

## Week 6

# Intro to Long Reports

### 6.1 Lecture 10: Scientific Visual Communication

- 2/7:
- Long report submissions delayed until Friday.
    - The content of today may be useful!
  - Thursday.
    - Anna Wuttig on the current state of EChem.
    - Tokmakoff will stick around after for us to chat about our reports with him.
  - There are many aspects beyond *visual* communication, but this is one that isn't always seen, so Tokmakoff decided to focus on it today.
  - Take all the guidelines and extra chapters seriously; they're exactly what is being graded for.
  - We should care about communication because it's as important to our career development as anything.
    - Our science must be distributed; otherwise, we're just a hobbyist.
  - We need to convey very complicated, quantitative information to other scientists, management, government agencies, policy makers, investors, and the general public.
  - Reduce complex quantitative data accurately into clear, concise messages: Data interpretation.
  - Often, there are real requirements on content and formatting.
  - Excellence in communication.
    - Content is key, but saying it well will really level you up.
    - It develops *trust* in your methods, results, and communications.
    - A well-communicated report and graphic can change the world, e.g., the hockey stick curve.
  - **Communication:** The means of exchanging information.
  - **Medium:** Any channel of communication.
  - Media we will discuss.
    - Print (text, graphics).
      - Graphics are how people digest scientific information.
    - Oral (in person with visual support).
    - Never use double columns if you want transport to online.

- The common starting point for all communication.
  1. Audience.
    - Identify; sets the objective, expectations, language, and aspects of your work to focus on.
    - You need to know if you're talking to fellow bench scientists, or senior management.
  2. Message.
    - What are you trying to say? Just say what you need to, and get rid of the rest.
    - When your TA or Tokmakoff reads your report, what are they going to think of my magenta line.
  3. Media.
    - What tools are at your disposal, and how are they best employed.
- Visual presentation tips for text and graphics.
  - Our goal: Communicate quantitative information clearly and concisely.
  - Make your viewer's life easy (be consistent, define the purpose of each element, etc.).
  - Simplicity is good; clutter is bad.
  - Color should be chosen with a real focus in mind.
- Typefaces and fonts.
  - The visual representation of language. Its style should help, not interfere, with your communication.
- **Typeface**: The design elements for lettering. A collection of glyphs.
- **Glyph**: A single representation of a character.
- **Font**: A variation of a typeface like size, weight, and spacing.
- Classes of typefaces: **Serif** and **sans serif**.
  - Sans-serif is good for titles, headings, and labels.
  - Serifs are good for presenting large amounts of text.
- History of typefaces.
  - Use legacy typefaces; they're still supported.
  - "Microsoft is your friend."
  - Computers revolutionized typography; Microsoft drove the development with proprietary stuff, which eventually caused them to lose the edge, and now there's great open-source fonts.
- Typefaces for equations.
  - Times New Roman and Garamond have full math support.
  - Computer modern ( $\text{\TeX}$ ) is probably still the best in terms of being able to distinguish things since it includes so many helpful flourishes.
    - You're probably encountered difficulties with the lab manual (e.g.,  $v$  vs.  $\nu$ ) because it's not in Computer modern.
- Tokmakoff's recommendations for formatting: Typed  $8.5 \times 11$  documents should have a...
  - Single column format.
  - 1" margins.
  - 11-12 point type.

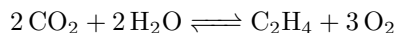
- $\sim 90$  characters per line including spaces (15 characters per linear inch).
  - 4-5 lines per vertical inch.
- Why worry about font size?
  - Legibility vs. readability; too small impacts legibility, and too big impacts readability.
- Why worry about line spacing?
  - $1.5\times$  is Tokmakoff's recommendation.
  - $2\times$  is legacy from typewriters, when single and double were the only options.
- