Green Chemistry

Inorganic II

CHEM 3740

UNIVERSITY of Prince Edward ISLAND

Green Chemistry – Learning Objectives

Outline

In this unit we will focus exploring the principles of green chemistry, green metrics, life cycle analysis, systems thinking, *two-eyed seeing*, and their applications in inorganic chemistry. We will consider current global challenges and the drawbacks/benefits of current systems.

Topics

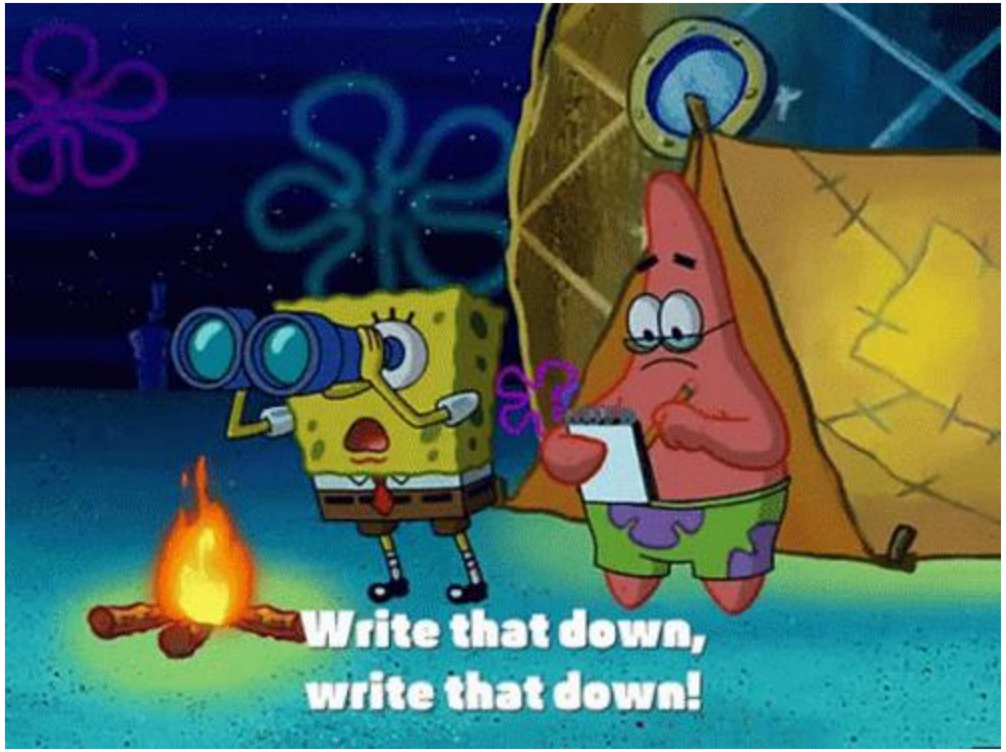
- Equity, Diversity, Inclusivity, Accessibility, and Reconciliation in sustainable research
- Systems Thinking and *Two-Eyed Seeing*
- 12 Principles of Green Chemistry
- Life cycle analysis and green chemistry metrics
- Applications of green chemistry in catalysis

Learning Objectives

1. To understanding the application and importance of green chemistry metrics
2. To analyse current systems and propose alterations to improve sustainability
3. To explore the landscape of green chemistry in inorganic chemistry and new areas of research

Presentation Navigation

- Exam Questions/Content
- Skills Worth Practicing
- Laboratory Content



Sustainable Development

"Sustainability focuses on meeting the needs of the present without compromising the ability of future generations to meet their own needs."

~ United Nations Brundtland Commission, 1987

3 GOOD HEALTH AND WELL-BEING

16 PEACE, JUSTICE AND STRONG INSTITUTIONS

Sustainable Development

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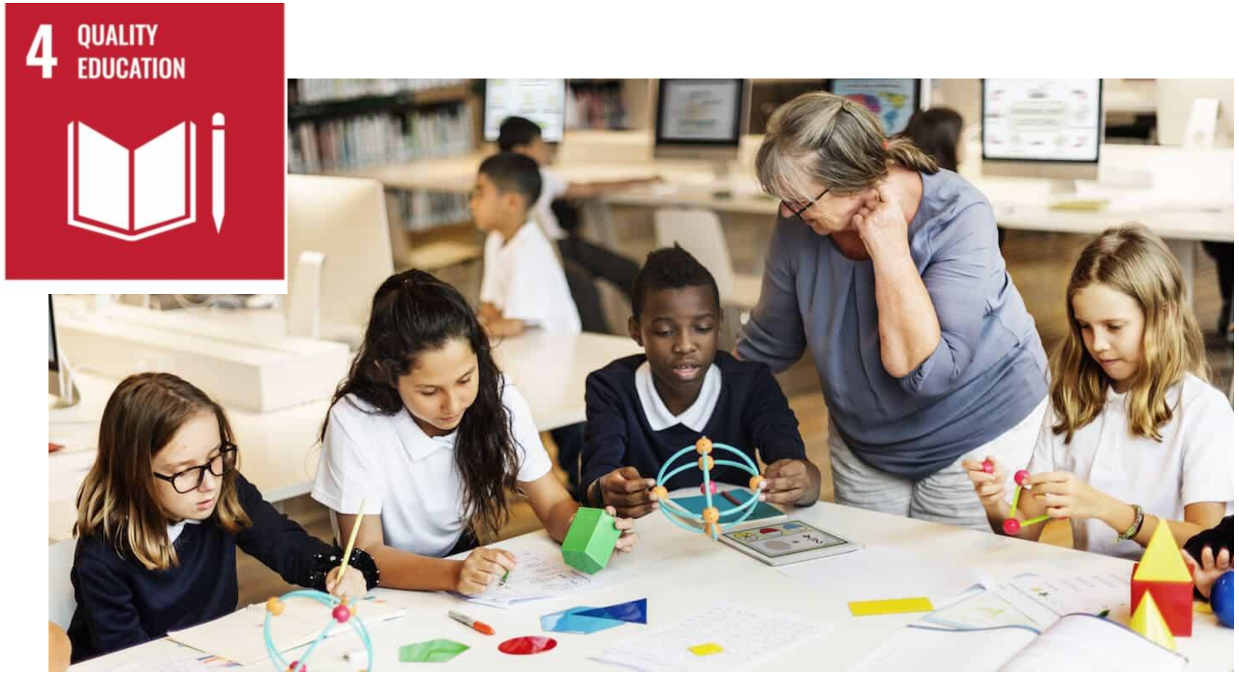
~ United Nations Brundtland Commission, 1987



United Nations Sustainability Goals

https://sdgs.un.org/goals.

United Nations Sustainability Goals

"The problem as I see it is that there's a view of scientists – science is impartial and shouldn't have politics. Therefore, scientists must be amorphous, faceless things without any identity or any politics or any this that or the other, and that's not true. **It's the scientists who do the science and we do better science when we're comfortable.**"

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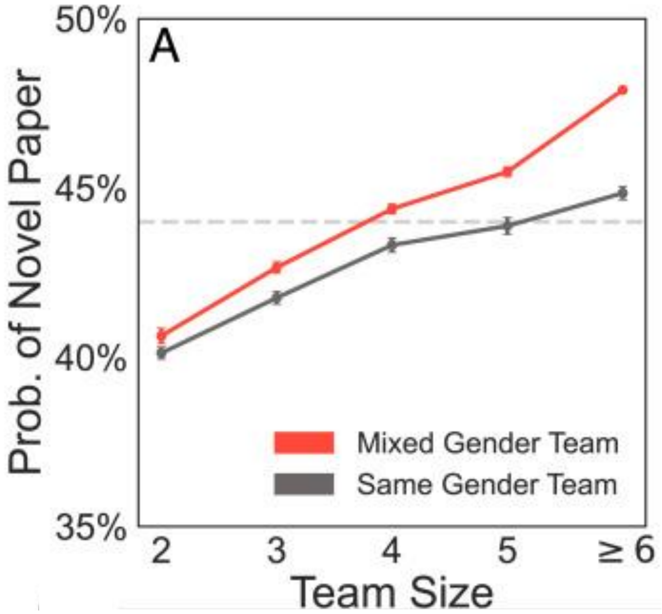
https://www.rsc.org/policy-evidence-campaigns/inclusion-diversity/resources/lgbt-toolkit/

EDI-AR: A Driver In Sustainable Development

"Diversity—defined as differences in how we see the world, how we think about the world, how we try and solve problems, the analogies we use, the metaphors, the tools we acquire, the life experiences we have—makes us better at what we do."

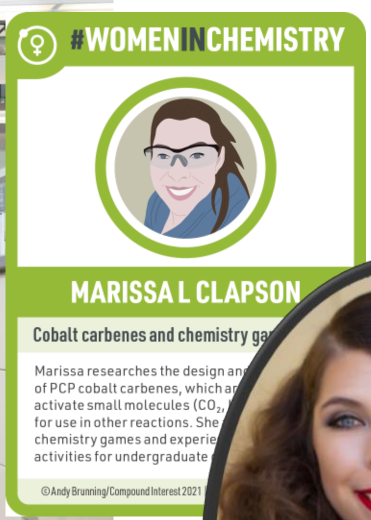
Data Driven Support:

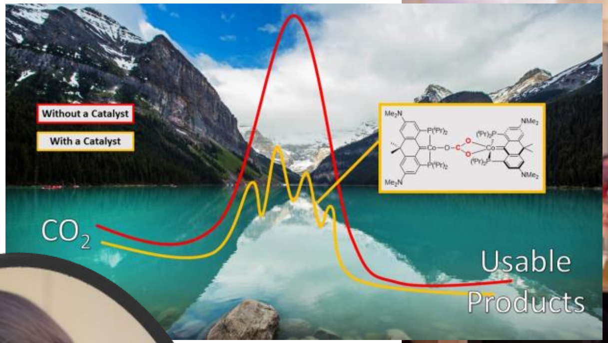
1. Diverse teams outperform less diverse teams and are associated with better problem solving and improved innovation.
2. Ethnically diverse teams publish more and in higher impacts journals.
3. Large mixed-gender scientific teams publish more, are 9.1% more likely to publish a novel paper, and have 34% more citations.
4. Underrepresented groups draw relations between ideas and concepts that have been traditionally missed or ignored.



Swartz, T. H.; Palermo, A. S.; Masur, S. K.; Aberg, J. A. *Journal of Infectious Diseases* **2019**, *220, 2*, S33-S41.
AlShebli, B. K.; Rahwan, T.; Woon, W. L. *Nat Commun.* **2018**, *9, I,* 5163.
Yang, Y.; Tian, T. Y.; Woodruff, T. K.; Jones, B. F.; Uzzi, B. *Proc. Natl. Acad. Sci. USA*, **2022**, *119, 36,* e2200841119.
Campbell, L. G.; Mehtani, S.l Dozier, M. E.; Rinehart, J. *PLOS ONE*, **2023**, *8, 10*, e79147.
Hofstra, B.; Kulkarni, V. V.; Galvez, S. M-N.; He, B.; Jurafsky, D.; McFarland, D. A. *Proc. Natl. Acad. Sci. USA*, **2020**, *117, 17,* 9284 – 9291.

Bringing Your Full Self





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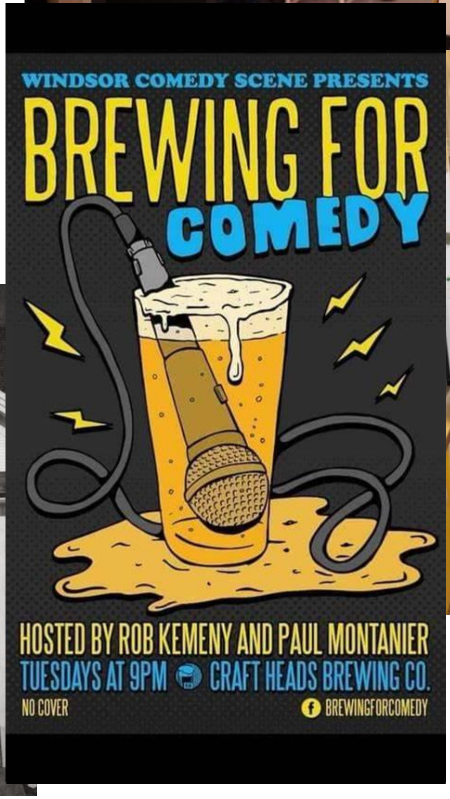

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Defining Sustainability

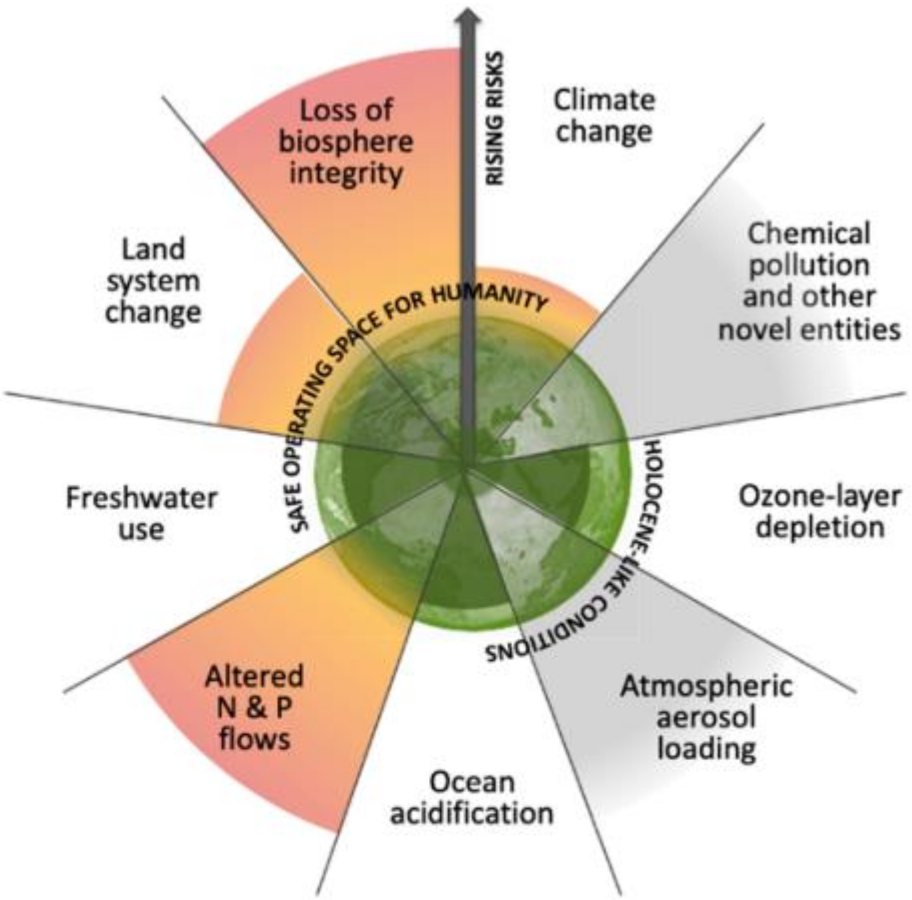
"Sustainability is the process of living within the limits of available physical, natural, and social resources in ways that allow the living systems in which humans are embedded to thrive in perpetuity."

– University of Alberta

What does global sustainability and sustainability in chemistry mean to you?

- Green chemistry principles

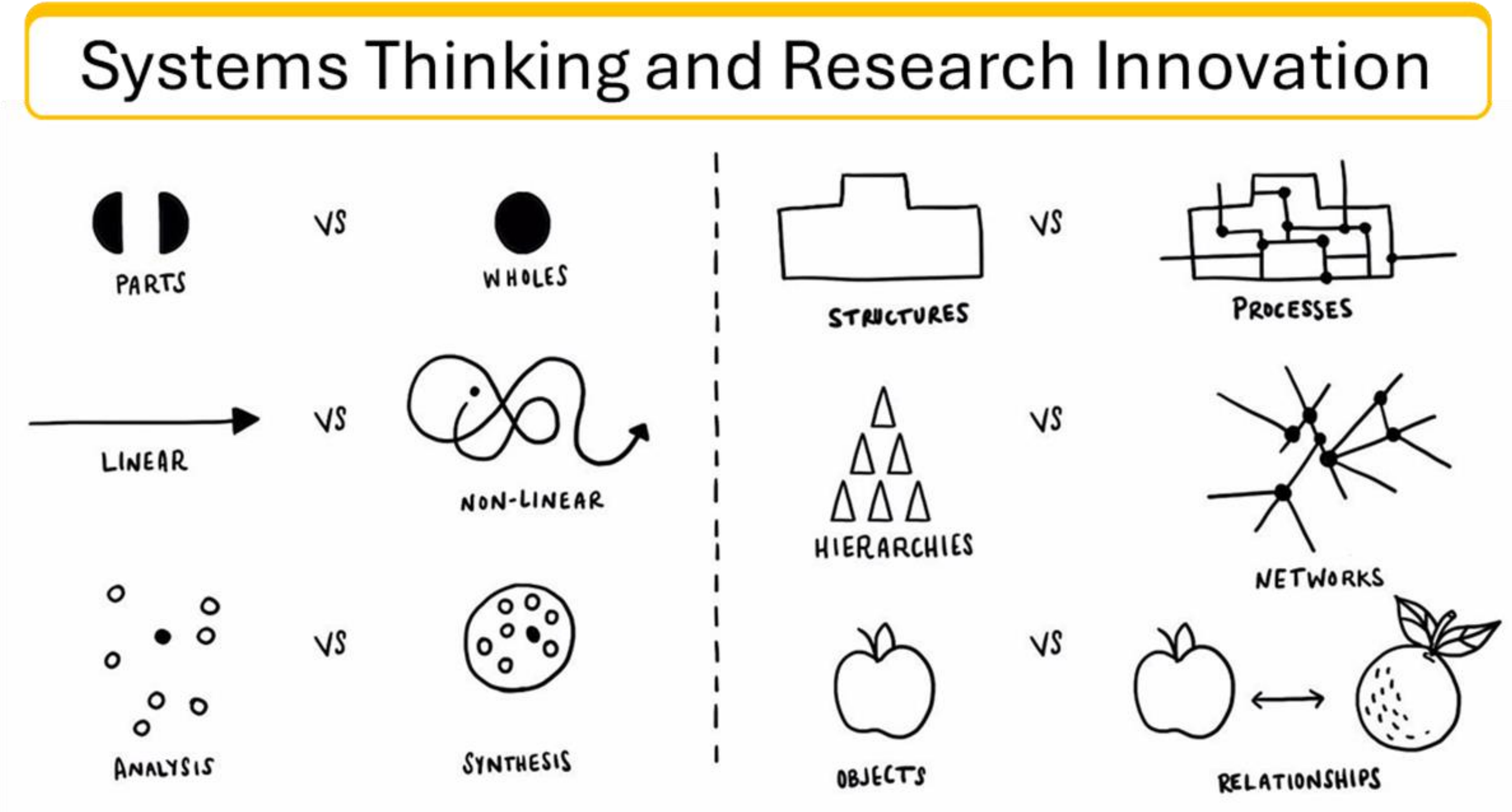
Planetary Boundaries



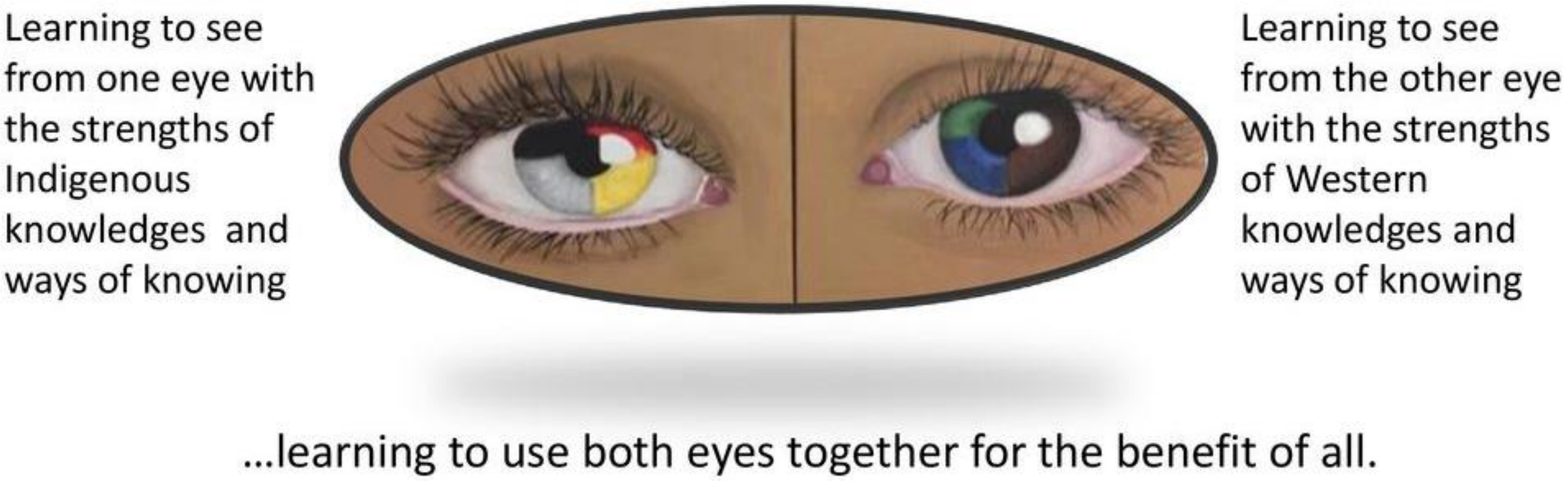
Variable:	Indicator measured	Below boundary (safe)	In zone of uncertainty (increasing risk)	Beyond zone of uncertainty (high risk)	Boundary not yet quantified globally	Important opportunities for chemistry contributions
Atmospheric aerosol loading:	Aerosol Optical Depth (AOD), but much regional variation					Better understanding of formation of atmospheric aerosols as suspensions of liquid, solid, or mixed particles; and of processes to prevent them
Biogeochemical flows:	Nitrogen: industrial & intentional biological fixation	62 Tg/yr		152 Tg/yr		Sustainable synthesis and applications of NH_3
	Phosphorus: flow from freshwater systems into ocean	11 Tg/yr		22 Tg/yr		Sustainable synthesis and applications of P compounds
Change in biosphere integrity:	Genetic diversity (extinction rate)	<10 E/MSY		100-1,000 E/MSY (E/MSY: extinctions per million species-years)		
	Functional diversity (Biodiversity Intactness Index)					
Climate change:	Atmospheric CO_2 concentration	350 ppm	398.5 ppm in 2015 (rose to 412.5 ppm in 2020)			Reduction of CO_2 production/ elimination of atmospheric release. Prevention of atmospheric release of CH_4, N_2O, NOx, C-F gases
	Energy imbalance at top of atmosphere (radiative forcing)	1.0 W m^{-2}		2.3 W m^{-2}		
Freshwater use	Maximum amount of consumptive blue water use (km^3 yr^{-1})	4000 km^3 yr^{-1}	2,600 km^3 yr^{-1}			Development of new, low-cost, sustainable processes for water purification
Land-system change	Area of forested land as % of original forest cover	75 %	62 %			
Novel entities in environment:	[Chemical pollution] renamed: 'Novel entities' – not yet defined					Application of sustainability principles, systems thinking, environmental impact assessments to ensure
Ocean acidification	CO_3^{2-} concentration, average global surface ocean saturation state with respect to aragonite	≥80 % PIA	84 % PIA (PIA = % of pre-industrial aragonite saturation state of mean surface ocean)			Reduction of CO_2 production/elimination of atmospheric release.
Stratospheric ozone depletion:	Stratospheric O_3 concentration, Dobson Units (DU)	<5% rpi	Variable (rpi: % reduction from preindustrial level of 290 DU, assessed by latitude)			Ceasing all use of CFCs, HFAs, HCFAs. Prevention of atmospheric release of N_2O, NOx.

Matlin, S.; Cornell, S.; Krief, A.; Hopf, H.; Mehta, G. *Chemical Sciences*, **2022**, *13* (40), 11710 - 11720.
MacDonald, R. P.; Pattinson, A. N.; Cornell, S. E.; Elgersma, A. K.; Greidanus, S. N.; Visser, S. N.; Hoffman, M.; Mahaffy, P. G. *J. Chem. Educ.* **2022**, *99* (10), 3530 – 3539.

Systems Thinking



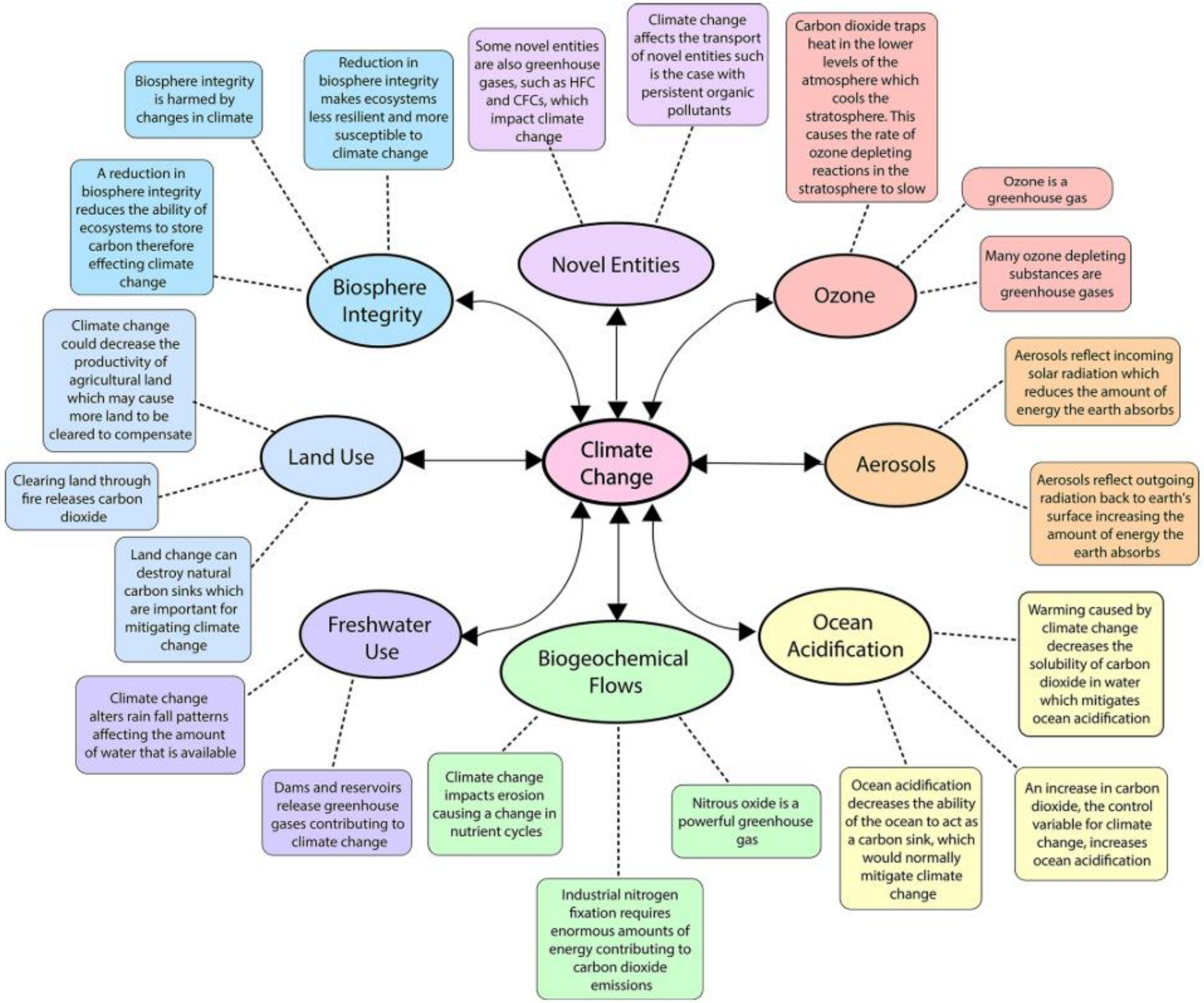
Etuaptamumk: Two-Eyed Seeing



A reminder of the benefits of traditional knowledge and how we can co-opt these learning with more “classical” views of chemistry to achieve modern goals.

Decolonizing the Colonized Mind, CTLT@UNBC
Smith, C.; Diver, S.; Reed, R. *Environmental Planning F,* **2023**, *2(1-2),* 121 – 143.

Building the Web – Climate Change



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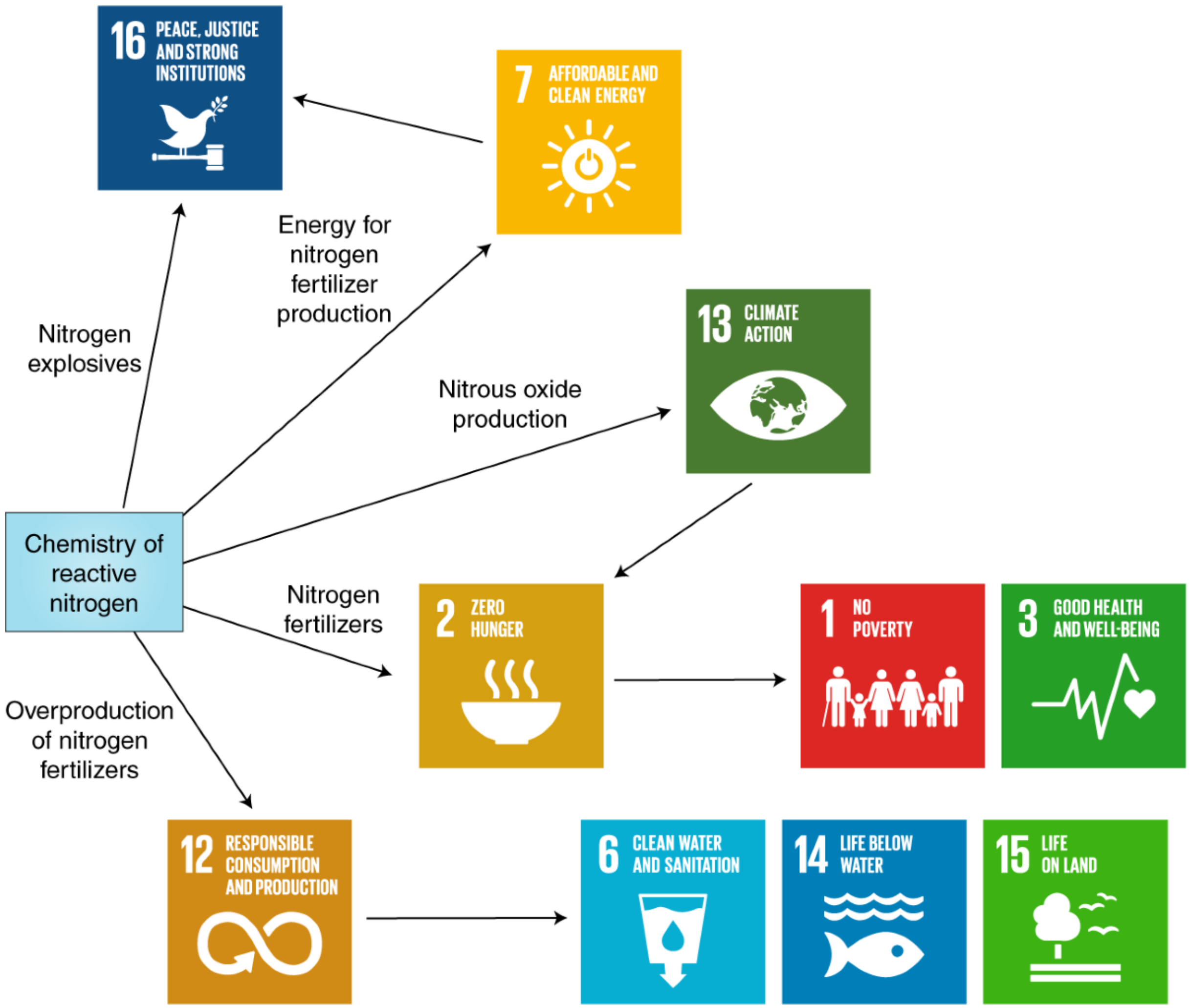
How Does Your Chemistry Learning Relate to Sustainability?



- What types of chemistry research am I interested in learning?
- What are the later impacts that type of chemistry can have?
- How does my personal experience allow me to relate to these goals to global sustainability/green chemistry?

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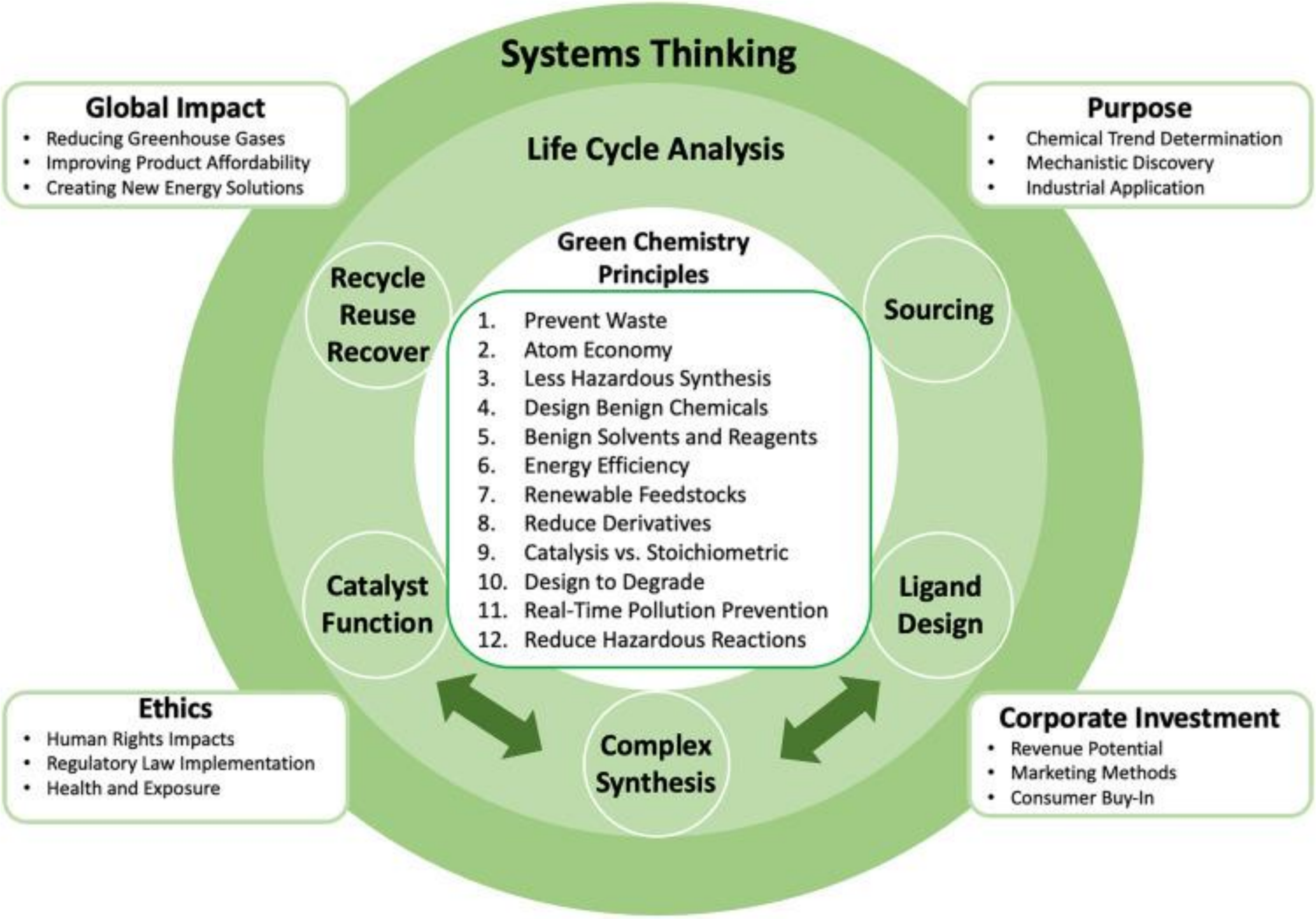
Mahaffy, P.G., Matlin, S.A., Holme, T.A. *Nat Sustain*, **2019**, *2*, 362–370.

Sustainability and Green Chemistry



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Clapson, M. L.; Durfy, C. S.; Facchinato, D.; Drover, M. W. *Cell Reports Physical Science*, **2023**, *4*, 9, 101548..

The 12 Green Chemistry Principles

1. WASTE PREVENTION

Prioritize the prevention of waste, rather than cleaning up and treating waste after it has been created. Plan ahead to minimize waste at every step.

2. ATOM ECONOMY

Reduce waste at the molecular level by maximizing the number of atoms from all reagents that are incorporated into the final product. Use atom economy to evaluate reaction efficiency.

3. LESS HAZARDOUS CHEMICAL SYNTHESIS

Design chemical reactions and synthetic routes to be as safe as possible. Consider the hazards of all substances handled during the reaction, including waste.

4. DESIGNING SAFER CHEMICALS

Minimize toxicity directly by molecular design. Predict and evaluate aspects such as physical properties, toxicity, and environmental fate throughout the design process.

5. SAFER SOLVENTS & AUXILIARIES

Choose the safest solvent available for any given step. Minimize the total amount of solvents and auxiliary substances used, as these make up a large percentage of the total waste created.

6. DESIGN FOR ENERGY EFFICIENCY

Choose the least energy-intensive chemical route. Avoid heating and cooling, as well as pressurized and vacuum conditions (i.e. ambient temperature & pressure are optimal).

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https://www.acs.org/greenchemistry/principles/12-principles-of-green-chemistry.html

The 12 Green Chemistry Principles

7. USE OF RENEWABLE FEEDSTOCKS

Use chemicals which are made from renewable (i.e. plant-based) sources, rather than other, equivalent chemicals originating from petrochemical sources.

8. REDUCE DERIVATIVES

Minimize the use of temporary derivatives such as protecting groups. Avoid derivatives to reduce reaction steps, resources required, and waste created.

9. CATALYSIS

Use catalytic instead of stoichiometric reagents in reactions. Choose catalysts to help increase selectivity, minimize waste, and reduce reaction times and energy demands.

10. DESIGN FOR DEGRADATION

Design chemicals that degrade and can be discarded easily. Ensure that both chemicals and their degradation products are not toxic, bioaccumulative, or environmentally persistent.

11. REAL-TIME POLLUTION PREVENTION

Monitor chemical reactions in real-time as they occur to prevent the formation and release of any potentially hazardous and polluting substances.

12. SAFER CHEMISTRY FOR ACCIDENT PREVENTION

Choose and develop chemical procedures that are safer and inherently minimize the risk of accidents. Know the possible risks and assess them beforehand.

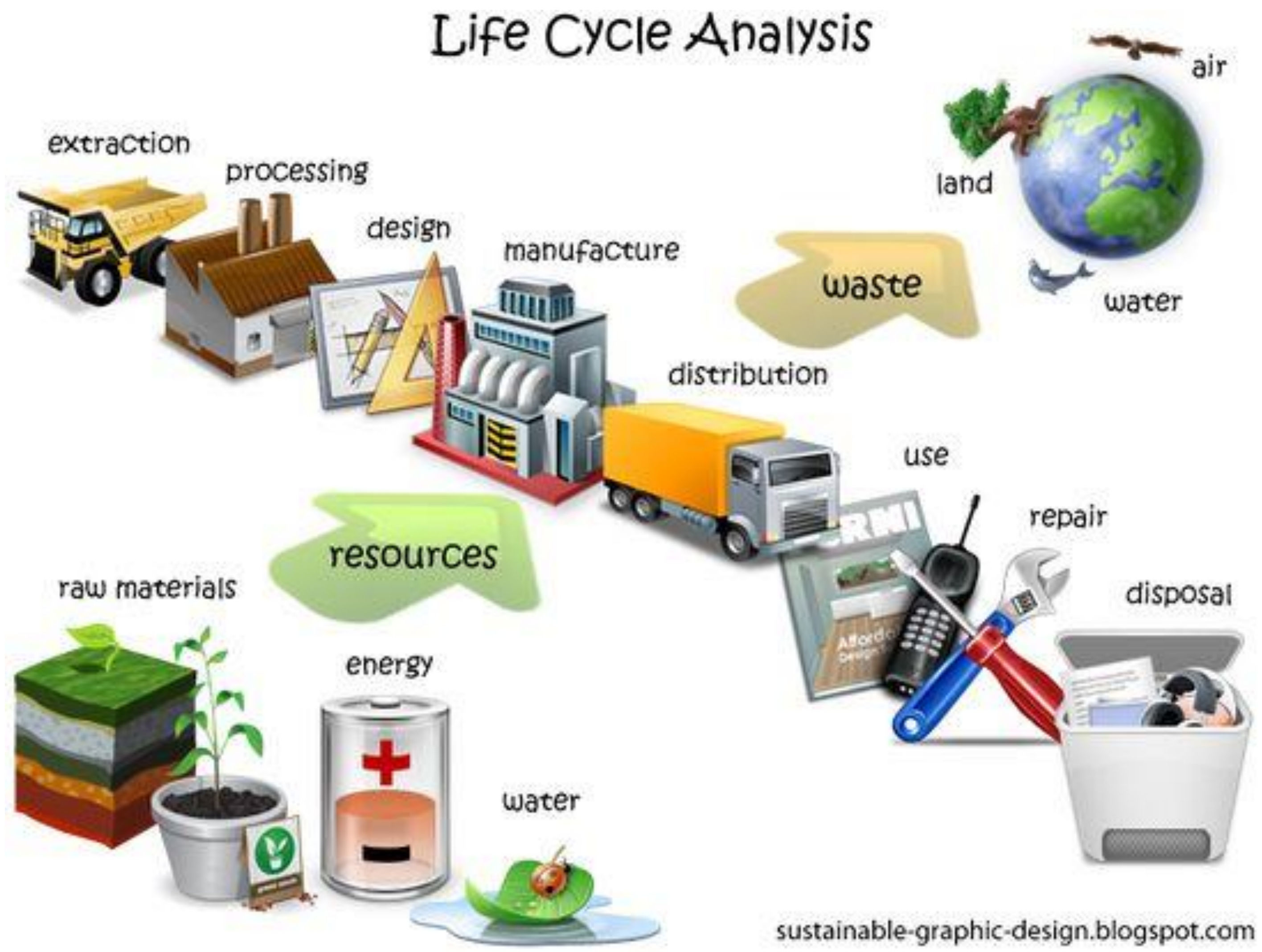
https://www.acs.org/greenchemistry/principles/12-principles-of-green-chemistry.html

Life Cycle Analysis

A full life cycle analysis considers a product from **"cradle" to "grave"**.

In a green application, one would want to extend a product to be **"cradle to cradle"** meaning that the end product can be recycled, reused, of decomposed to its material components and utilized in the system again.

In research, a full life cycle analysis is not always feasible, but we can do a truncated version to assess specific molecules in the lab.



Green Chemistry Metrics

Acidification Potential (AP): the potential for a gaseous compound to generate acid rain relative to an equal mass of SO_2. If the gaseous chemical is a Brønsted acid or can be transformed into a Brønsted acid upon oxidation and hydration in the atmosphere than an AP value is calculated.

$$AP = \frac{\alpha(Mw)}{\alpha_{SO2}(Mw_{SO2})}$$

α = number of dissociable protons in the strong acid form (ex. α_{SO2} = 2 because it forms H_2SO_4).
Mw = molecular weight of the gaseous compound.

To calculate the index of a green metric, the metric is multiplied by the mass (m) of the compound.

$$I_{AP} = APm$$

Global Warming Potential (GWP): a ratio of the irradiative forces (e.g. ability to cause global warming) of a gaseous or volatile chemical over time compared to an equal mass of carbon dioxide.

$$GWP = \frac{NC(Mw)}{NC_{CO2}(Mw_{CO2})}$$

NC = number of carbon atoms in the compound.

Human Toxicity by Inhalation Potential (INHTP): the ratio of the concentration of a compound in the air in relation to the toxicity of the reagent (LC_{50} rat, g/m^3 4h) compared to an equal mass of toluene (a standard).

$$INHTP = \frac{C_a/LC_{50})}{C_{a,tol}/LC_{50,tol})}$$

C_a = airborne concentration of the chemical.
LC_{50} = toxicity for the chemical to a rat, g/m^3 4h.

Atom Economy (AE): the number of reagents incorporated into the desired product. A value of 1 is the best possible value.

$$AE = \frac{Mw_{Product}}{\sum Mw_{Reagents}}$$

Carbon Efficiency (CE): the amount of carbon from the reagents maintained in the desired product.

$$CE = \frac{CN_{Product}}{\sum CN_{Reagents}}$$

Process Mass Intensity (PMI): a measure of the mass of reagents used in the formation of the final desired product compared to the mass of the desired product.

$$PMI = \frac{\sum m_{Reagents}}{m_{Product}}$$

Environmental Factor (E-Factor): the amount of waste generated compared to the amount of desired product.

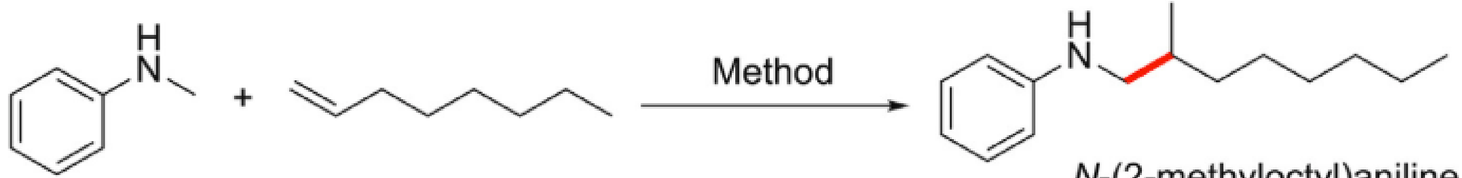
$$E - Factor = \frac{\sum m_{waste}}{m_{Product}}$$

Reaction Mass Efficiently (RME): an inverse E-factor that can be used to analyze specific parts of a reaction processes.

$$RME = \frac{m_{Product}}{\sum m_{Reagents}}$$

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

Example LCA Comparing Two Catalysts

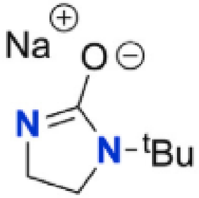


N-(2-methyloctyl)aniline

A Tantalum-catalyzed synthesis

- ☒ 3 step synthesis to metal starting material
- ☑ 1 step ligand synthesis
- ☒ H_2SO_4 required for ligand synthesis

[**Ta**($CH_2SiMe_3)_3Cl_2$] (5 mol%)
L1 (5 mol%)
110 °C, 1 h
toluene (0.867 M)

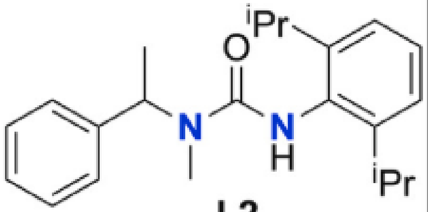


L1

B Titanium-catalyzed synthesis

- ☑ commercially-available starting material
- ☑ 1-step ligand synthesis
- ☒ HCl generated from ligand synthesis

[**Ti**($NMe_2)_4$] (5 mol%)
L2 (5 mol%)
160 °C, 2 h
toluene (1.0 M)



L2

Route	I_{AP}	I_{OD}	I_{SF}	I_{GW}	I_{INHT}	I_{INGST}	PER	ACCU log K_{ow}	I_{AD}	CO_2 (kg)	EF	RME
Ta	80	0	60	70 000	3000	2×10^5	Months	4	2	70	7	40%
Ti	30	0	5	100	30	5×10^9	Very long-lived	4	0.005	50	5	80%

ManBen, M; Scott, S. S.; Deng, D.; Zheng, C. H. M.; Schafer, L. L. *Green Chem.* **2023**, *25*, 2629 – 2639.

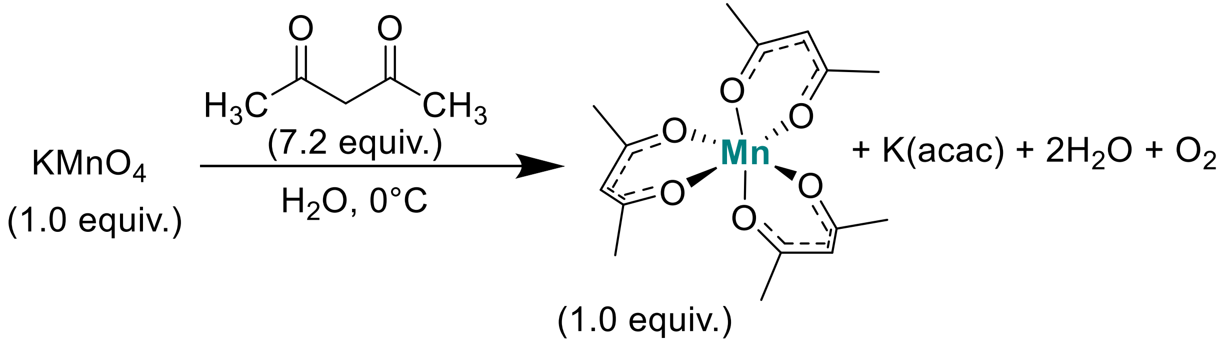
How to Perform a Truncated Life Cycle Analysis

A truncated life cycle analysis looks at only a portion of a system.
For example, just the synthesis of a material (not including sourcing the starting materials or disposal at the end).

Step 1: Write out ALL of the starting materials, solvents, and products of the reaction.

Synthesis and Isolation of Tris(acetylacetonato)manganese(III), Mn(acac)$_3$.

Add 0.75 g of potassium permanganate ($KMnO_4$) and 15 mL of distilled water to a 50 mL beaker. Heat the solution on a hot plate to 80°C while stirring continuously with a stir bar until all the solid is completely dissolved. Cool the solution to room temperature in an ice bath. After cooling, stir the solution rapidly and gradually slowly add 3.5 mL of acetylacetone (pentane-2,4-dione) in small aliquots to prevent excessive foaming, which could cause the solution to overflow the flask. Once the addition is complete, boil the solution for 5 minutes, then cool the beaker in an ice bath. Collect the product using a Buchner funnel and wash with three 5 mL portions of cold distilled water. Thoroughly dry the crystals by pulling air through the funnel for at least 10 minutes.



CO_2 is included in the list whether or not it appears in the reaction equation; the quantity of CO_2 produced is that due to energy consumption plus any produced in the reaction.

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Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

How to Perform a Truncated Life Cycle Analysis

Step 2: Scale the reaction to produce 1 kilogram of product. Assume 100% conversion to products.

Synthesis and Isolation of Tris(acetylacetonato)manganese(III), Mn(acac)$_3$.

Add 0.75 g of potassium permanganate ($KMnO_4$) and 15 mL of distilled water to a 50 mL beaker. Heat the solution on a hot plate to 80°C while stirring continuously with a stir bar until all the solid is completely dissolved. Cool the solution to room temperature in an ice bath. After cooling, stir the solution rapidly and gradually slowly add 3.5 mL of acetylacetone (pentane-2,4-dione) in small aliquots to prevent excessive foaming, which could cause the solution to overflow the flask. Once the addition is complete, boil the solution for 5 minutes, then cool the beaker in an ice bath. Collect the product using a Buchner funnel and wash with three 5 mL portions of cold distilled water. Thoroughly dry the crystals by pulling air through the funnel for at least 10 minutes.

1. $KMnO_4$ is the limiting reagent (Mw = 158.03 g/mol).

$$n = \frac{m}{Mw} = \frac{0.75\ g}{158.03\ g/mol} = 0.00475\ mol$$

2. Amount of Mn(acac)$_3$ (Mw = 355.28 g/mol) produced.

$$m = n(Mw) = 0.00475\ mol\left(355.28\frac{g}{mol}\right) = 1.686\ g$$

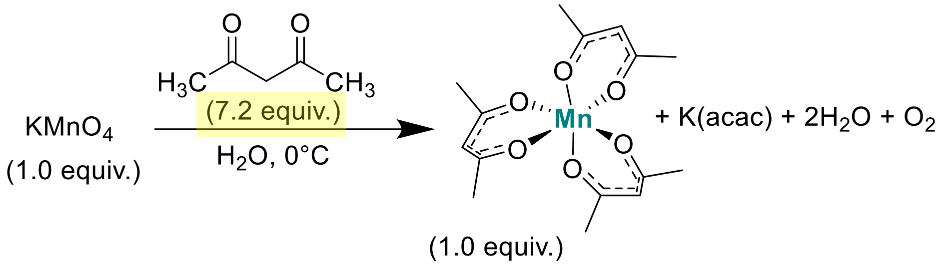
3. Scaling the reaction to produce 1 kilogram of product.

$$Multiplication\ Factor = \frac{1000\ g}{1.686\ g} = 593.09$$

4. Multiply all masses and volumes by 593.09 to scale the reaction to 1 kilogram.

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

How to Perform a Truncated Life Cycle Analysis



Only 3 equiv. of acac are incorporated into the product, the rest is waste.

Compound	Role	Mass Used/kg	Mass Produced/Kg	Mass Emmitted/Kg
Potassium permanganate	Reagent	0.445		0.445
Acetylacetone	Reagent	2.024	1.1779	1.179924
Tris(acetylacetonato)manganese(III)	Product		1	
Potassium acetatylacetonate	Byproduct		0.44	0.44
Oxygen	Byproduct		0.09	0.09
Water	Byproduct		0.051	0.000051
Water	Solvent	8.896		0.008896
Carbon Dioxide (from heating)	Energy Byproduct		86.03	86.03

Assume that the generation of 1 kJ of energy generates 0.042 g of CO2
* Heating 8896.4 g of water at 80°C for 20 minutes = 2048.218 KJ = 86.03 g CO2 produced

It is assumed that 0.1% of the mass of every compound used is emitted to the environment if the compound can be incinerated afterward (e.g., organic solvents, organic byproducts) and 100% is emitted if the compound cannot be incinerated (e.g., inorganic compounds, gases, drying agents).

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.
https://gettopics.com/en/calc/water-heating-calculators

How to Perform a Truncated Life Cycle Analysis

Step 3: Compile a table of compounds and their potentials. NOTE: not all potentials apply to all compounds.

Compound	AP	ODP	SFP	GWP	INHGT (mg/Kg)	INHTP (mg/L)	PER	ACCU Log Kow	ADP
Potassium permanganate	0	0	0	0	?	n/a	n/a	n/a	0.0000138
Acetylacetone	0	0	0	2.197928	652.4594	0.016416977	weeks	-0.167491087	0.000001
Tris(acetylacetonato)manganese(III)	0	0	0	0	?	?	months	n/a	n/a
Potassium acetatylacetonate	0	0	0	0	?	?	weeks	?	n/a
Oxygen	0	0	0	0	0	0	n/a	0	n/a
Water	0	0	0	0	0	0	n/a		n/a
Water (Solvent)	0	0	0	0	0	0	n/a		0.000001
Carbon Dioxide (from heating)	0	0	0	1	0	0	n/a	n/a	0.000001

Assume that AP, ODP, SFP, GWP, and INHTP are zero for compounds that have negligible volatility. Enter "n/a" (not applicable) for inorganic compounds in the PER and ACCU columns and for products, byproducts, and intermediates in the ADP column.

This is the most time-consuming step as multiple calculations need to be performed. Use reference 1 as a guide.

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.
https://gettopics.com/en/calc/water-heating-calculators

How to Perform a Truncated Life Cycle Analysis

Step 4: Compile a table of compounds and their indexes based on the mass of compound emitted.

Compound	I_{AP}/g	I_{ODP}/g	I_{SFP}/g	I_{GWP}/g	I_{INHGT}/g	I_{INHTP}/g	PER	ACCU Log K_{ow}	I_{ADP}/g
Potassium permanganate	0	0	0	0.0	?	n/a	n/a	n/a	0.006141
Acetylacetone	0	0	0	4.4	1320.6	3.3E-02	weeks	-0.17	0.000002
Tris(acetylacetonato)manganese(III)	0	0	0	0.0	?	n/a	months	n/a	n/a
Potassium acetatylacetonate	0	0	0	0.0	?	n/a	weeks	?	n/a
Oxygen	0	0	0	0.0	0.0	0.0E+00	n/a	0.00	n/a
Water	0	0	0	0.0	0.0	0.0E+00	n/a		n/a
Water (Solvent)	0	0	0	0.0	0.0	0.0E+00	n/a		0.000009
Carbon Dioxide (from heating)	0	0	0	86030.0	0.0	0.0E+00	n/a	n/a	0.086030
Sum	**0**	**0**	**0**	**86034.4**	**1320.6**	**3.3E-02**	**months**	**-0.17**	**0.092182**

Note: PER and ACCU Log K_{ow} are not summed. The largest value is the total for the reaction.

Colour coding is mainly to compare, there is no hard cut off for what is yellow vs. red for example.

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Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.
https://gettopics.com/en/calc/water-heating-calculators

How to Perform a Truncated Life Cycle Analysis

Step 5: Compile a table of representing the efficiency of the reaction.

Yield, g	% yield	mass reagents, g	mass waste, g	E-Factor	Reaction Mass Efficiency	Atom Economy	Carbon Efficiency	Process Mass Intensity
1.046	62	4.163	18.17	17.37	0.25	0.775	1	3.98

Atom Economy (AE): the number of reagents incorporated into the desired product. A value of 1 is the best possible value.

$$AE = \frac{Mw_{Product}}{\sum Mw_{Reagents}}$$

Carbon Efficiency (CE): the amount of carbon from the reagents maintained in the desired product.

$$CE = \frac{CN_{Product}}{\sum CN_{Reagents}}$$

Process Mass Intensity (PMI): a measure of the mass of reagents used in the formation of the final desired product compared to the mass of the desired product.

$$PMI = \frac{\sum m_{Reagents}}{m_{Product}}$$

Environmental Factor (E-Factor): the amount of waste generated compared to the amount of desired product.

$$E - Factor = \frac{\sum m_{waste}}{m_{Product}}$$

Reaction Mass Efficiently (RME): an inverse E-factor that can be used to analyze specific parts of a reaction processes.

$$RME = \frac{m_{Product}}{\sum m_{Reagents}}$$

Note: To calculate these values, you must use your data.

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

The Drawbacks of a Truncated Life Cycle Analysis

1. The is insufficient data for less-common chemicals.

2. The influence of inorganic substrates is often not reflected.

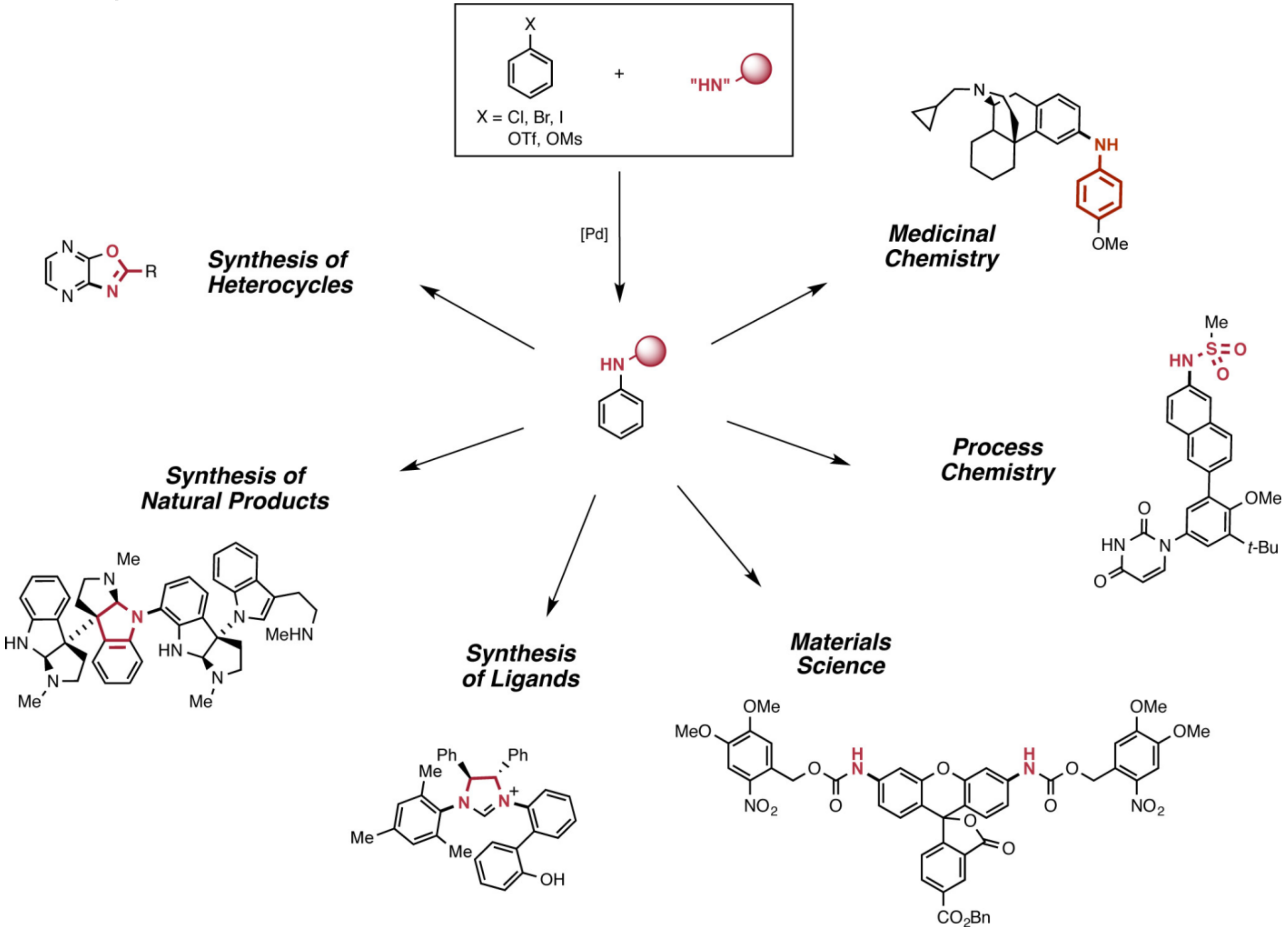
3. The toxicity effects of solids dissolved in water is not considered.

