Evidence of Students' Engagement in Green Chemistry Using Engineering Practices

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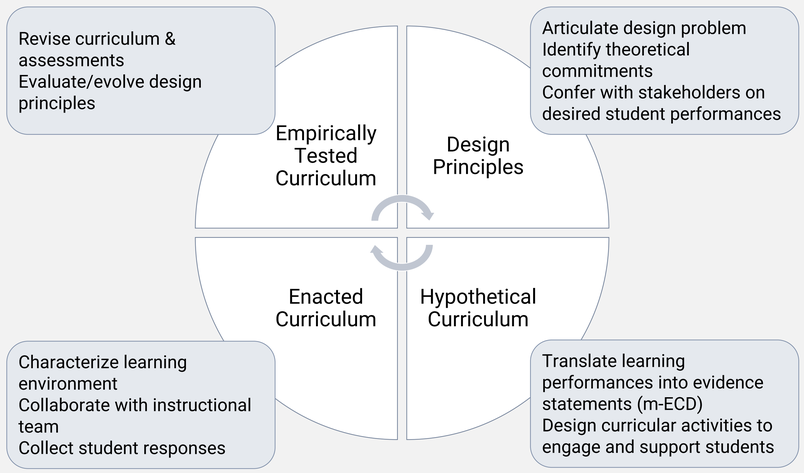
Design-Based Research:[1-3]

Methodological framework for designing and optimizing learning environments to support and elicit evidence of desired learning performances



Articulate Design Problem:

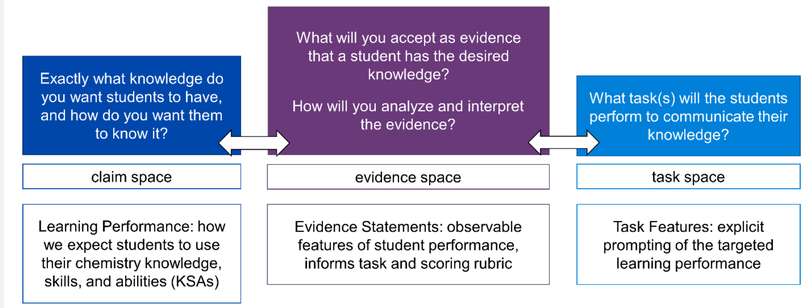
Verification-style labs and lecture materials do not engage students in sustainable thinking or decision making; how to design such that students must *use* their chemistry knowledge to model, predict, explain and *engineer* a greener outcome?

Theoretical Commitments – How People Learn:[4]

Design principles based on learning theory, evidence, and commitment to green and sustainable chemistry

Evidenced-Centered Design[8-9] of Assessment Items:

Identify claims about student performance to test via the curriculum; set evidence through iterative design of assessment prompts and supportive scaffolding



Green Organic Project-Based Chemistry Labs:[10-11]

Using chemistry CIs to tackle projects in the scientific practices that chemists do; uses greener solvents and green metrics for students' decision-making

Course Context: This course serves as the organic chemistry laboratory for BA chemistry, biology and pre-health professional majors and serves approximately 600 students per semester. Taken concurrently with Organic Chemistry II, students enrolled in this laboratory course receive 2 credit hours for a dedicated 3 hours in a laboratory setting and a 1-hour laboratory-specific lecture. Many students have taken 1-2 General Chemistry laboratory courses in the same project-based style.

cooperative organic chemistry

student teams work on a multi-week project in which each student takes on a specific role to contribute to the overall investigation to answer the driving question

Identification of an Unknown Organic Solid (1) — Introduces organic laboratory techniques – melting point determination, ^{1}H-NMR, TLC, etc. – in the context of a familiar project scenario. Students use **structure-property CI** to justify how their evidence supports their chemical identity claim.

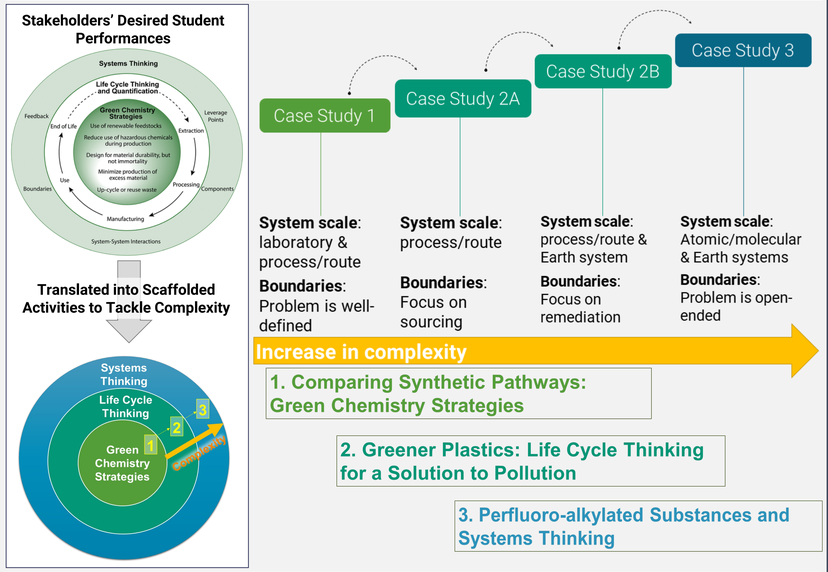
Synthesis & Analysis of Painkillers (2) — Uses these laboratory skills and techniques to investigate (greener) catalysts for a synthesis and a multi-component analysis. Uses **electrostatics CI** and **green metrics** as evidence in their argumentation.

Extraction of Caffeine (3) — Engages in extraction and separations techniques valued by stakeholders. Builds on repertoire of techniques in a more challenging problem that requires **structure-property CI** to separate and purify.

Amide Synthesis (4) — Builds on repertoire of laboratory skills and techniques to investigate different amide reagent combinations. Uses **electrostatics CI** and **green metrics** as evidence in their argumentation.

Sustainability Case Studies:[12]

Use chemistry CIs and SEPs in a multi-week case studies of sustainable chemistry at scales beyond the bench; overall set scaffolds towards performing systems thinking



Scaffolded-Decision Making Using Engineering Practices:[5, 12]

Defining Sustainability Problems and Evaluating/Designing Solutions

When student are **Defining a Problem**, they should:

1. Describe the problem and the **boundary conditions** (*i.e.*, scale, time point, etc.) of the problem
2. Give the **social and/or environmental context** for why the problem matters
3. Define the chemistry of the **physical system** and its components
4. Identify to whom this problem matters (**stakeholders**)
5. Specify what needs to be considered (**criteria, constraints**) for an acceptable solution to the problem

When student are **Evaluating a Solution**, they should:

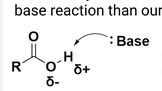
1. Generate a list of what needs to be considered (**criteria, constraints**) for an acceptable solution to the problem
2. Gather all relevant data and scientific information
3. **Assign priorities** for the evaluation of possible solutions
4. Analyze the **strengths and weaknesses** of each solution with respect to the **criteria/constraints**
5. Provide an **evidence-based decision** of which solution is optimal, including the **strengths/weaknesses** (**cost and benefits**) of each solution

Design activities and assessments to elicit evidence:

Excerpts from "Comparing Synthetic Pathways"[13] Case Study 1 in which students use their chemistry knowledge to define a problem

Week 1: Constructing an Explanatory Model of the Amide Bond-Forming Mechanism

If we tried to form an amide bond by reacting a carboxylic acid and an amine, the resonance stabilization afforded to the carboxylic acid makes it more likely to undergo an acid-base reaction than our intended nucleophilic substitution.



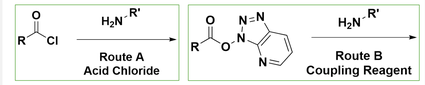
1. We can deprotonate the acidic proton, so the acid-base product does not happen before the amide product

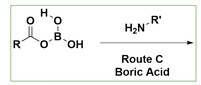
2. We can make the carbonyl more reactive by adding an electron-withdrawing groups so less energy is required to initiate the nucleophilic substitution

X = electron-withdrawing group

3. Molecules that exhibit resonance are more stable and less reactive; therefore, we can increase the reactivity of the carbonyl by ensuring it does not undergo resonance.

The carbonyl compounds in Routes A, B, and C are more reactive than a carboxylic acid. What's the general model?





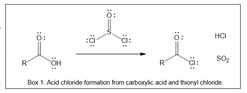
In the **BLUE** box below, draw an arrow-pushing mechanism to show how the amine reacts with these carbonyl compounds in Routes A-C.

Using the reaction mechanisms you drew in the box above, **construct an explanation** in the **PURPLE** box for how the various structural features (R group, C=O, X group) impact the activation of the carbonyl and therefore its reactivity.

Week 2: Defining the Problem and Evaluating Solutions (Reaction Schemes)

As your team uses the chemistry knowledge to engineer an acceptable solution for the pharmaceutical company, an important first step is to **define the problem** in the **GREEN** box below.

