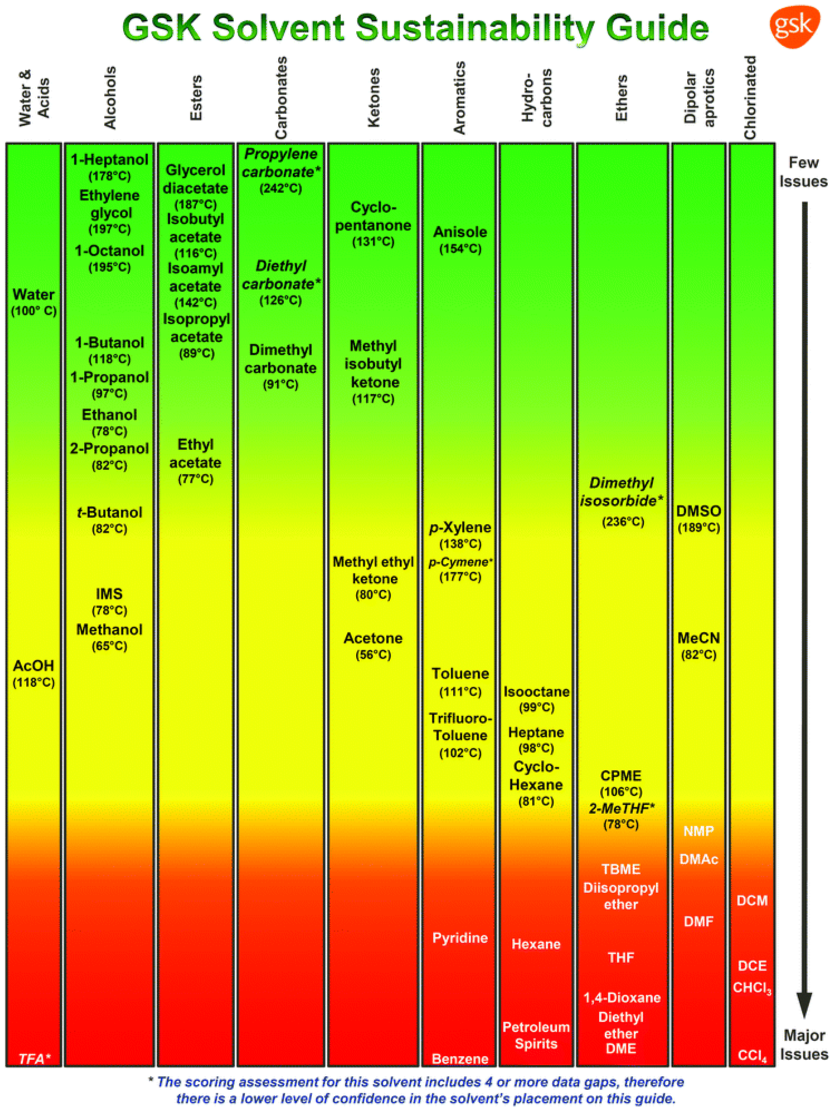
For additional reading :
- https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-1996-designing-greener-chemicals-award
- https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-2010-designing-greener-chemicals-award

5. Do we need it, or is it just convenient?

Principle 5: The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used.

Do we need it, or is it just convenient?

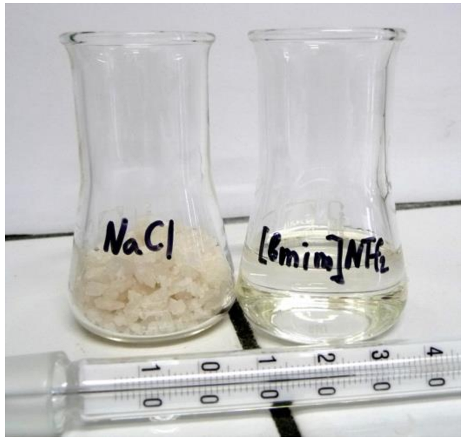
Solvents are everywhere, but they have very different risk profiles.

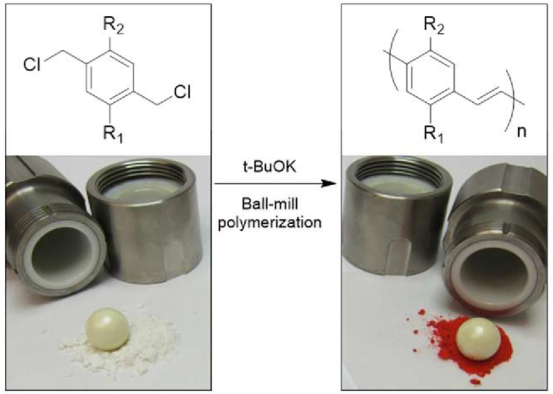


Do we need it, or is it just convenient?

Evaluating alternatives is very important:

Ionic Liquids





Solventless

Supercritical CO_2

6. Energy has a cost and an impact!

Principle 6: 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.

Energy has a cost and an impact!

A reaction or chemical process needs energy, but we need to identify the most energy-efficient process and minimize the impact.

Ideally, (almost) no equipment is needed for mechanical cooling, heating, or stirring.

For additional reading :

- https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-2006-greener-reaction-conditions-award

7. Renewable is better than depleting!

Principle 7: A raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable.

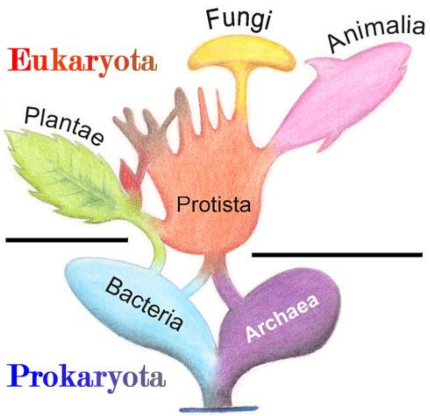
Renewable is better than depleting!

Pollution and Climate Change

Generating Circularity

CO_2

Products

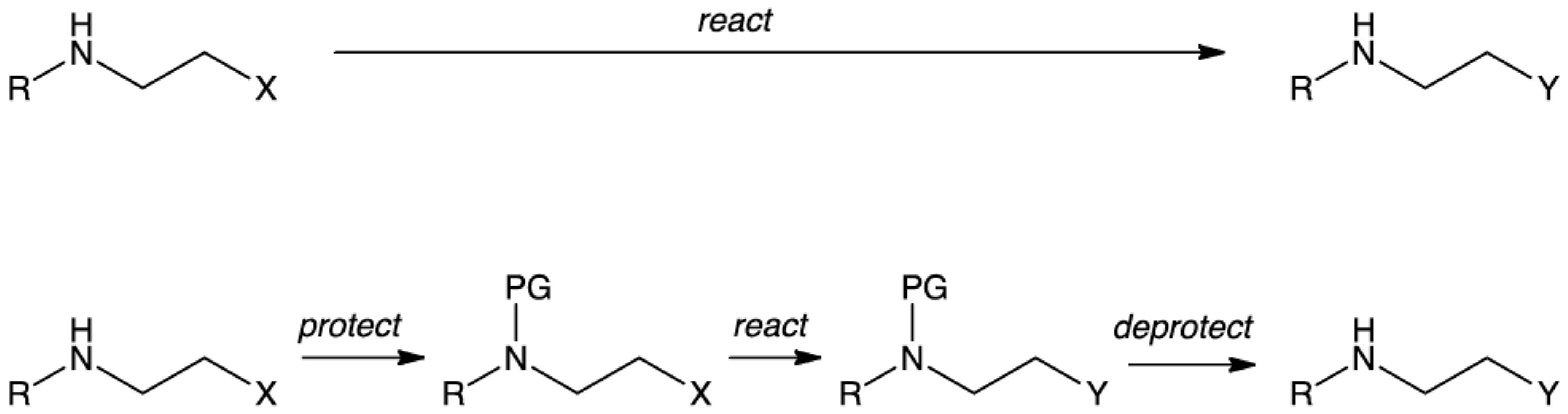


8. If there is a direct way, use it!

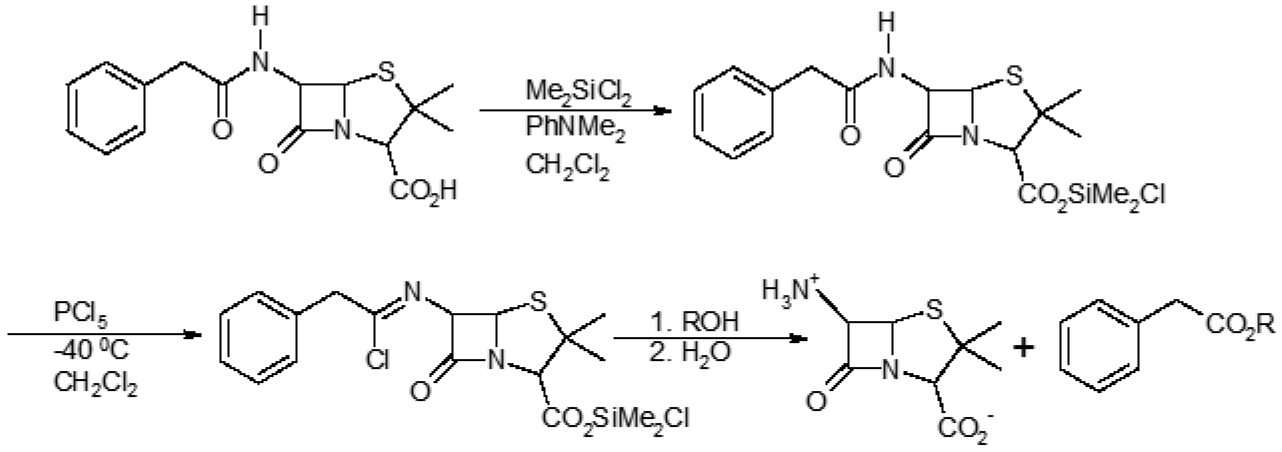
Principle 8: Unnecessary derivatization (use of blocking groups, protection/deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible.

If there is a direct way, use it!

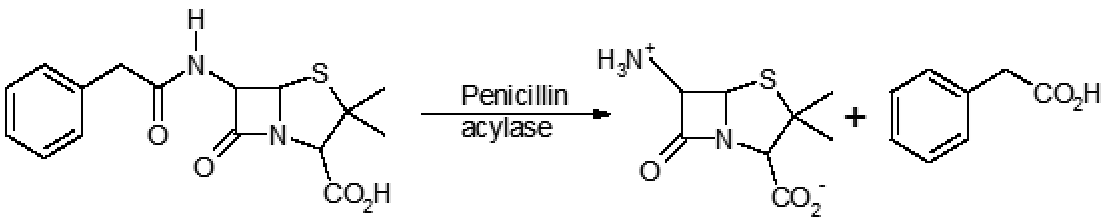
It is important to emphasize the difference between a temporary modification and a reaction



If there is a direct way, use it!



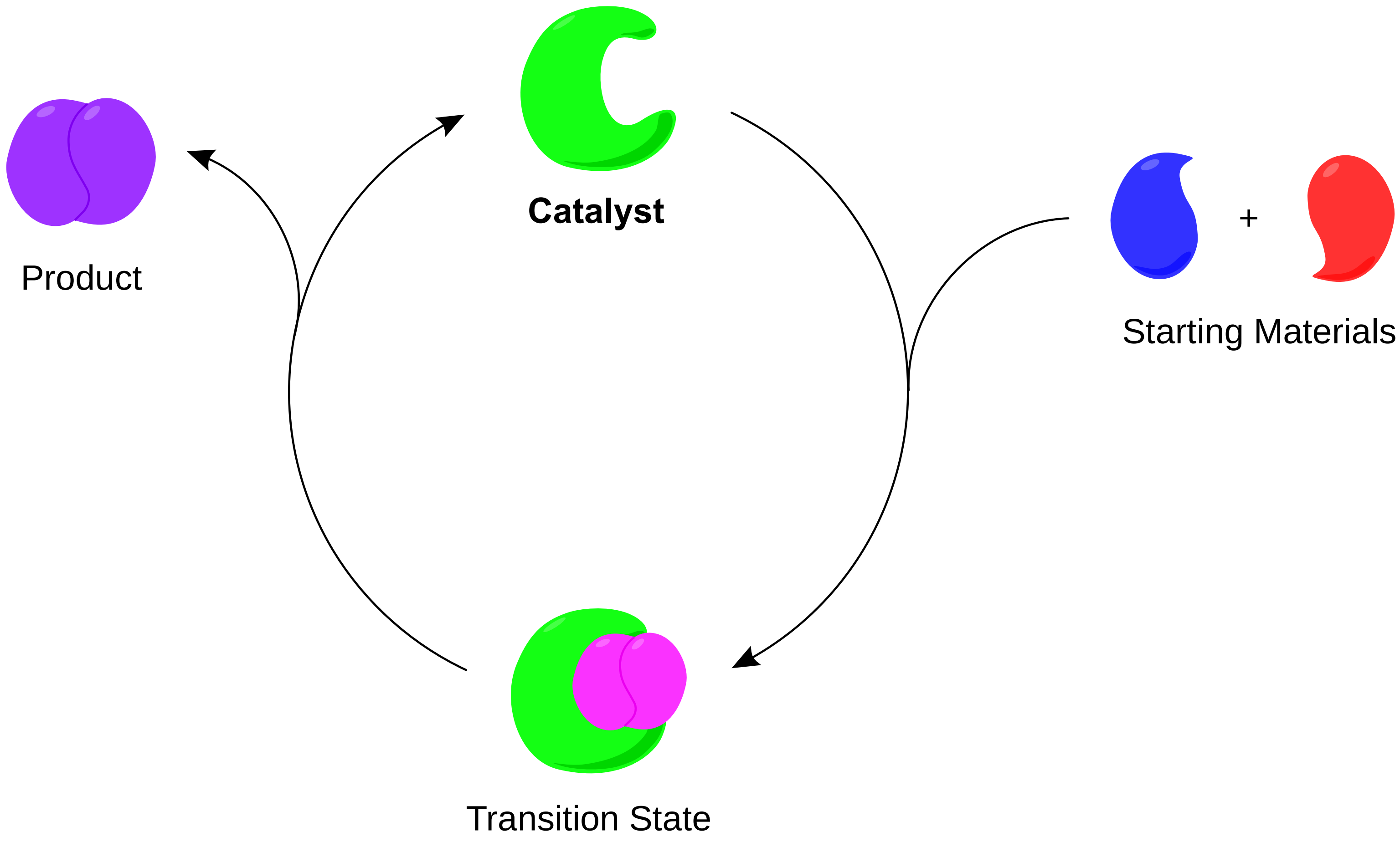
Penicilin deacylation: The same chemical reaction but realized in two drastically different ways.



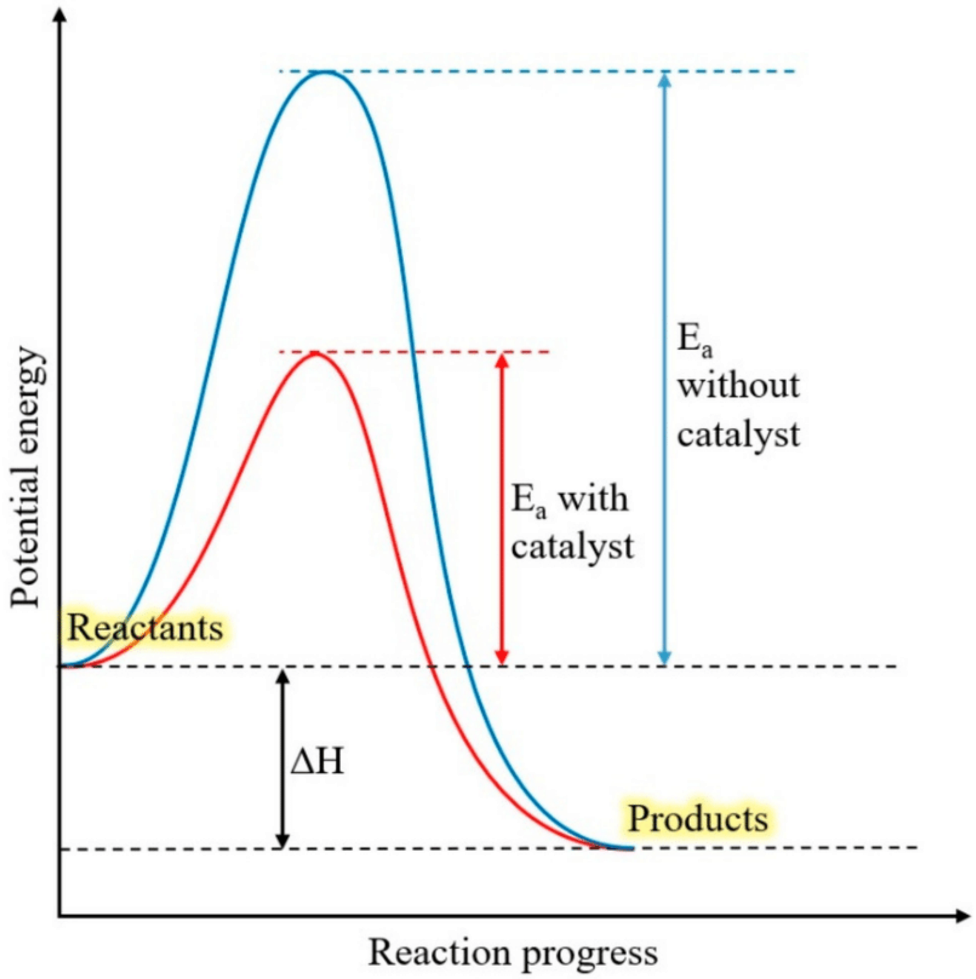
9. If you can, use a catalyst!

Principle 9: Catalytic reagents (as selective as possible) are superior to stoichiometric reagents.

9. If you can, use a catalyst!



9. If you can, use a catalyst!



3 Types of Catalysts:

Metal Catalysts
(Pd, Pt, Ni)

Biocatalysts
(Enzymes)

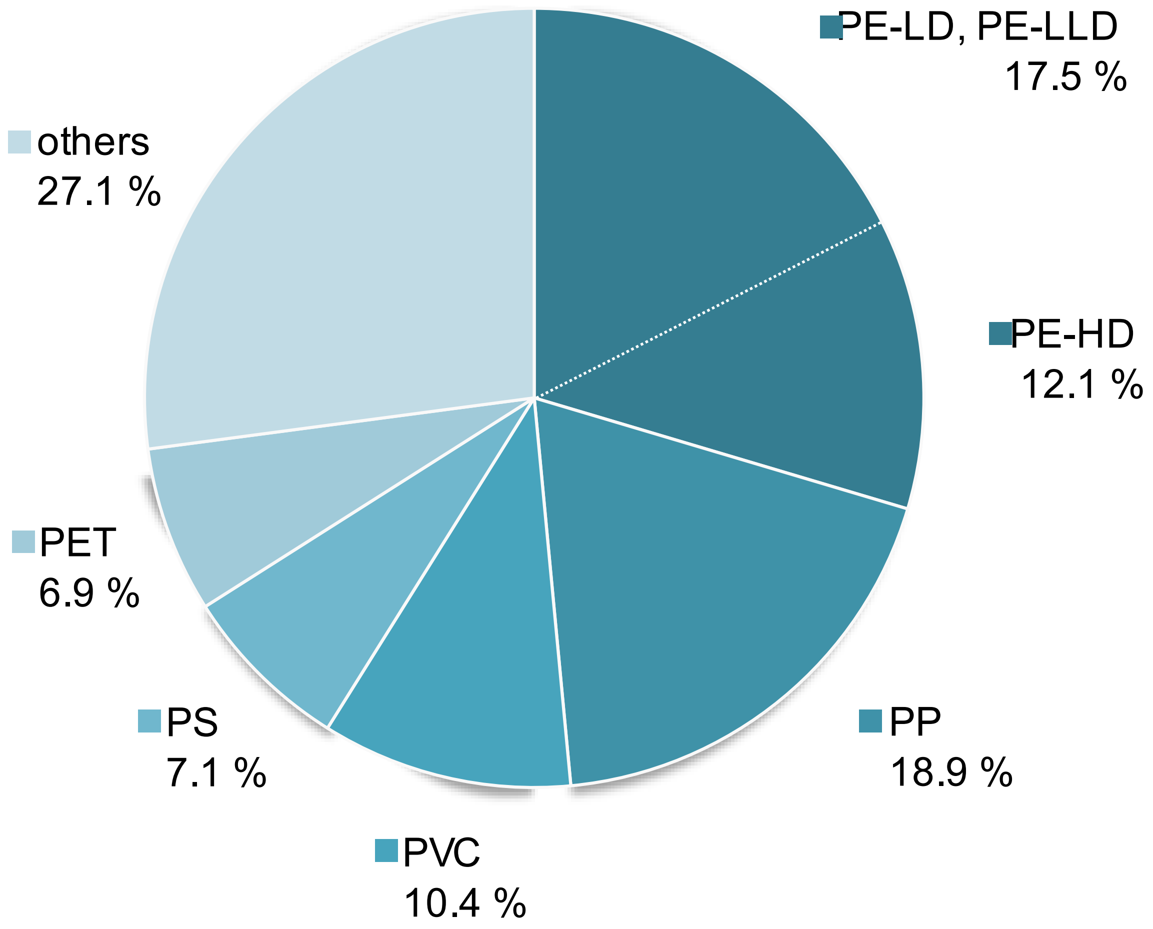
Organocatalysts
(Small Molecules)

10. Think about the future!

Principle 10: Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment.

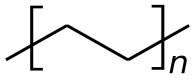
Think about the future!

We have many different plastics….

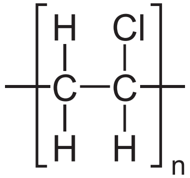


Think about the future!

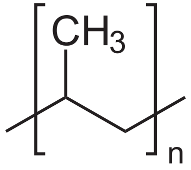
And few of them were designed to be degradable….



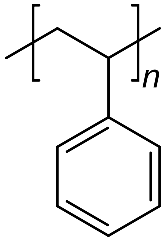
Polyethylene
PE (80 Mio. t)



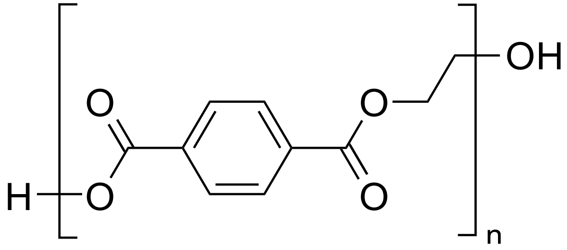
Polyvinyl Chloride
PVC (40 Mio. t)



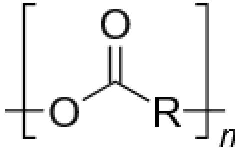
Polypropylene
PP (78 Mio. t)



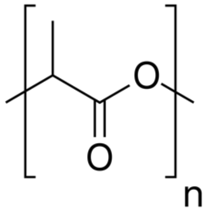
Polystyrene
PS (15 Mio. t)



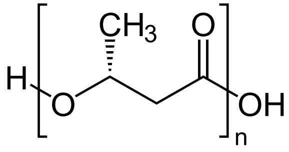
Polyethylene Terephthalate
PET (30 Mio. t)



Polyester (50 Mio. t)



Polylactic Acid
PLA (<0.5 Mio. t)



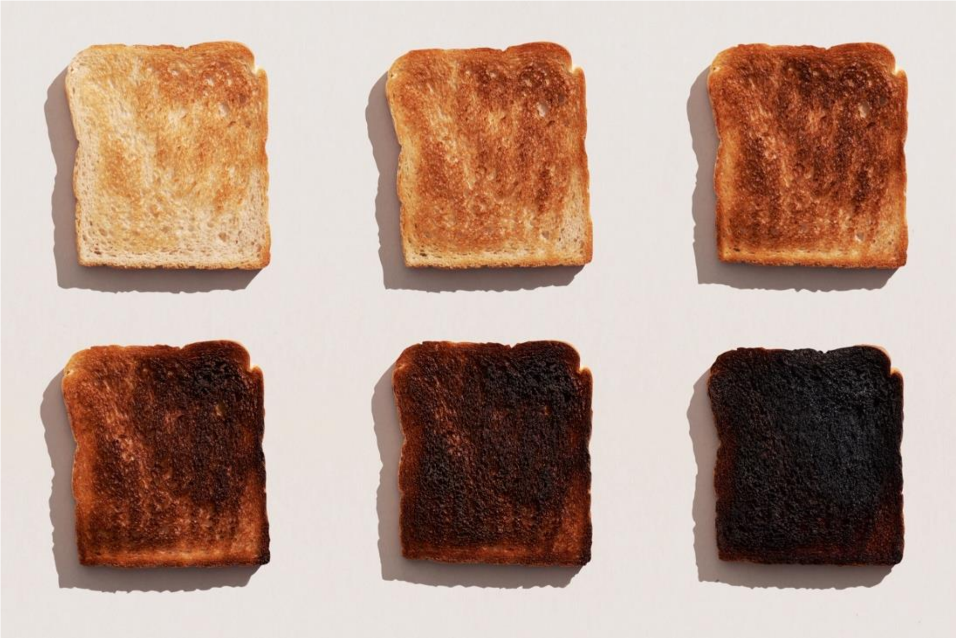
Polyhydroxyalkanoates
PHA (<0.5 Mio. t)

11. Think about the present!

Principle 11: Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances.

Think about the present!

In a kitchen we can simply monitor a 'reaction' aka the cooking process with our eyes:



Think about the present!

- Real-time analysis refers to the control of a chemical reaction while it is occurring.

- In a chemical laboratory there are solutions and technologies to help us control in real-time the chemical reaction, the formation of waste, and ultimately save time, energy and resources. Examples are HPLC, GC, IR, NMR, etc.

12. Learn from the past!

Principle 12: Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires.