4. Poorly documented synthetic procedures (ex. how much silica and solvent is used for a column separation? How much drying agent is used?) result in estimated values.

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

Sustainable Transformations: C-N Bond Formation

The formation of carbon-nitrogen (C-N) bonds is crucial in synthetic chemistry



Due to the large utility of C-N bonds there is a push to develop catalysts that can perform this chemistry efficiently using greener chemistry methods.

Existing Chemistry

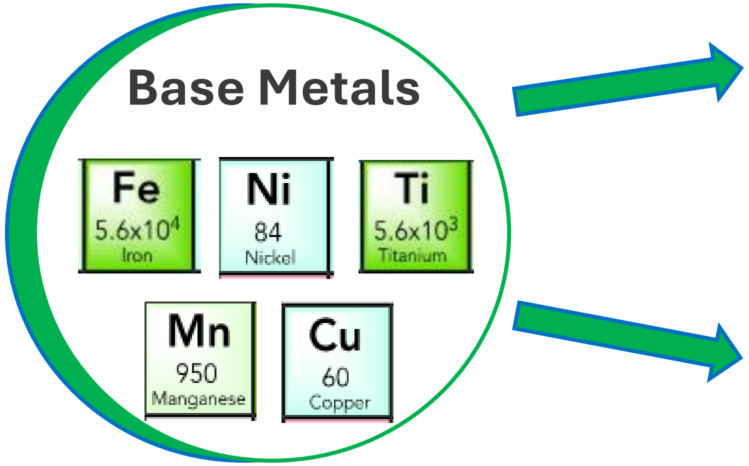
- Relies on precious metals (Pd, Ir, Rh)
- Products are difficult to purify
- Low catalyst recover and recyclability

Ruiz-Castillo, P.; Buchwald, S. L. *Chem. Rev.* **2016**, *116*, *19*, 12564-12649

Green Catalyst Development

Sustainable Transformations: Catalysts that allow for less solvent, safer reagents, and improved efficiency for commercial transformations.

Green Catalyst Development: Working to create greener catalysts through improved ligand synthesis and the application of base metals or main group catalytic species.



Replacing precious metals (Pt, Pd, Ir) performing 2-electron chemistry

Harnessing 1-electron chemistry to perform novel transformations

Sustainable Targets: Catalyst development to target sustainable transformations such as CO_2 reduction (zero-carbon cycles), nitrogen reductions/ammonia oxidation (NH_3 as an alternative fuel), biofuel synthesis, biopolymer synthesis, etc.

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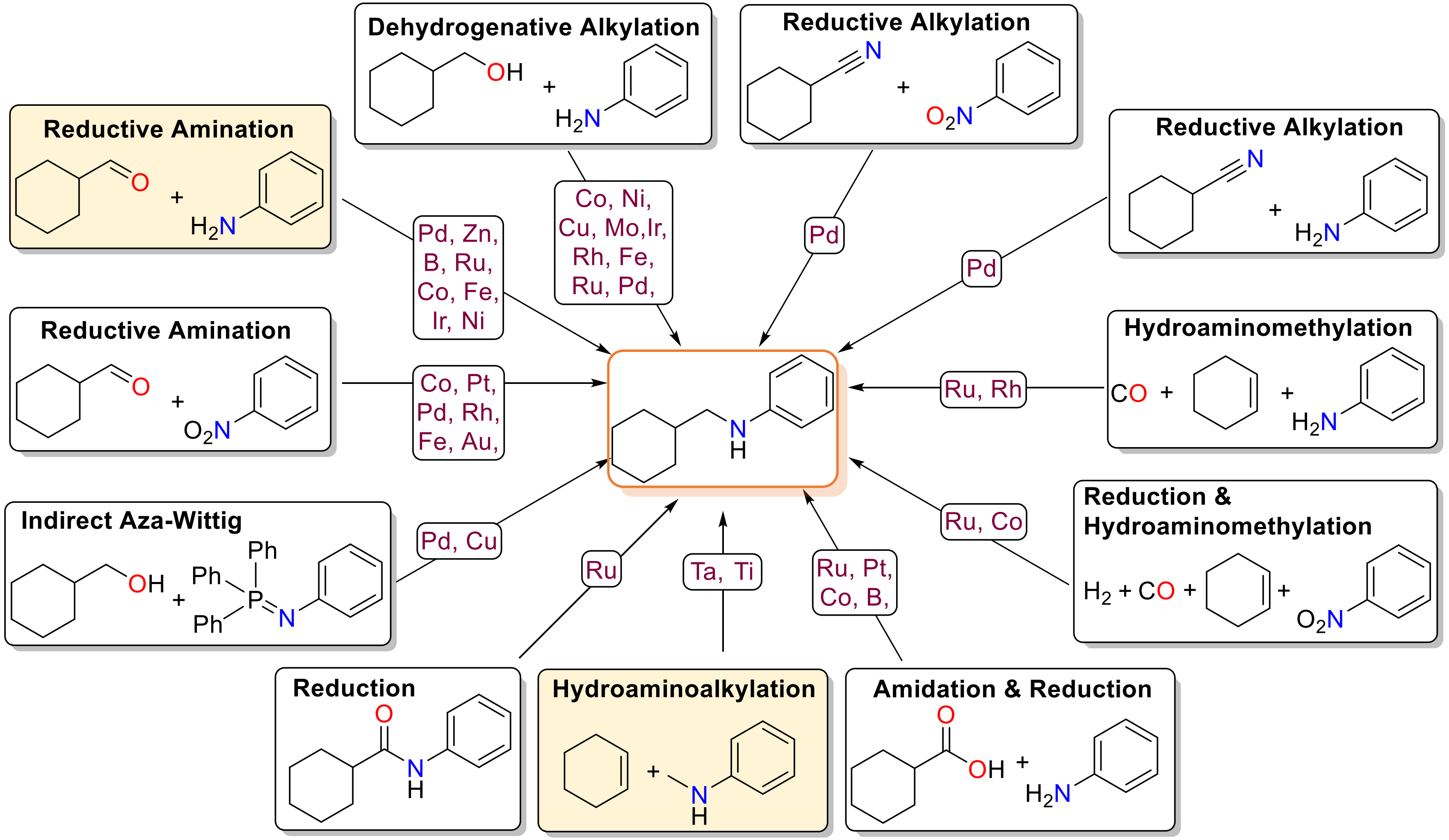
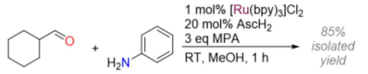
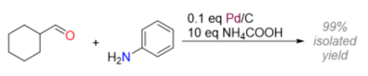
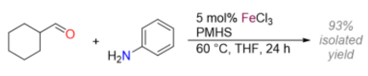
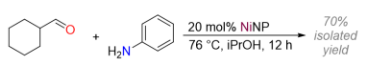
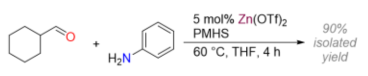
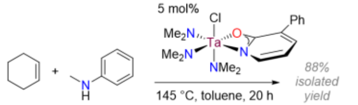
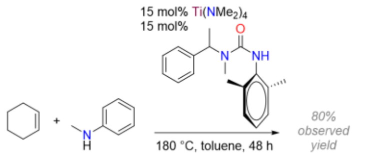
Clapson, M. L.; Durfy, C. S.; Facchinato, D.; Drover, M. W. *Cell Reports Physical Science*, **2023**, *4*, 9, 101548..

Choose the Greenest Catalyst – Emerging Chemistry



Clapson, M. L.; Davy, E.; Durfy, C.; Schechtel, S.; Scott, S. An Interactive Exploration of the Societal Impacts of Inorganic Chemistry - A Base Metal View on Sustainable Catalysis. **2024**, *J. Chem. Educ*. [In Revisions].

Catalytic Systems Life Cycle Analysis Table

Entry	Route	I_{AP} (g)	I_{ODP} (g)	I_{SFP} (g)	I_{GWP} (g)	I_{INGTP} (g)	I_{INHTP} (g)	PER	ACCU Log K_{ow}	I_{ADP} (g)	CO_2 (kg)	RME	EF	AE	Ref.
1		0	0	2	800	$7x10^{-4}$	1000	months	-0.7	500	0.8	30%	10	90%	2
2		2	0	6	2000	60	3000	months	6	50	2	20%	2	90%	3
3		0	0	100	5000	10000	7000	months	4	0.8	5	40%	50	90%	4
4		0	0	6	2000	-20000	-4000	months	10	0.04	2	60%	20	90%	5
5		0	0	50	700	300	900	months	3	0.2	0.6	40%	50	90%	6
6		4	0	2000	9000	700	200	very long-lived	6	20	7	30%	50	100%	7
7		200	0	4000	10000	3000	80	very long-lived	20	0.06	10	30%	100	100%	8

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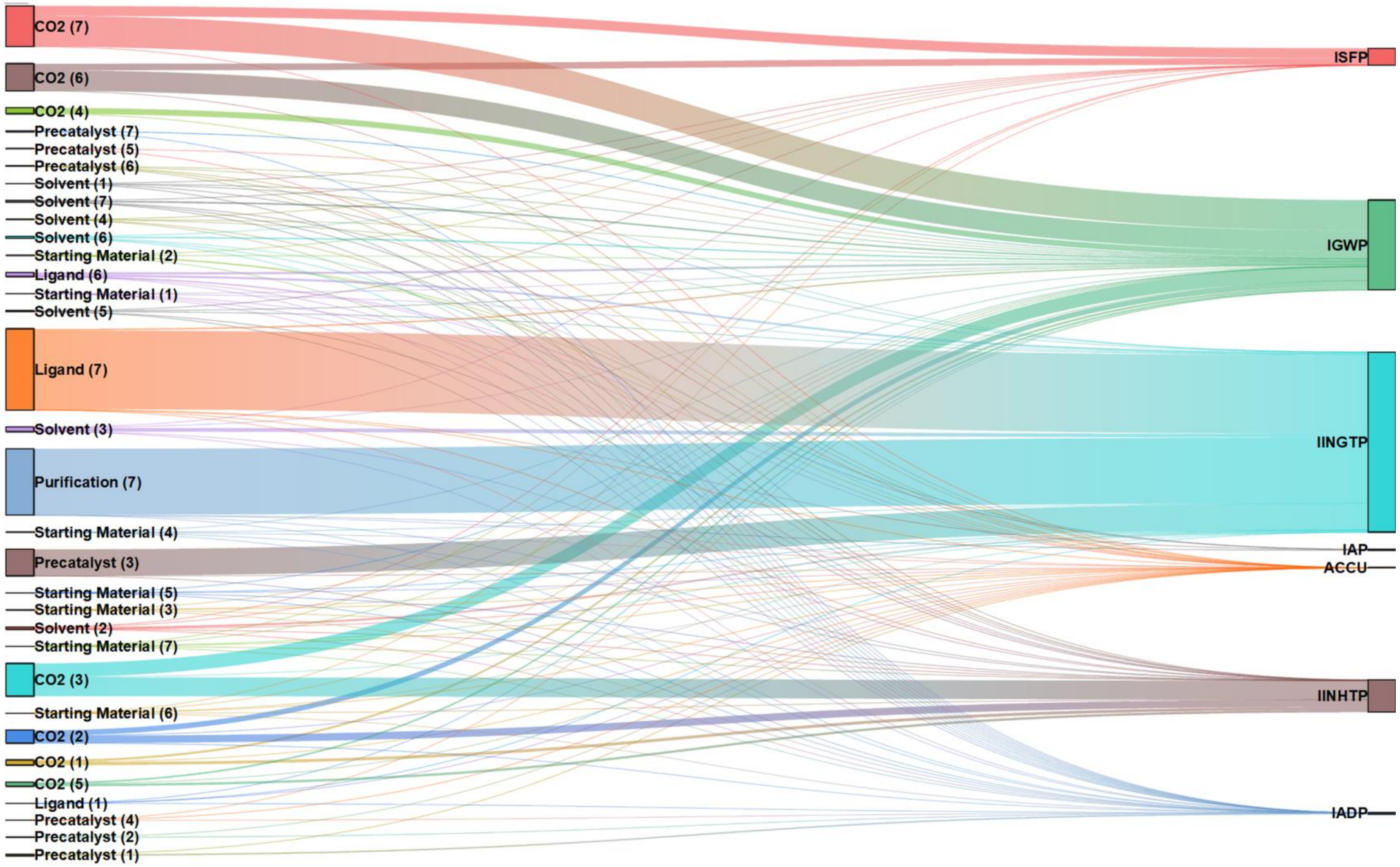
Clapson, M. L.; Davy, E.; Durfy, C.; Schechtel, S.; Scott, S. An Interactive Exploration of the Societal Impacts of Inorganic Chemistry - A Base Metal View on Sustainable Catalysis. **2024**, *J. Chem. Educ*. [In Revisions].

Looking Deeper at the LCA Data

Sankey diagram categorizing influence of method subsection with sustainability metrics.



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Clapson, M. L.; Davy, E.; Durfy, C.; Schechtel, S.; Scott, S. An Interactive Exploration of the Societal Impacts of Inorganic Chemistry - A Base Metal View on Sustainable Catalysis. **2024**, *J. Chem. Educ*. [In Revisions].

Choose the Greenest Catalyst - You Might Have Noticed

- Comparing the I_{ADP} of each route the base metal and early transition metal pathways tend to be less resource depleting than the late-row transition metal catalyzed methods.