The synthesis of acid chloride is shown in Box 1. This route produces two key toxic, gaseous by-products: HCl and SO_2 (a greenhouse gas). Typical industrial scale reactions are done on the "ton scale" with 1,000 kg of reactant.



Box 1. Acid chloride formation from carboxylic acid and thionyl chloride.

As a model for what this would do to our waterways, calculate how the amount in moles of HCl produced would change the pH of a typical 60,000L backyard pool.

Moles HCl = 6,658.8 mol

Molarity HCl = 0.11 M of H^+

pH pool = 0.95 (highly acidic)

Stakeholder Analysis: Synthesis Team

Synthetic Route	Theoretical Yield (1000 kg scale)	Percent Yield	Actual Yield (amide product)
Route A (Acid Chloride)	1593.6 kg of amide product	73%	1,163.3 kg
Route B (Coupling Reagent)		82%	1,306.8 kg
Route C (Boric Acid)		64%	1,019.9 kg

Stakeholder Analysis: Economic Team

Synthetic Route	Solvent Cost (per 1000 kg)	Reactants Cost (per 1000 kg)	Workup Cost (per 1000 kg)	Total Cost (per 1000 kg)
Route A (Acid Chloride)	$2.736 million	$2.746 million	$13.574 million	$19.056 million
Route B (Coupling Reagent)	$5.347 million	$12.535 million	$12.398 million	$30.280 million
Route C (Boric Acid)	$3.134 million	$9.633 million	$11.079 million	$23.846 million

Stakeholder Analysis: Environmental Team

Synthetic Route	Solvent Waste	By-Products	By-Product Major Hazards
Route A (Acid Chloride)	• DCM • DMF (catalytic) • 0.1 M sodium bicarbonate ($NaHCO_3$) • 1.0 M hydrochloric acid (HCl)	• Carbon dioxide (CO_2 - gas) • Carbon monoxide (CO - gas) • HCl (gas)	• CO_2 – greenhouse gas • CO – poisonous, flammable gas • HCl – irritant and toxic to aquatic life
Route B (Coupling Reagent)	• DMF • Ethyl acetate (EtOAc) • sat. $NaHCO_3$ • 1.0 M HCl	• Tetramethylurea • Two organic salt products	• Tetramethylurea – reproductive toxicity, skin/eye irritant, and toxic to aquatic life • Two organic salt products – skin/eye irritants
Route C (Boric Acid)	• Toluene (PhMe) • Boric acid (catalytic) • Hexane • Water	• Water	• Water is non-toxic

Design assessment to elicit evidence:

Engaging in Evidence-Based Decision Making[12]

Based on your team's exploration of this case study, write a **decision memo**[14] to communicate your understanding of the problem, evaluate the solutions, and make a recommendation. The structure of your memo should follow:

Recommendation: Communicate your decision as to which synthetic route the company should use.

Background: Provide a relevant and concise background that summarizes the problem definition, the stakeholders' criteria and constraints, *and* briefly explains the underlying chemistry.

Evidence: Summarize key evidence needed to address problem and stakeholders, prioritizing the most relevant evidence. Use of figure or table is encouraged, and if used they should be easy to read from a glance and include definitions of any abbreviations.

Conclusion & Implementation: End with a summary of the conclusions your team has drawn and briefly describe the next steps for implementing your recommendation.

Teams generally chose Route C.
Here's an exemplar from a team from Spring 2023:

> "Our pharmaceutical company has concerns regarding the most efficient and environmental [sic] friendly way of synthesizing amide-containing molecules[…] Presently, at the forefront of the company's minds [sic] […] is how to synthesize amides while lowering the impact on human and environmental health as well as lowering the cost for the company. Therefore it is essential we choose the synthetic pathway that satisfies all aspects of the company's concerns. The company believes that Route C should be used to reduce the chances of pollution, to save money, and to offer the highest yield of product with the least amount of waste generated."

This recommendation outlines **criteria and constraints** from the various **stakeholders**. It also shows students have **implicit prioritization** of these criteria, despite wanting to achieve "all aspects". Their **evidence** heavily relied on yield, cost, and formation of by-products as they outlined the **strengths and weaknesses** of each route.

Open Educational Resources:

Making the curricular materials available for adoption and adaptation

Libraries MICHIGAN STATE UNIVERSITY

GCTLC

Our IUSE research team is committed to open educational resources (OERs). The textbook *Cooperative Organic Chemistry* will be published through MSU Libraries. The project-based labs, case studies, and related journal articles from this research will be published open access through Beyond Benign's Green Chemistry Teaching and Learning Community (GCTLC).

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