Learn from the past!

<u>The tragedy of Bhopal, India (1984):</u>

Methyl isocyanate caused a thermal runaway.

> 3000 thousand dead instantly

> 500,000 people with sequelae

Learn from the past!

<u>What happened?</u>

- Methyl isocyanate (MIC) was stored in large quantities.
- Water entered the storage tank.
- MIC reacted exothermically with water.
- Security systems failed, were inoperative, or were ignored.
- The thermal runaway caused an increase in temperature, generating a large amount of toxic gas that was released into the surrounding region.

For additional reading on another example:

- https://www.epa.gov/greenchemistry/presidential-green-chemistry-challenge-2016-greener-synthetic-pathways-award

Twelve Principles…Isn't that how it is done?

- Industry is still geared toward cleaning up after wasteful chemical syntheses.
- Scientific literature is filled with approaches that are inefficient by design.
- Reagents or solvents are seldomly selected with regard to hazard.
- Industrial chemicals do not have minimal hazard as a performance criterion.

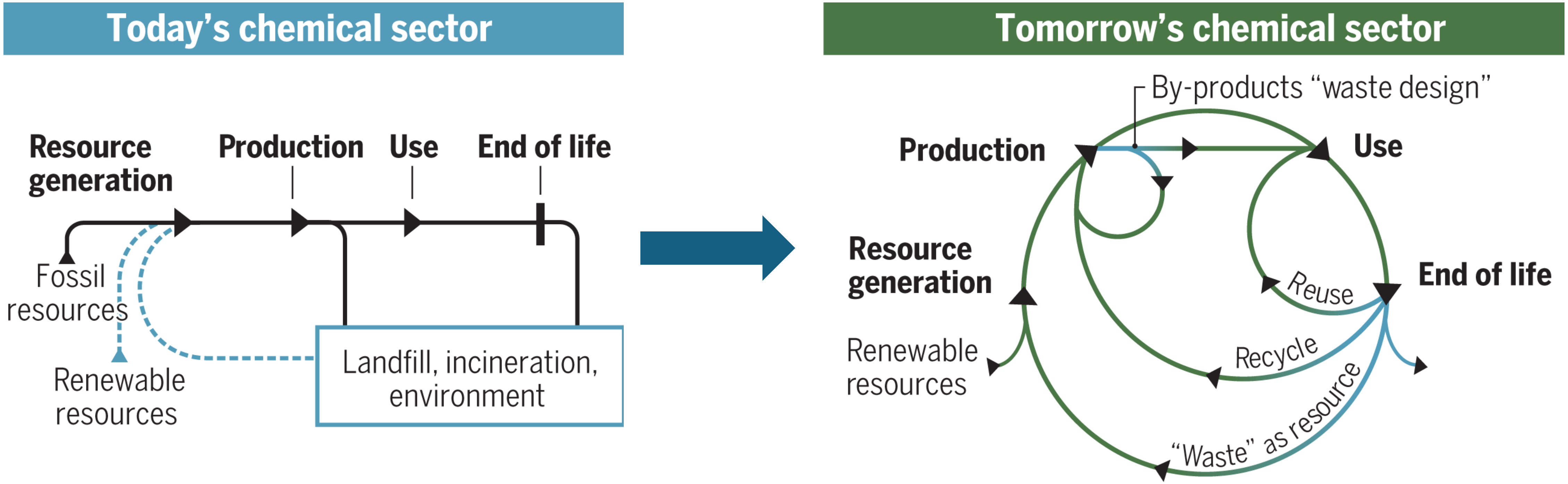
Twelve Principles…Isn't that how it is done?

- Persistence of chemicals in the biosphere and in our bodies is a major global health issue (CDC >250 of chemicals invented since 1945).
- The vast majority of organic chemicals are still made from depleting non-renewable feedstocks
- Our chemical industry still largely deals with safety through engineering.

For additional reading on another example:

- https://www.acs.org/content/dam/acsorg/membership/acs/benefits/discovery-reports/green-chemistry-applications.pdf
- https://www.youtube.com/watch?v=NSozp4_QeLI

Green Chemistry – How it should be done



Instead of thinking linearly....

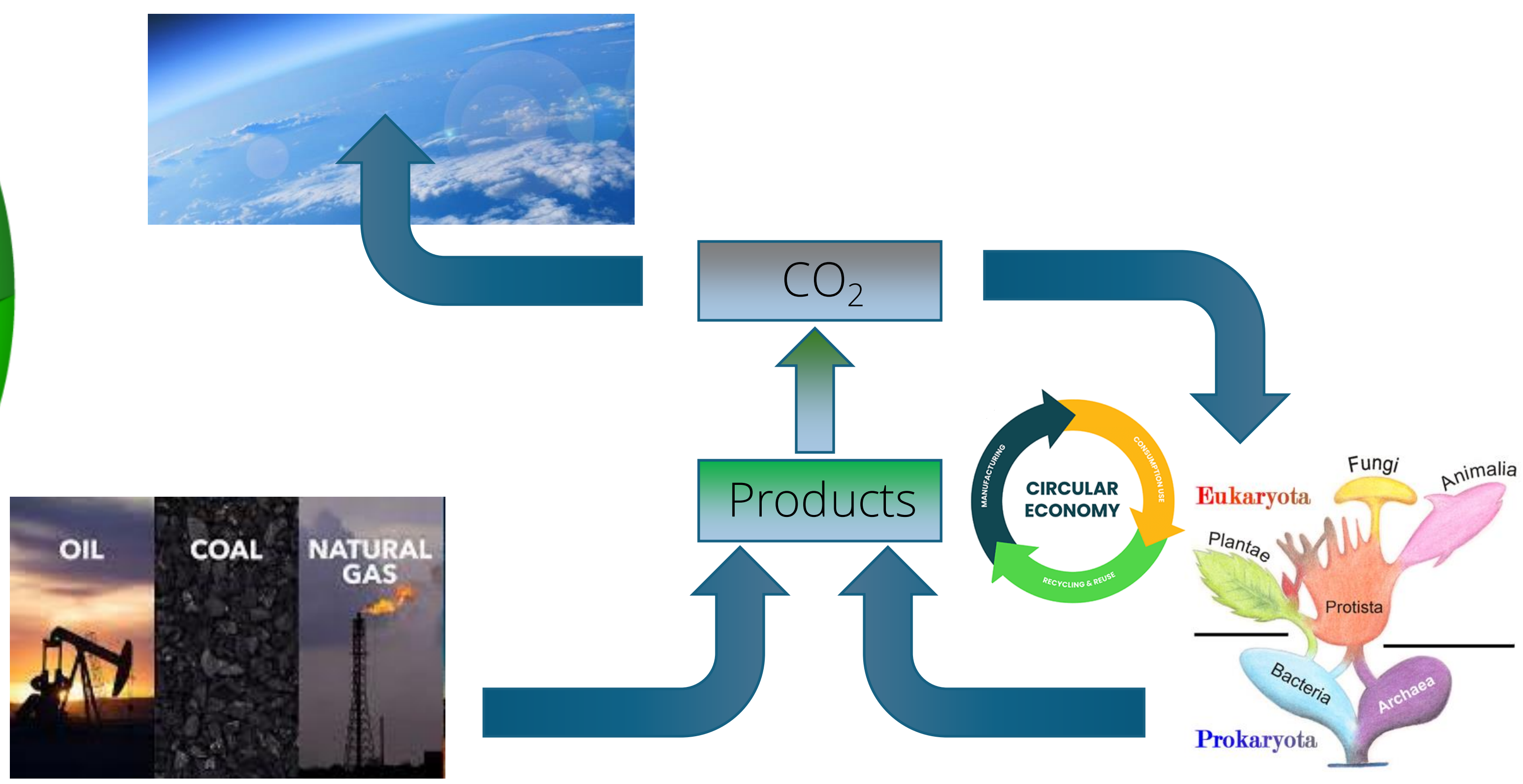
....we need to start think in systems.

Toolbox for Sustainability

It is important to understand that the 12 principles are interlinked, using one often implies using some of the others.

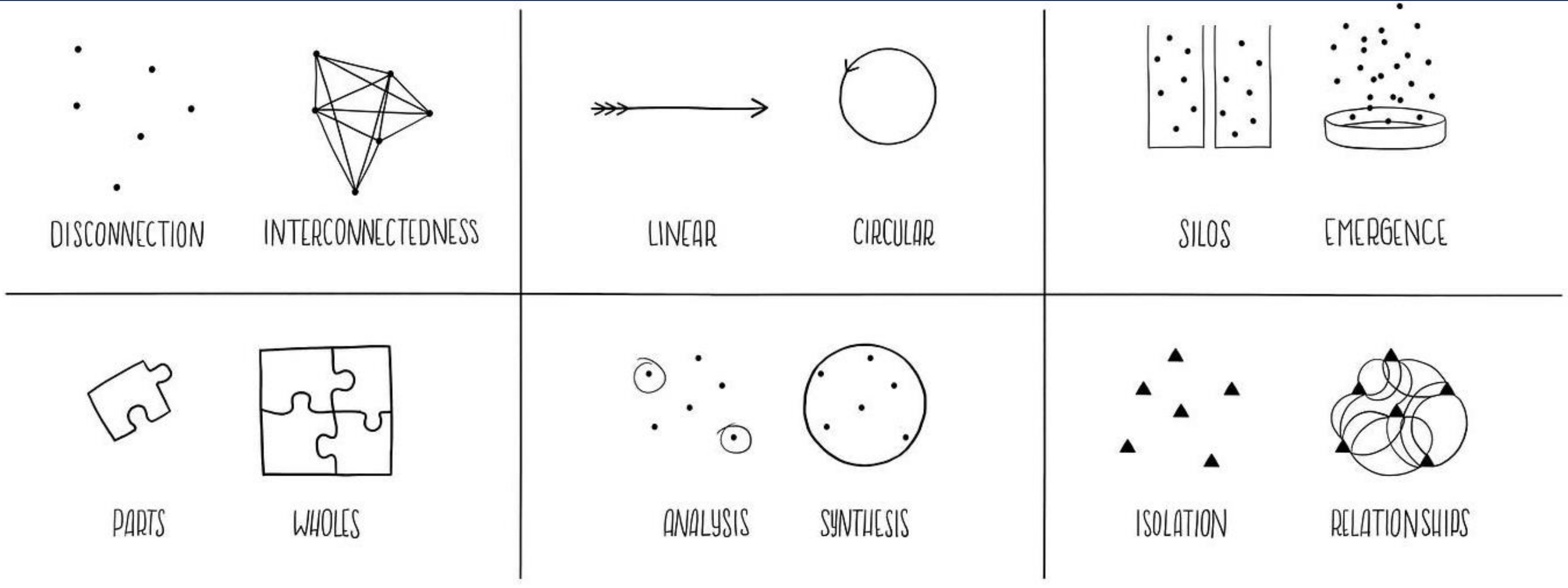
Green Chemistry can change paradigms...

“Open” system → “Closed” system



Systems Thinking

The "What happens when..."



https://medium.com/disruptive-design/tools-for-systems-thinkers-the-6-fundamental-concepts-of-systems-thinking-379cdac3dc6a

DISRUPT DESIGN

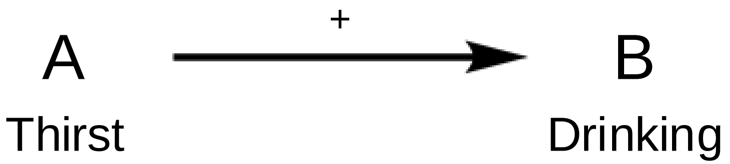
"What happens when..."

To solve today's problems, we need to address these thinking about them as systems:

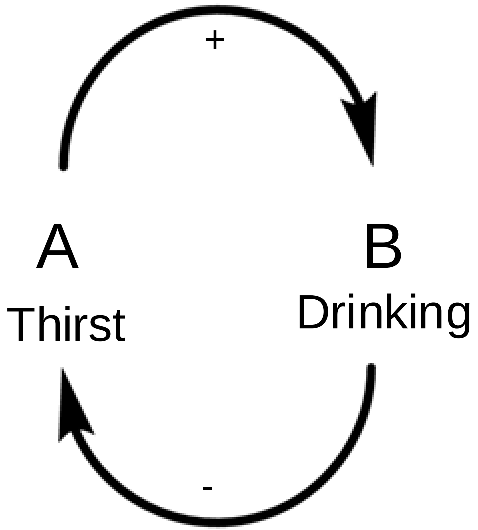
- It's essential to recognize that (basically all) things are part of a system.
- If we don't think in systems, good intentions can bring about unintended negative consequences.

Simple system: Cause-Effect Relationships

The reductionist approach in chemistry does not consider cause and effect relationships.



In reality the same relation is probably linked in a cause-effect-relationship where A causes B, but then either directly or indirectly B influences A.



Complex Cause and Effect Relationships

Each chemical has a certain toxicity

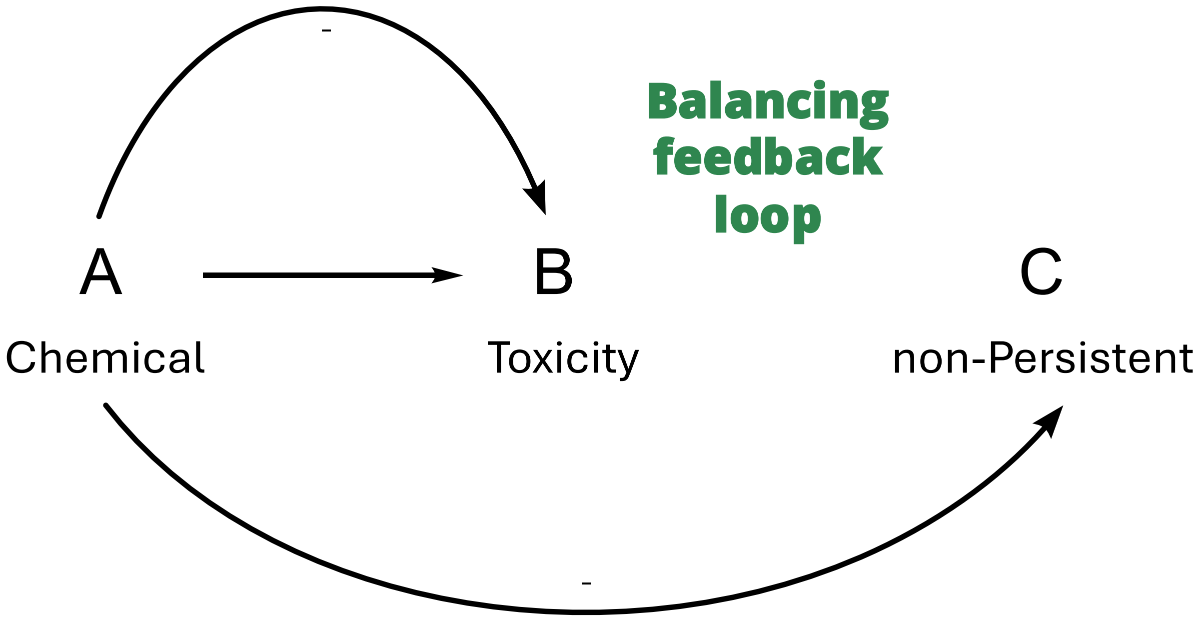
- If the chemical is **non-persistent**, it will degrade and concentration is lowered
- This will finally lower toxic effects
- If the influx is lower than its degradation, toxicity effects will lower as well

- If the chemical is **persistent**, it will not degrade
- It's toxic effects will stay the same
- **Any** influx of the chemical will increase its concentration, ultimately increasing its toxic effects

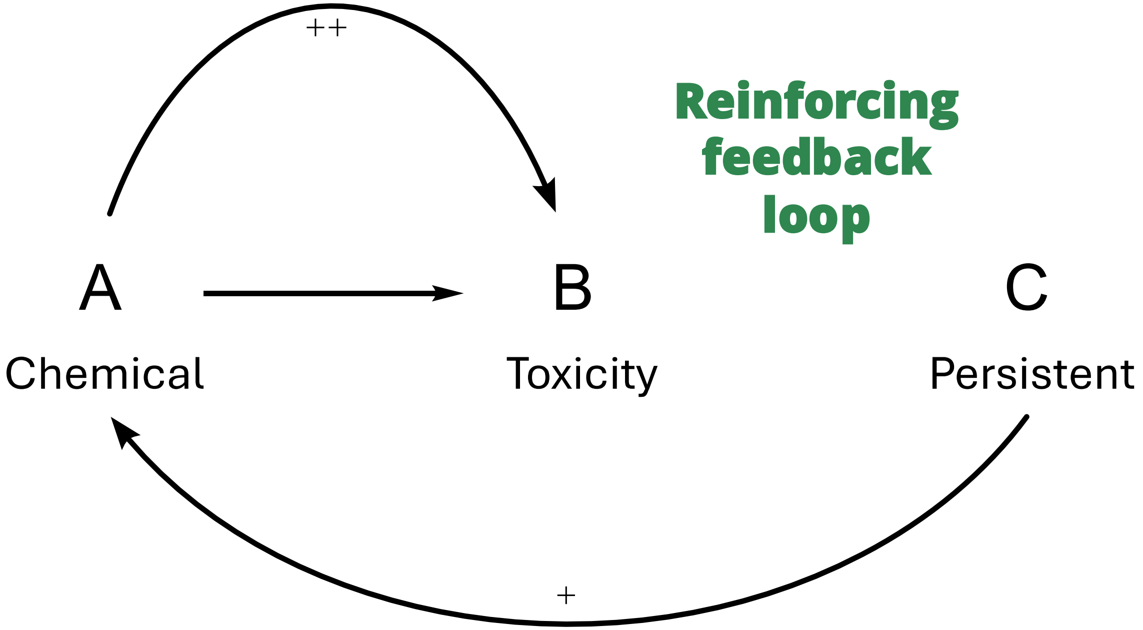
How would this look like in a simple systems diagram?