- The use of ligands or the need to generate specialized metal precursors tends to negatively impact the sustainability of the synthesis.
    - I_{AP}, I_{ODP}, I_{SFP}, I_{GWP}, I_{INGTP}, I_{INHTP}, PER, and ACCU Log K_{ow} are dictated by the organic synthesis portion of the methodology (the synthesis of a ligand).

- Reaction mass efficiency (RME) and environmental factor (EF) tend to be negatively influenced by the ligand synthesis.

- Atom economy (AE) is limited by the mechanism of the reaction:
    - hydroaminoalkylation uses the entire mass of the starting materials in the product,
    - reductive amination loses a small molecule as a by-product.

- CO_2 production is calculated using the number of solvents that need distilling prior to use in reaction and during isolation of products along with refluxing and heating of solvents. CO_2 production tends to be higher with air/water sensitive chemistry and ligand syntheses.

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Clapson, M. L.; Davy, E.; Durfy, C.; Schechtel, S.; Scott, S. An Interactive Exploration of the Societal Impacts of Inorganic Chemistry - A Base Metal View on Sustainable Catalysis. **2024**, *J. Chem. Educ*. [In Revisions].

Green Chemistry Metrics – A Simple View For Catalysts

1. Select an abundant catalytic center
    - Base metals
    - Main Group Elements

2. Design a ligand that requires minimal synthetic steps
    - Lower or eliminate solvent
    - Choose greener solvents/reagents
    - Improve safety

3. Aim for low impact reaction conditions
    - Low temperature and pressure
    - Electrocatalytic
    - Photocatalytic

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Clapson, M. L.; Durfy, C.; Facchinato, D.; Drover, M. W. *Cell Reports Physical Science*, **2023**, *4*, 101548.

Proposing Greener Alternatives

Some Considerations:

- First row metals are prone to one-electron chemistry compared to 2nd and 3rd row metals.
- More abundant does not mean less toxic.
- Not all ligands work the same on all metals.
- Not all chemistry (especially organometallic chemistry) can be performed in water/air.
- Water used in a reaction is contaminated and will have to be purified, so it still counts as waste.

Greener Solvent Guide

There is no universal approach to solvent selection. Solvent guides are resources that should be used by chemists to make the right choice for their specific chemistry.

Greener Solvents →

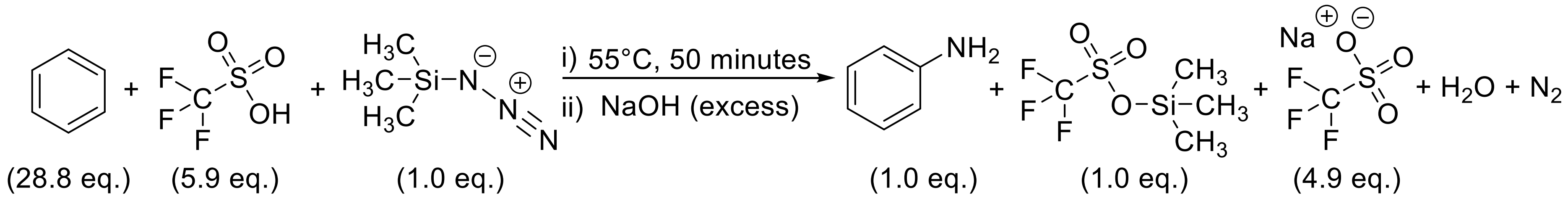
Hexane (s) Pentane	Heptane Isooctane	
DMF DMAc NMP	MeCN DMSO	Cyrene™ CPME
THF MTBE	2-MeTHF	CPME
Et_2O, Di-isopropyl ether MTBE	2-MeTHF	CPME
DME Dioxane MTBE	2-MeTHF	CPME
CCl_4* $CHCl_3$* CH_2Cl_2 DCE*		
CH_2Cl_2 **(extractions)** MTBE	2-MeTHF Toluene	EtOAc
CH_2Cl_2 **(chromatography)**	Heptane/EtOAc	3:1 EtOAc/EtOH
Benzene*	Toluene	
	Acetone	Ethyl lactate DMC
	Acetone **(washing)**	EtOH

***Indicates highly hazardous**

- Organic Acids: derived from natural sources (ex. citric acid, acetic acid, formic acid)
- Solid Acids: Acids supported on a substrate (ex. silica, zeolites)
- Lewis Acids: When applicable (ex. $AlCl_3$, $FeCl_3$)

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

Conversion of Benzene to Aniline: Proposing Green Alternatives



Procedure:

Benzene (75 mL, 0.842 mol) and triflic acid (20 mL, 0.22 mol) are warmed to 55°C. Trimethylsilyl azide (0.037 mol, 4.4 g) in 20 mL benzene (0.224 mol) is added. The mixture is stirred for 50 min until no more N_2 is given off. The mixture is then cooled to room temperature and poured over 100 g of ice. Unreacted benzene and other organics are extracted with three washings of dichloromethane and discarded. The aqueous layer is basified to pH ~13 and the aniline product is then extracted with three washings of dichloromethane, which are combined and dried with $MgSO_4$. The solvent is removed by distillation to give aniline in 95 % yield and 100% selectivity based upon the amount of azide used.

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Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

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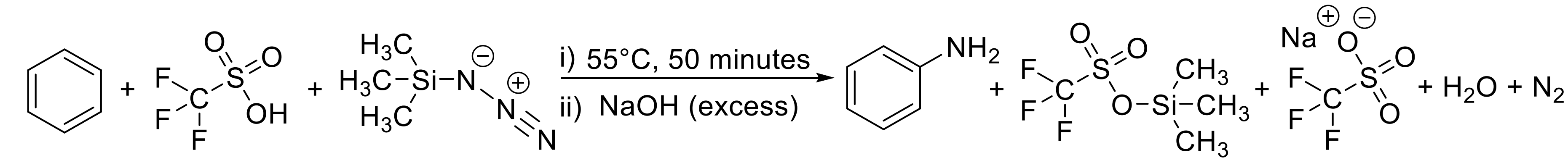

Table 1. Materials for Route 1

Material	Role	Mass Used/kg[a]	Mass Produced/kg	Mass Emitted/kg
Benzene	reagent/solvent	20	-	2.0×10^{-2}
Me_3SiN_3	reagent	1.3	-	1.30×10^{-3}
Triflic Acid	reagent	9.8	-	9.8×10^{-3}
$Me_3SiOSO_2CF_3$	byproduct	-	2.4	2.4×10^{-3}
$NaOSO_2CF_3$	byproduct	-	9.3	9.3
Dichloromethane	solvent	236	-	0.24
NaOH	reagent	2.3	-	0.12[b]
$MgSO_4$	drying agent	8.9	-	8.9
CO_2	energy byproduct	-	1.83	1.83

[a]For a 1 kg scale. [b]The amount of NaOH remaining after the balanced reaction and neutralization of the excess of triflic acid.

What green chemistry concerns do you see looking at this data?

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Conversion of Benzene to Aniline: Proposing Green Alternatives

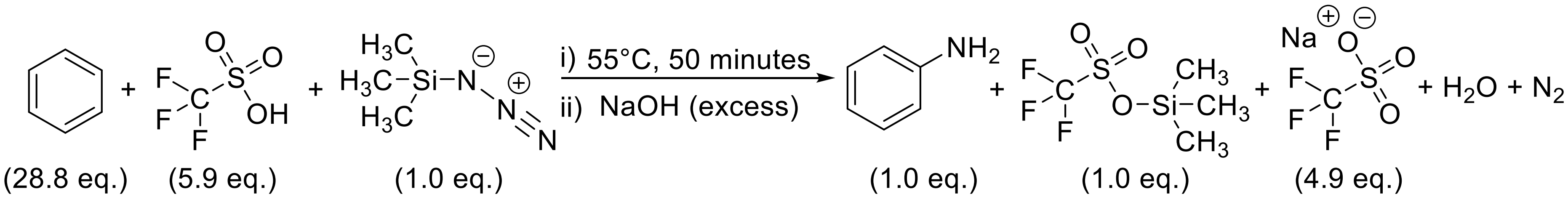
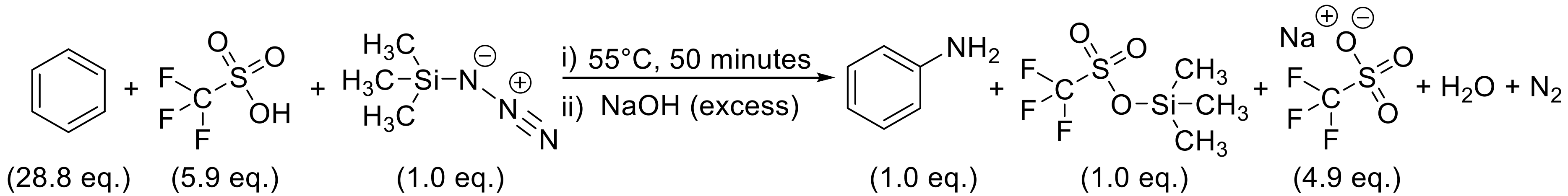


Table 3. Indices for Route 1

Material	I_{AP}/g	I_{OD}/g	I_{SF}/g	I_{GW}/g	I_{INHT}/g	I_{INGT}/g	PER	ACCU Log K_{ow}	I_{AD}/g
Benzene	0	0	2.8	66	240	19	months	2.1	0
Trimethylsilyl azide	0	0	0	0	0	?	months	2.3	0
Triflic Acid	0	0	0	0	0	0.5	weeks	-0.5	F: 0.011 S: 0.754
$Me_3SiOSO_2CF_3$	0	0	0	0	0	?	months	0.6	n/a
$NaOSO_2CF_3$	0	0	0	0	0	?	n/a	n/a	n/a
Dichloromethane	0	94	7.2	123	12	38,081	weeks	1.3	0
NaOH	0	0	0	0	0	?	n/a	n/a	0
$MgSO_4$	0	0	0	0	0	?	n/a	n/a	0.94
CO_2	0	0	0	1829	0	0	n/a	n/a	0
Sum	0	94	10	2018	252	38,100	months	2.3	1.7

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

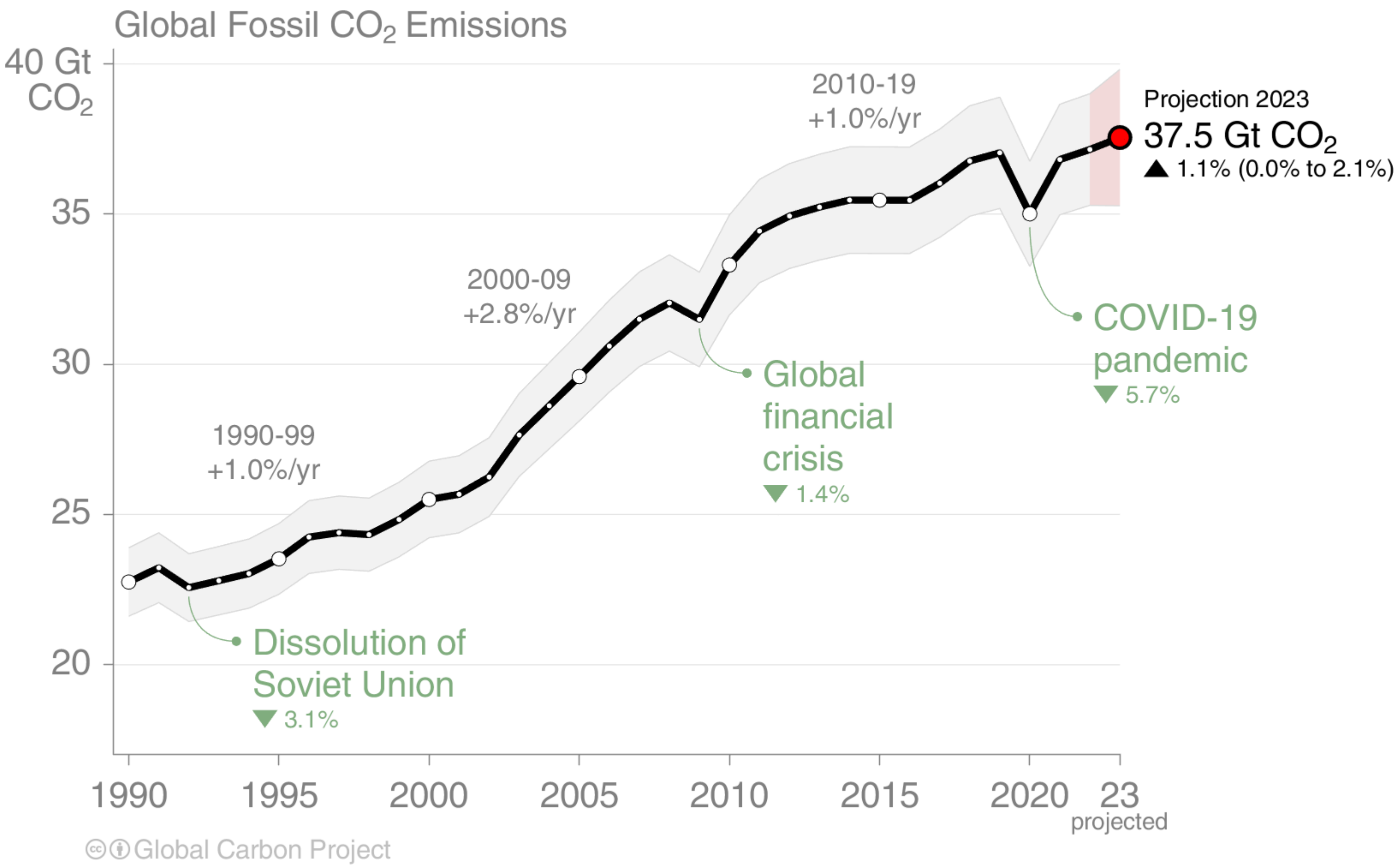
Conversion of Benzene to Aniline: Proposing Green Alternatives



Greener Chemistry Recommendations:

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

Sustainable Transformations – CO_2 Reduction



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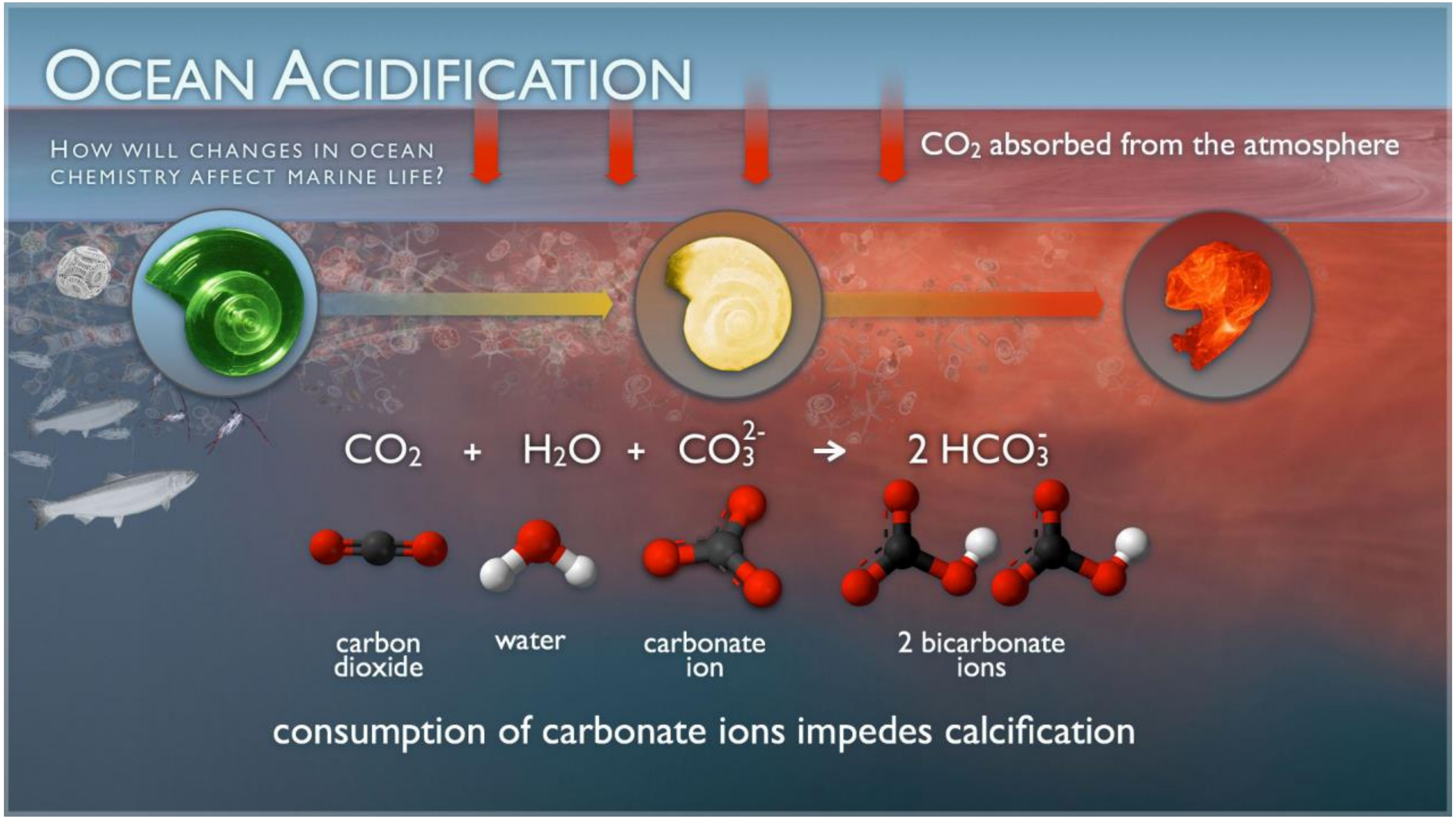
Green Transformations – CO_2 Reduction



https://www.noaa.gov/education/resource-collections/ocean-coasts/ocean-acidification

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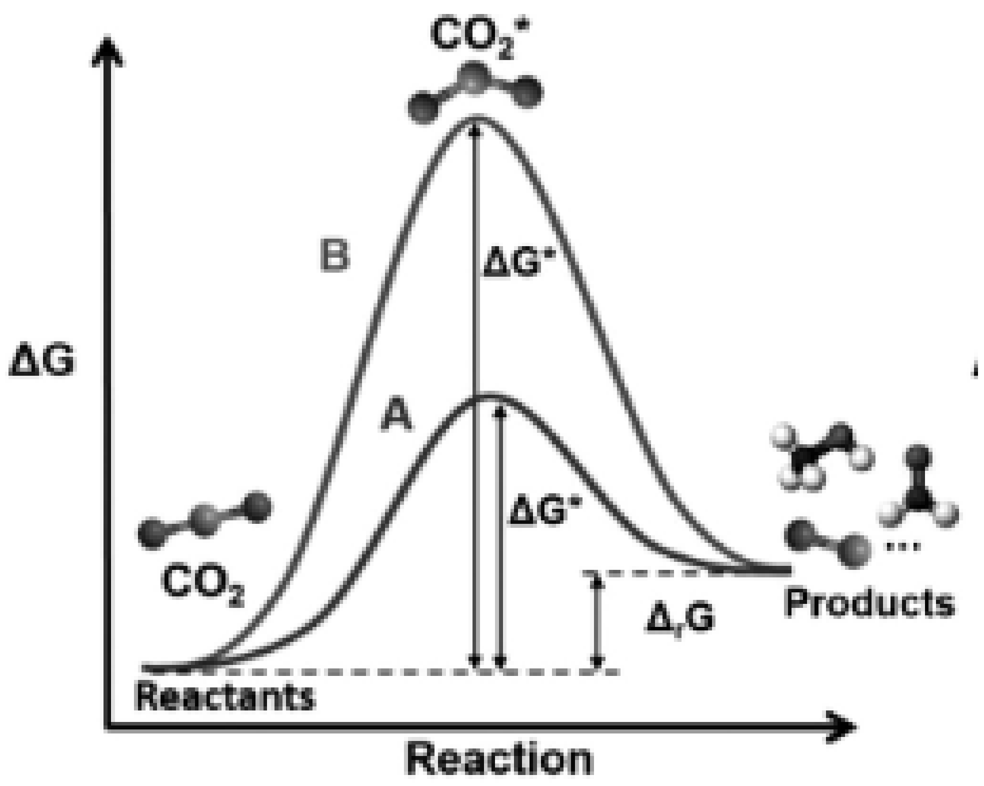
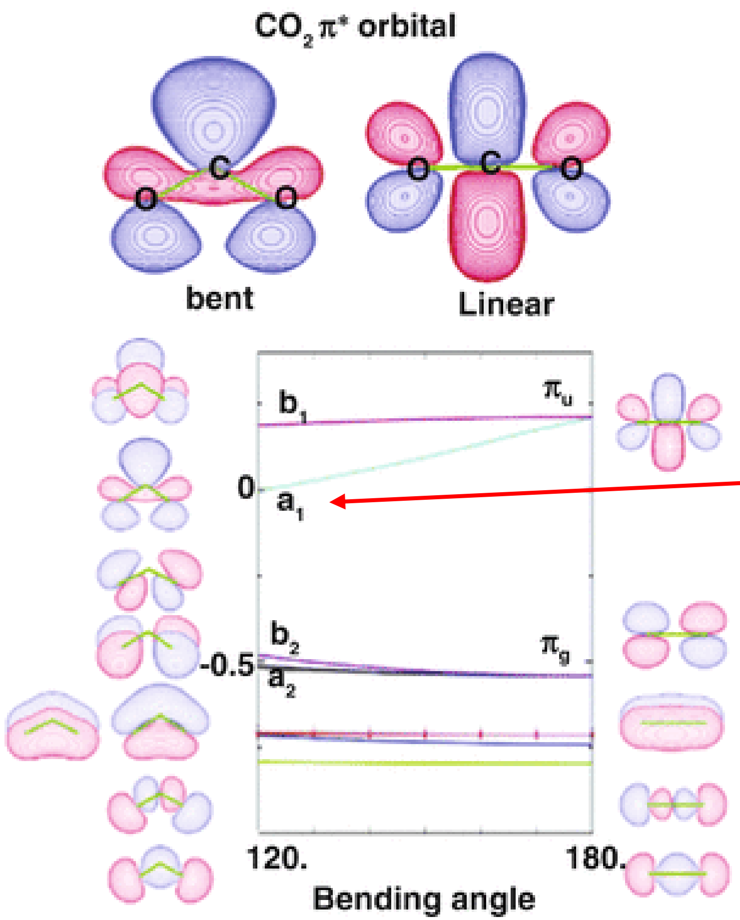
The Challenge: Stability of CO_2





Orbital of a_1 symmetry available for bonding

CO_2 is thermodynamically (strong C=O bonds) and kinetically (high activation barrier from linear to bent) stable.

Zheng, Y.; Yu, B.; Wang, J.; Zhang, J. Carbon Dioxide Reduction through Advanced Conversion and Utilization Technologies. **2019**, 1st Ed. CRC Press.

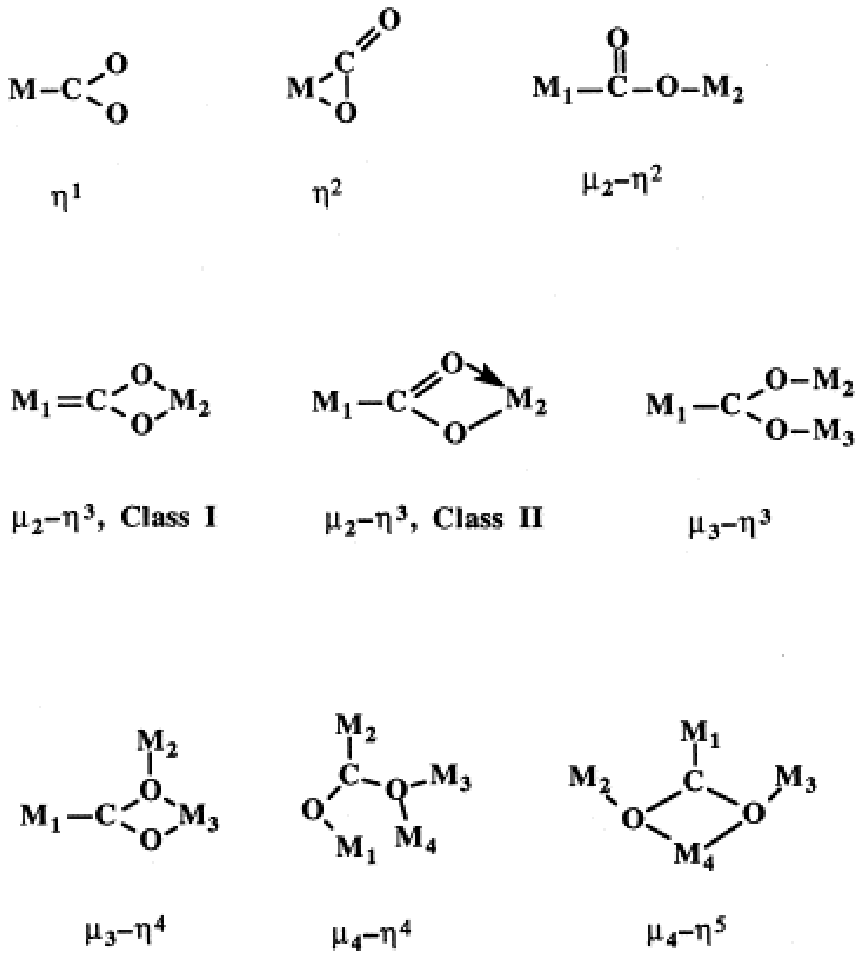
The Challenge: Thermodynamics of CO_2 Conversion

Calculated Thermodynamic Parameters (ΔG^0, ΔH^0, and ΔS^0) of Some CO_2 Conversion Reactions

Product	Net Reaction	ΔG^0 (kJ·mol^{-1})	ΔH^0 (kJ·mol^{-1})	ΔS^0 (J·mol^{-1}·K^{1})
Hydrogen	$H_2O \rightleftharpoons H_2\uparrow + 0.5O_2\uparrow$	237.17	285.83	163.30
Carbon monoxide	$CO_2 + H_2O \rightleftharpoons CO\uparrow + H_2O + 0.5O_2\uparrow$	257.38	283.01	86.55
Formic acid	$CO_2 + H_2O \rightleftharpoons HCOOH + 0.5O_2\uparrow$	269.86	254.34	–52.15
Formaldehyde	$CO_2 + H_2O \rightleftharpoons HCHO + O_2\uparrow$	528.94	570.74	140.25
Methanol	$CO_2 + 2H_2O \rightleftharpoons CH_3OH + 1.5O_2\uparrow$	701.87	725.97	80.85
Ethanol	$2CO_2 + 3H_2O \rightleftharpoons C_2H_5OH + 3O_2\uparrow$	1325.56	1366.90	138.75
Propanol	$3CO_2 + 4H_2O \rightleftharpoons C_3H_7OH + 4.5O_2\uparrow$	1962.94	2021.24	195.65
Methane	$CO_2 + 2H_2O \rightleftharpoons CH_4\uparrow + 2O_2\uparrow$	818.18	890.57	242.90
Ethane	$2CO_2 + 3H_2O \rightleftharpoons C_2H_6\uparrow + 3.5O_2\uparrow$	1468.18	1560.51	309.80
Ethylene	$2CO_2 + 2H_2O \rightleftharpoons C_2H_4\uparrow + 3O_2\uparrow$	1331.42	1411.08	267.30

Zheng, Y.; Yu, B.; Wang, J.; Zhang, J. Carbon Dioxide Reduction through Advanced Conversion and Utilization Technologies. **2019**, 1st Ed. CRC Press.

CO_2 Binding Modes and Reduction Potentials



Reaction	Reduction potential E° (V) at pH = 7 vs SHE
$CO_2 + 2\,H^+ + 2\,e^- \rightarrow CO + H_2O$	−0.52
$CO_2 + 2\,H^+ + 2\,e^- \rightarrow HCOOH$	−0.61
$CO_2 + 8\,H^+ + 8\,e^- \rightarrow CH_4 + 2\,H_2O$	−0.24
$2\,CO_2 + 12\,H^+ + 12\,e^- \rightarrow C_2H_4 + 4\,H_2O$	−0.34

Coordination of CO_2 to a metal or main group species can promote/stabilize a bent conformation allowing for further reactivity

Existing Chemistry

- Relies on precious metals (Pd, Ir, Rh)
- Has low selectivity
  - Competitive with H_2 reduction
- Transformations to alkanes/alkenes is harder
  - CO or formate more common

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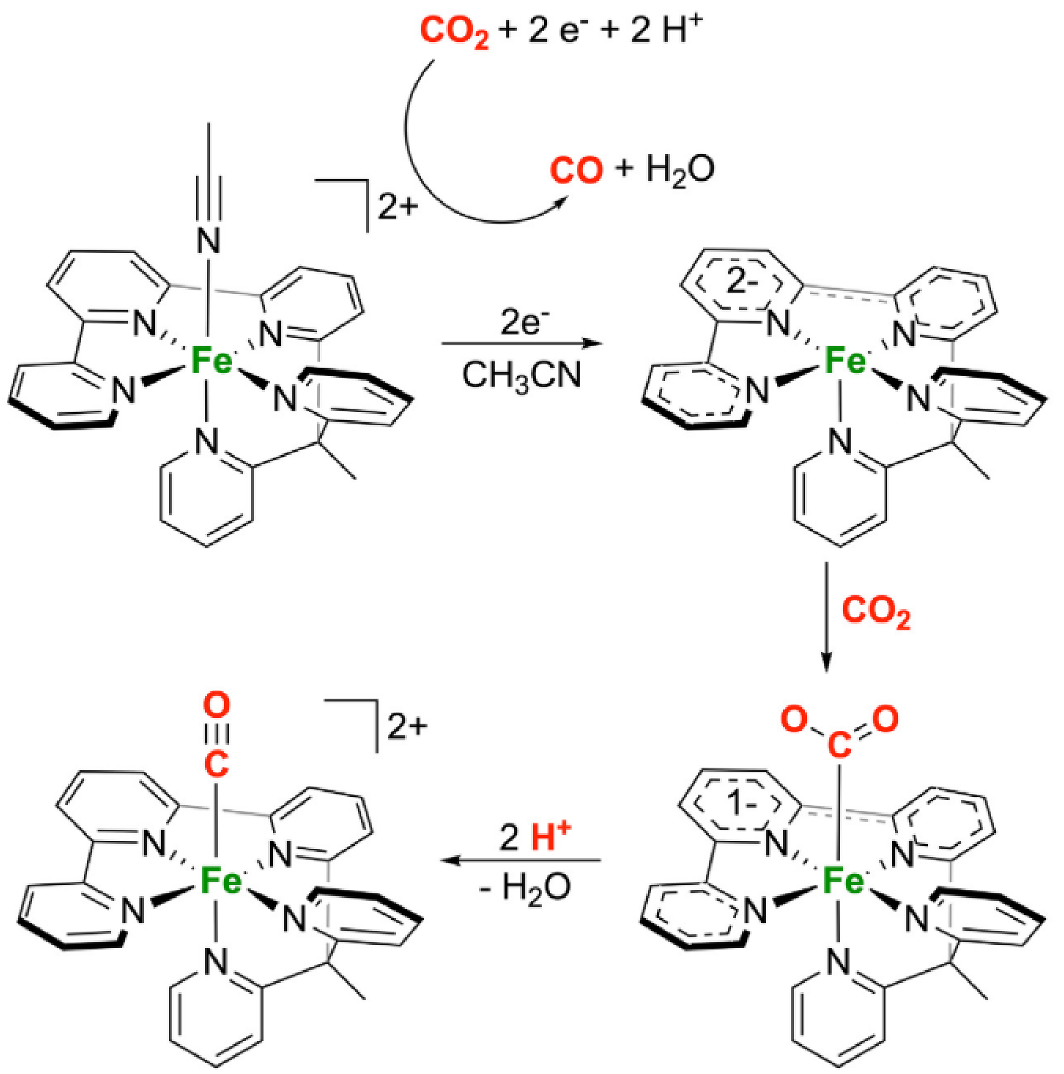
Emerging Trends: CO_2 Conversion to Water and CO



Redox Active Ligands: ligands that are able to be reduced and oxidized in place of the metal.

- Stabilizes reactive intermediates
- Allows for proton/electron shuttling

Single Site Reactivity: metal complexes that have a single vacant site for substrates to bind.

- Limits the binding modes that can occur, promoting specific reaction mechanism.
- Can improve substrate selectivity.

Electrochemistry: reactions performed by applying an external voltage.

- No external reducing agents required.
- Minimizes synthetic waste.
- Requires a green energy source to make a lasting impact.

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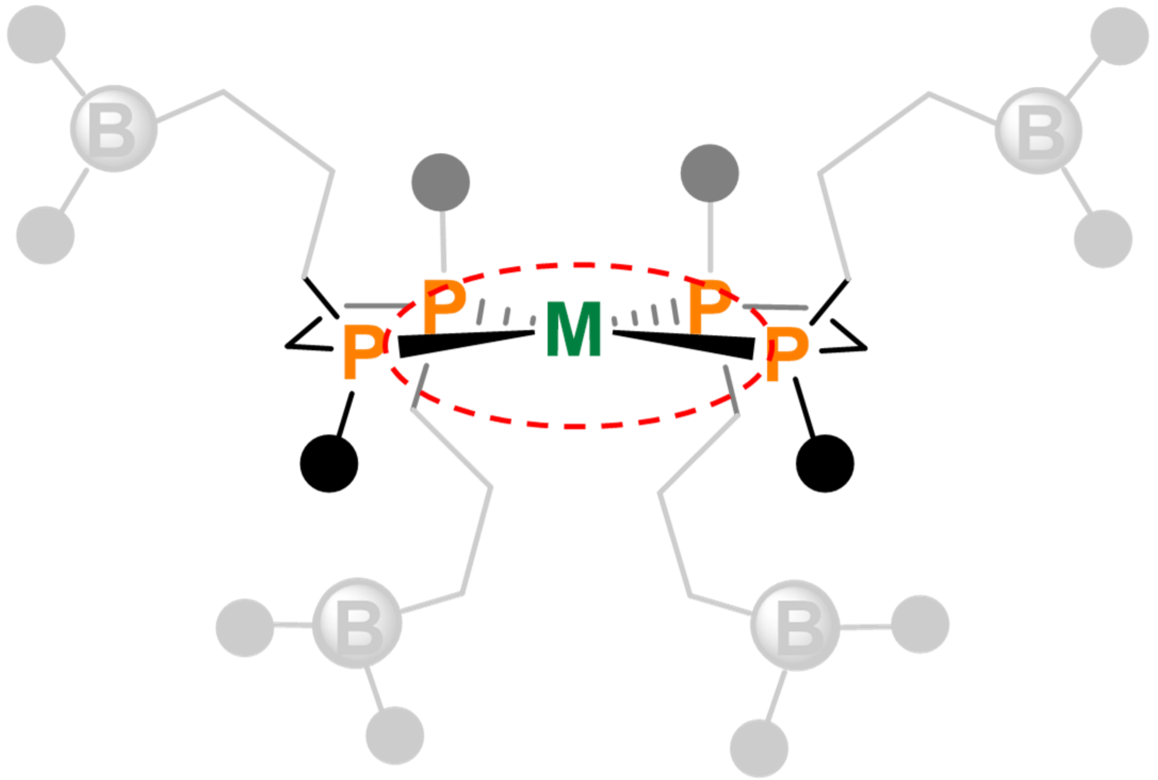
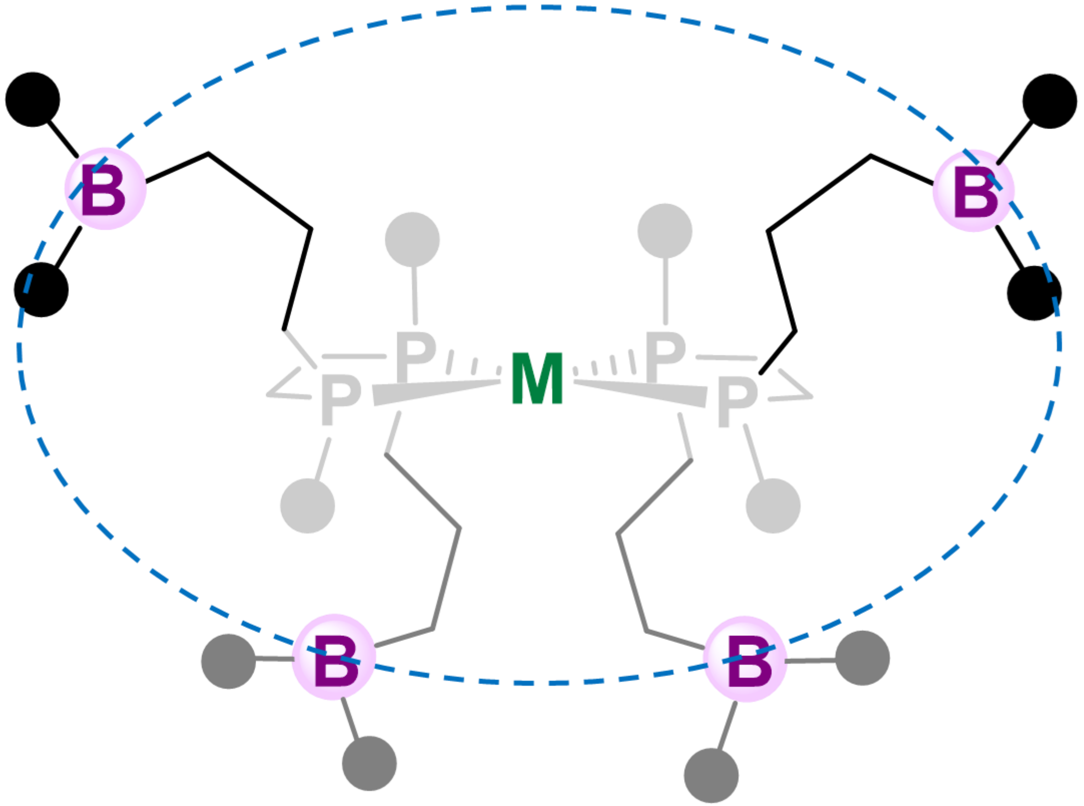
Loipersberger, M.; Derrick, J.S.; Chang, C.J.; Head-Gordon, M. *Inorg. Chem.* **2022**, *61*, 6919–6933.

Primary and Secondary Coordination Sphere



Primary Coordination Sphere (PCS)
Atoms bound directly to the metal center



Secondary Coordination Sphere (SCS)
Exterior atoms in the ligand scaffold

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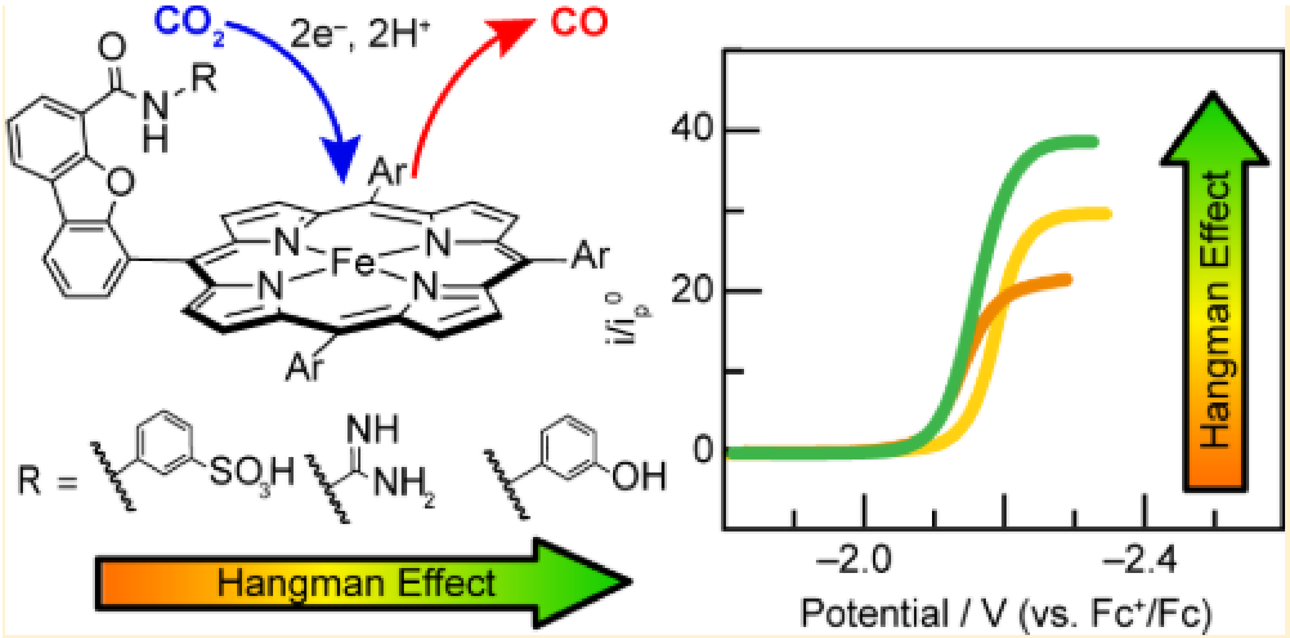
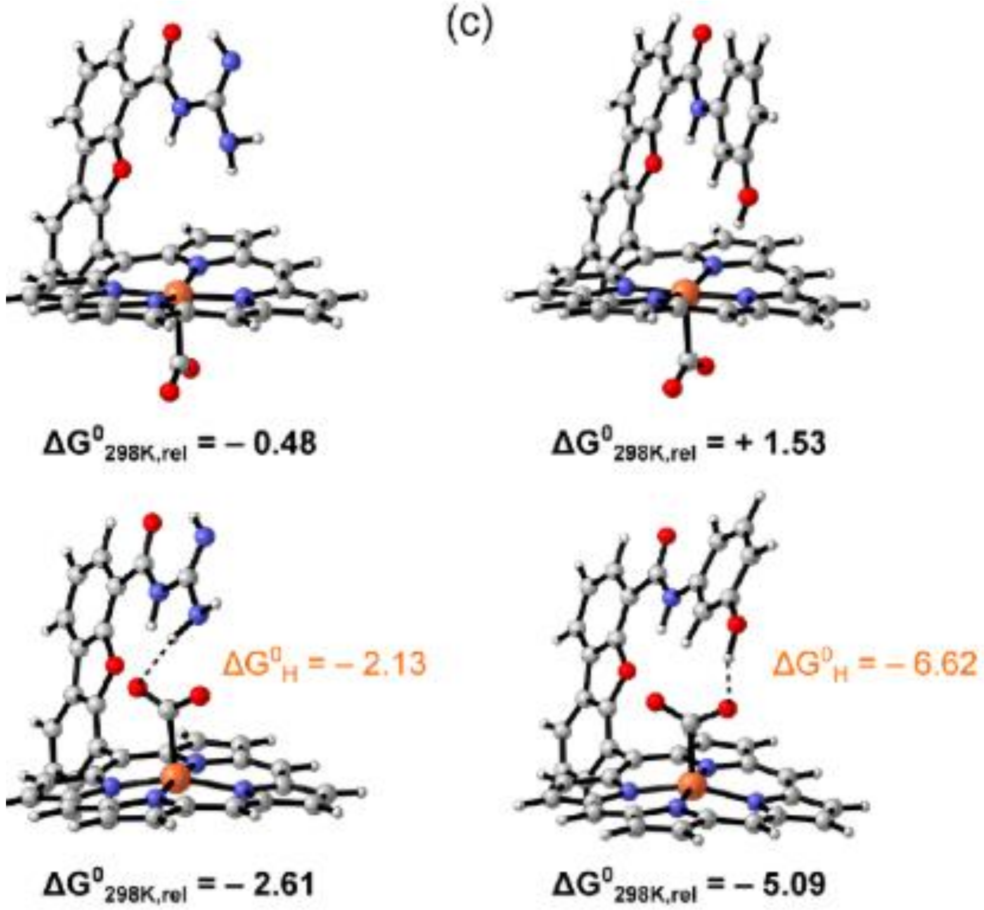
Zurakowski, J. A.; Austen, B. J. H.; Drover, M. W. *Trends Chem.* **2022**, *4* (4), 331–346.
Zurakowski, J.A.; Dufour, M.C.; Austen, B.J.H.; Spasyuk, D.M.; Nelson, D.J.; Drover, M.W. *Chem. -Eur. J.* **2021**, *27*, 16021-16027.
.

Emerging Trends: CO_2 Reduction Leveraging the SCS





Pros:

- Stabilizes reactive intermediates.
- Allows for proton/electron shuttling.

Cons:

- Ligands become more complex lowering "greenness".

Margarit, C. G.; Schnedermann, C.; Asimow, N. G.; Nocera, D. G. *Organometallics* **2019**, *38*, 1219−1223

Recommended Reading and Practice Questions

Mercer, S. M.; Andraos, J.; Jessop, P. G. *Journal of Chemistry Education*, **2012**, *89*, *2*, 215-220.

Interactive Systems Thinking Regarding Planetary Boundaries:
https://applets.kcvs.ca/sites/applets/PlanetaryBoundaries/

Clapson, M. L.; Durfy, C.; Facchinato, D.; Drover, M. W. Cell Reports Physical Science, 2023, 4, 101548

Ashley, A. E.; O’Hare, D. Top Curr Chem (2013) 334: 191–218

Durfy, C. S.; Zurakowski, J. A.; Drover, M. W. *ChemSusChem*, **2024**, *17,* (13), e202400039