Complex Cause and Effect Relationships

Toxicity of **non-persisten**t chemical:



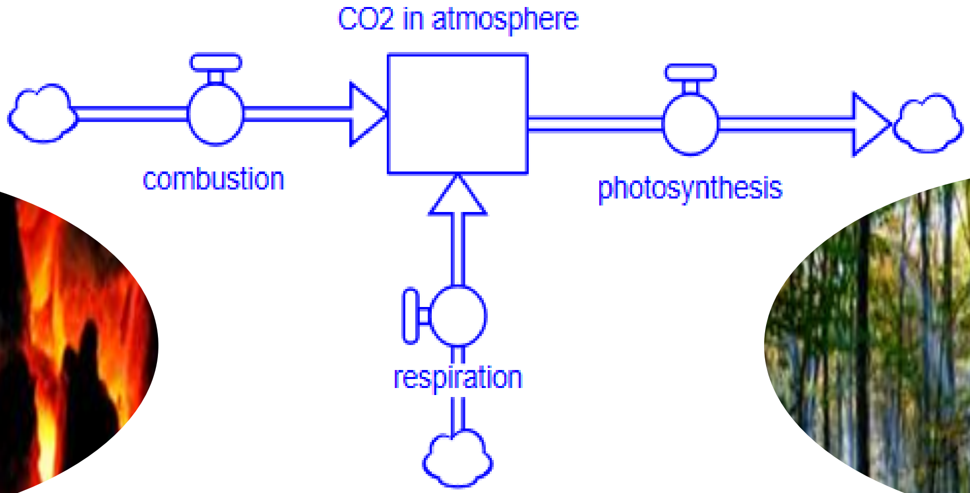
Toxicity of **persistent** chemical:



Visualization: Stock and Flow Diagrams

Stock-CO_2 in Earth's atmosphere

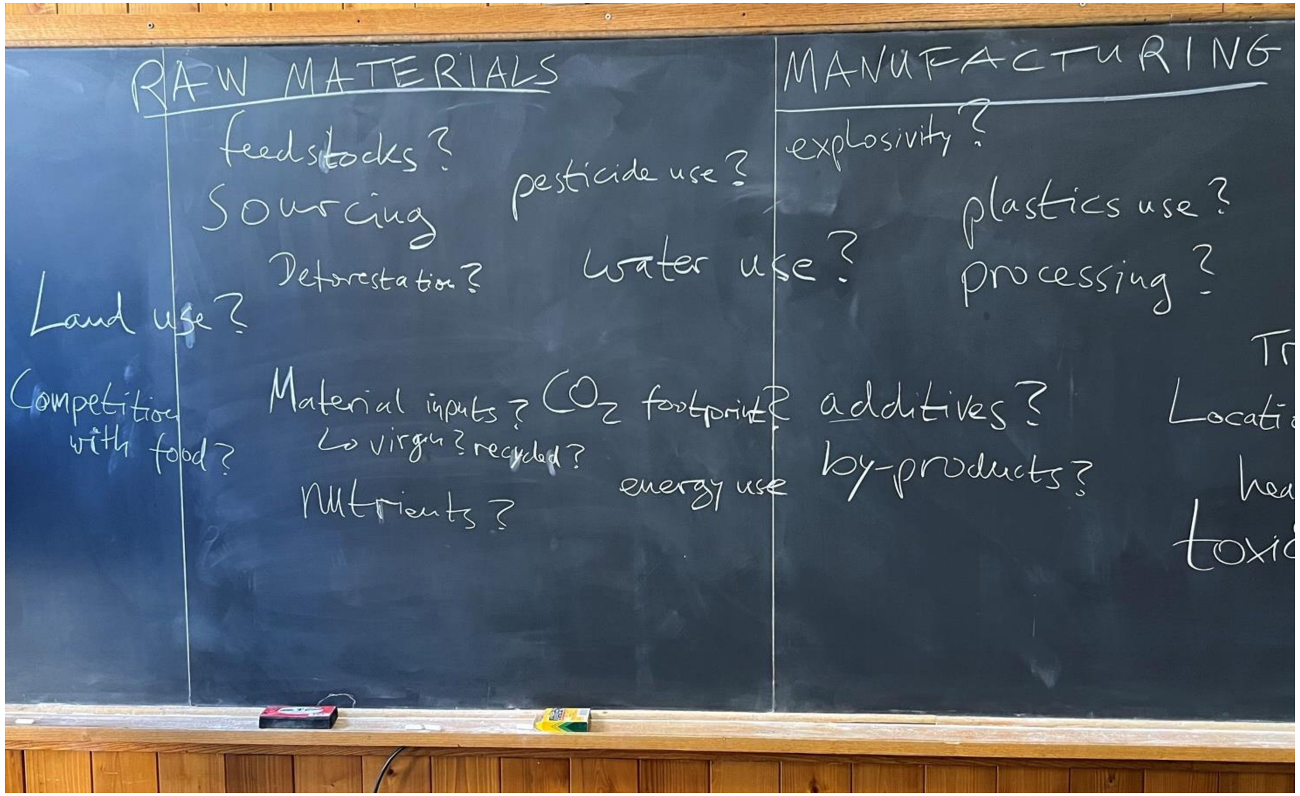
Flow: combustion, photosynthesis, respiration

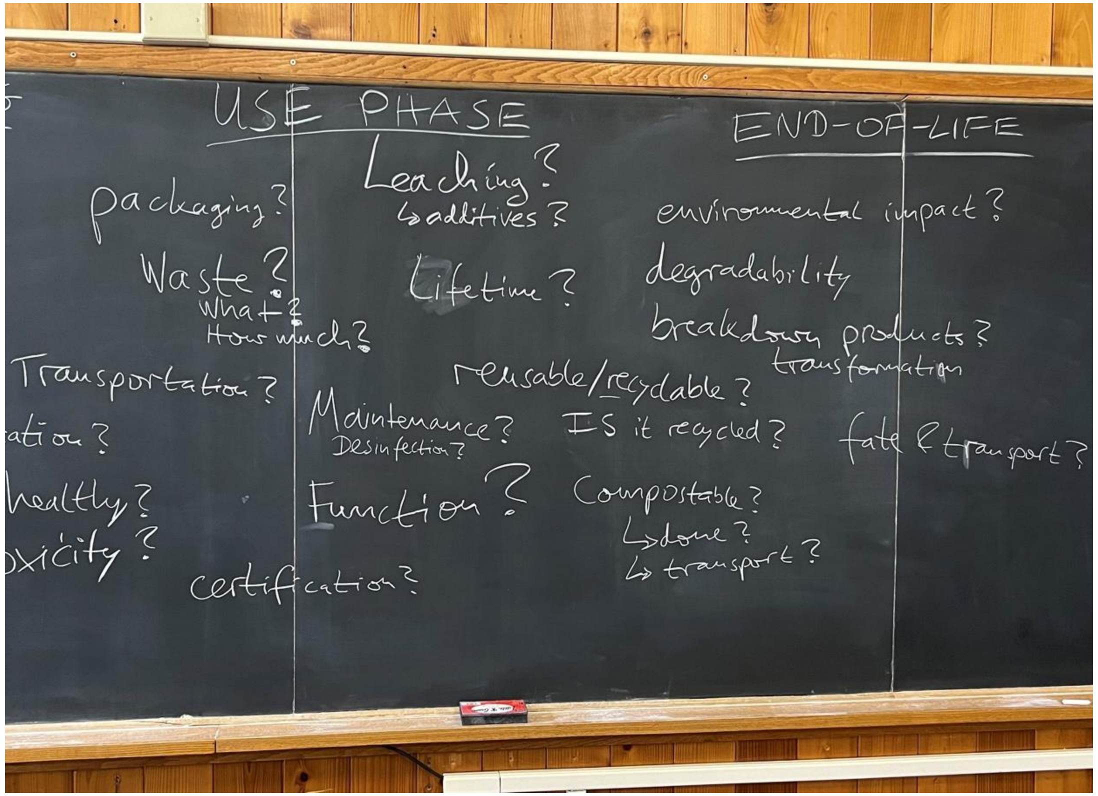


https://deq.nc.gov/about/divisions/air-quality
https://earthobservatory.nasa.gov/features/CarbonCycle

Organizing complex problems

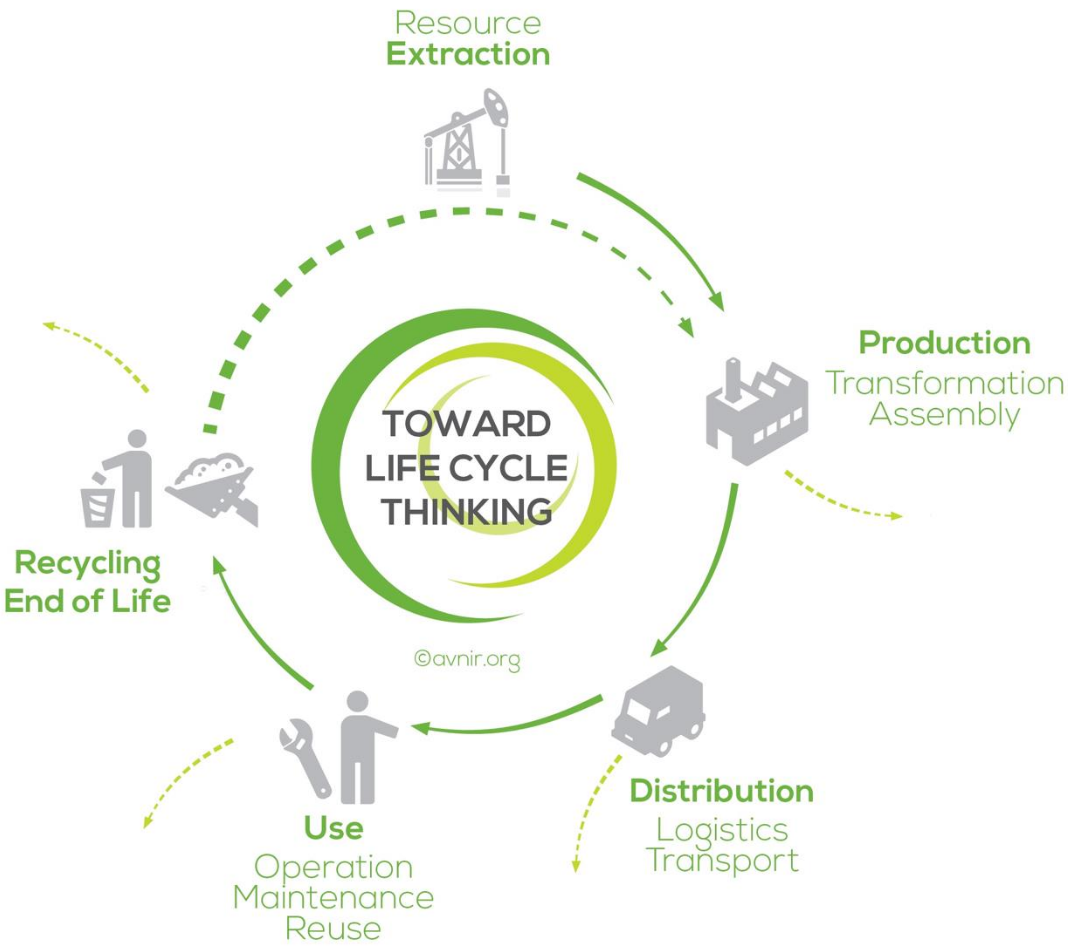
Systems visualizations are a great tool to understand complex problems, and the influence each component of a system can play.





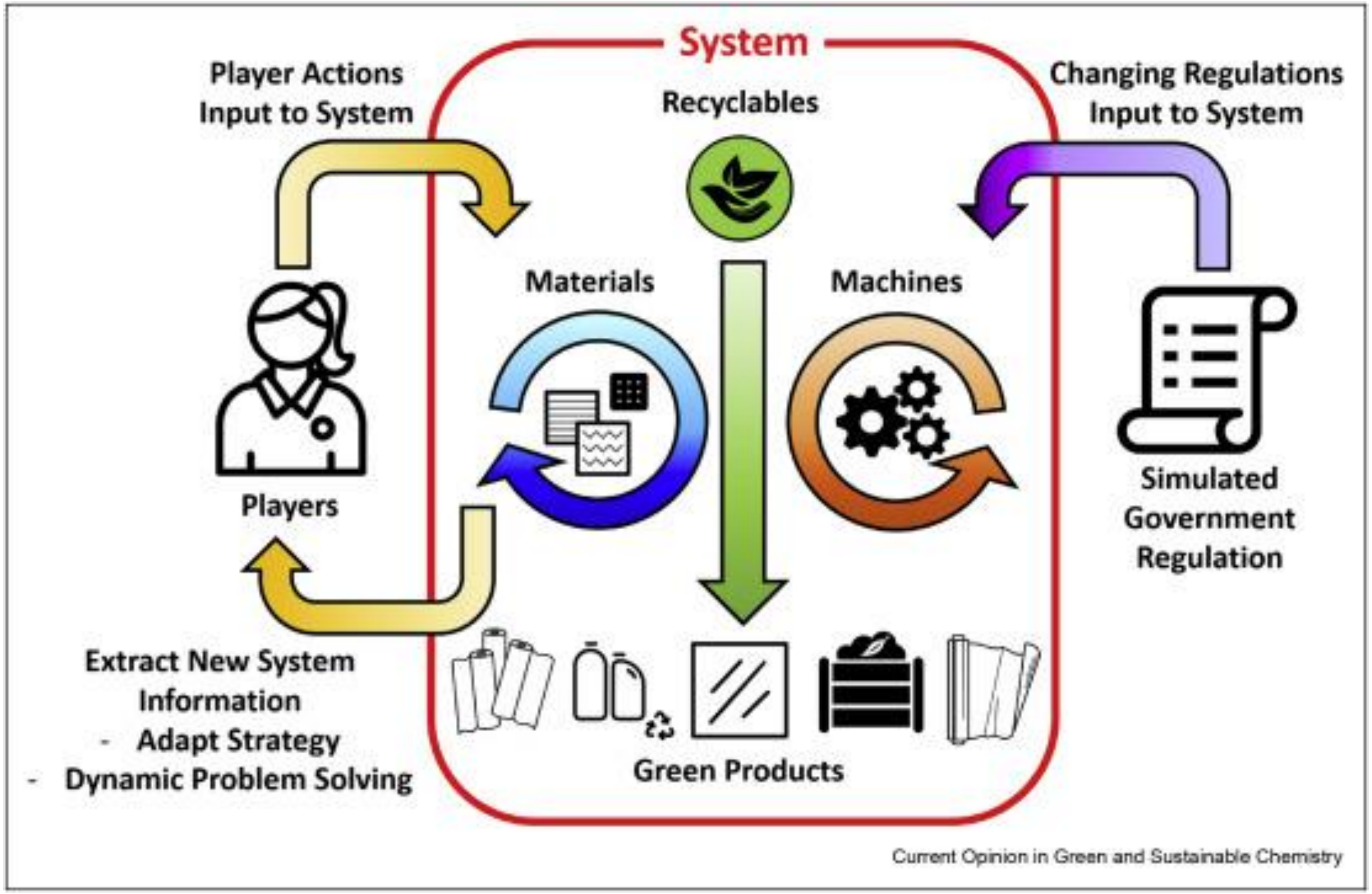
Organizing complex problems

Life cycle analysis (LCA) is a great example of this:



Organizing complex problems

The human component makes systems (even more) complex:



Hurst, G. A. (2020). Current Opinion in Green and Sustainable Chemistry, 21, 93–97.

From visualizing to measuring...

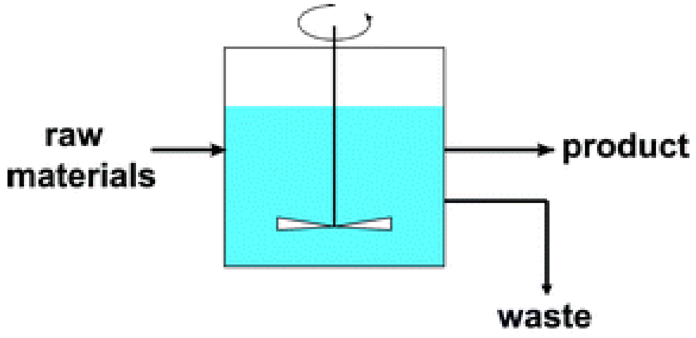
We have seen how factors relevant in Green Chemistry can relate to each other in a system.

Are there also ways to quantify (measure) Green Chemistry?

How can we measure Green Chemistry?

- E-Factor
- F-Factor
- Project Mass Intensity
- Energy Efficiency
- Life Cycle Assessment

E-Factor (Environmental)



$$E = \frac{\text{kg waste}}{\text{kg product}}$$

Sector	Product tonnage	E-Factor (kg waste per kg product)
Oil refining	10^6–10^8	<0.1
Bulk chemicals	10^4–10^6	<1 to 5
Fine chemicals	10^2–10^4	5 to >50
Pharmaceuticals	10–10^2	25 to >100

The oil refinery is very efficient (low price products)

Pharma industry is inefficient (high price products)

Sheldon, R. A., "The E-factor 25 years on," Green Chemistry, 19, 18-43, 2017.

F-Factor (Functional)

$$F = \frac{\text{Fulfilled Function}}{\text{kg product}}$$

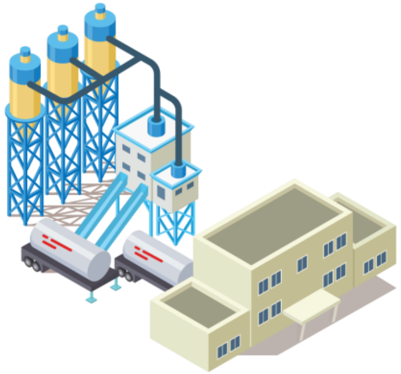
Example: Two different products (A or B) can be used for cleaning window surfaces, but have to be used in different quantities.

$$F_A = \frac{100 \text{ windows}}{1 \text{ kg}_A} = 100$$

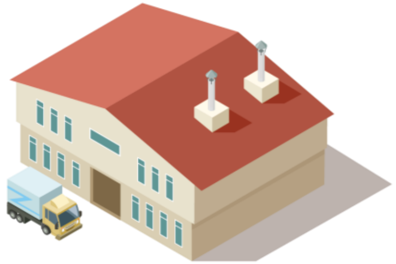
$$F_B = \frac{100 \text{ windows}}{0.2 \text{ kg}_B} = 500$$ ✓

F-Factor (Functional)

The F-Factor is a key concept underlying chemical leasing:



Provides not only chemicals but also expertise and services to optimize chemical use.



CHEMICAL SUPPLIER
A manufacturer/distributor/trader of chemicals

Know-how: More efficient and safer application of chemicals to the specific process

Benefit: Long-term business relation and better market competitiveness, higher profit, experience

MOTIVATION IS ALIGNED:
Both partners are interested in achieving better performance and desired quality by using
LESS CHEMICALS

Pays for function/services rendered by chemicals and not for the volume.

CHEMICAL USER
A company that uses chemicals in operations

Know-how: Specifics of the process where chemicals are used

Benefit: Economic, environmental, health and safety benefits; sustainable chemical management, specific knowledge

Important concept: Functional Unit

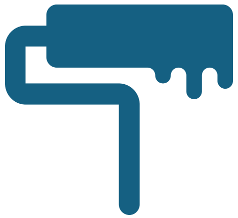
A functional unit is a unit of measure of material which inherently fulfills a defined primary function

A functional unit is the basis of an LCA and also a key out of F-Factor calculation!
Example of primary function: disinfecting 1 m^2 of counter top for 1 month

A functional unit does not contain a technical solution

Spray: need 10 cm^3 of liquid, applied daily

300 cm^3 per FU



Paint: need 30 cm^3 of liquid, applied monthly

30 cm^3 per FU

https://tristarmarblestone.ca/

PMI (Process Mass Intensity)

$$PMI = \frac{\text{total mass used in synthesis (kg)}}{\text{mass of product (kg)}}$$

The PMI is a metric which accounts for yield, reaction and reagent stoichiometry, catalysts and solvent and is often used in industry.

$$\text{Mass productivity} = \frac{1}{PMI} \times 100 = \frac{\text{mass of product (kg)}}{\text{total mass used in synthesis (kg)}} \times 100$$

Energy Efficiency

Energy efficiency is an important engineering metric that can have a profound impact on the efficiency of a process or reaction.

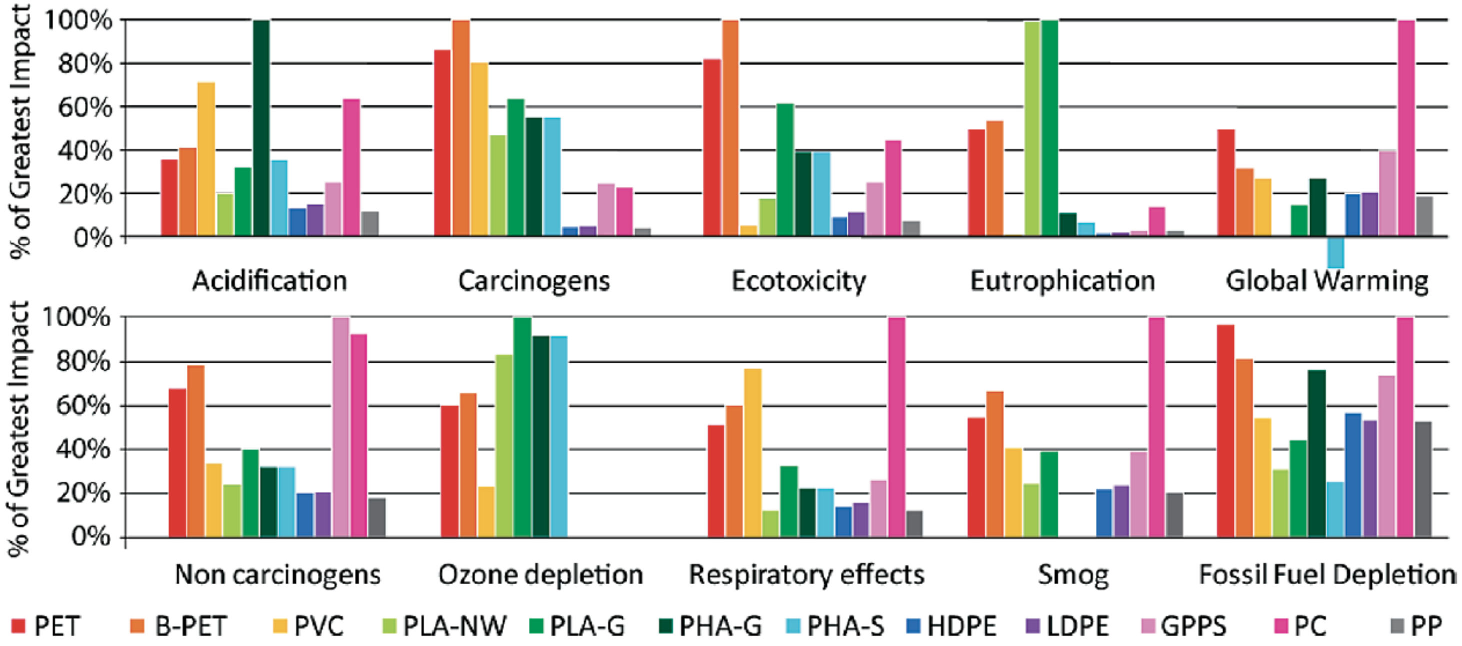
Most energy is used to heat/cool, pressurize/depressurize, or agitate a chemical reaction, and can be calculated in most cases.

$$q = \int_{298}^{T_m} c_{p,sol}(T)dT + \int_{T_m}^{T_b} c_{p,liq}(T)dT + \int_{T_b}^{T_{rxn}} c_{p,gas}(T)dT + \Delta H_{fus} + \Delta H_{vap}$$

Life Cycle Analysis: the bigger picture

LCA looks at many other factors, such as environmental impact and waste, toxicity, etc.

A **life-cycle assessment** (LCA, also known as life-cycle analysis, ecobalance, and cradle-to-grave analysis) is a technique to assess environmental impacts associated with all the stages of a **product's life from-cradle-to-grave** (i.e., from raw material extraction through materials processing, manufacture, distribution, use, repair and maintenance, and disposal or recycling).



M. D. Tabone, J.J. Cregg, E.J. Beckman, A. Landis, Environ. Sci. Technol. 2010, 44, 8264–8269.

In summary

Green Chemistry is a great tool for global sustainability.

- Evolution of Chemistry Knowledge
- The beginnings of Green Chemistry
- 12 Principles of Green Chemistry
- Green Chemistry – How it should be done!
- Systems Thinking
- Green Chemistry Metrics

Yale School of the Environment

Center for Green Chemistry & Green Engineering at Yale

Advance Science

Catalyze Implementation

Prepare the next generation

Raise Awareness

Thank You!

For questions, please reach out:

greenchemistry@yale.edu

https://www.globalgreenchem.com

https://www.chemistryforsustainability.org

https://greenchemistry.yale.edu/

@GREENCHEMISTRY.YALE

Executed by:

Center for Green Chemistry & Green Engineering at Yale

Implemented by:

UNIDO

Financed by:

gef global environment facility INVESTING IN OUR PLANET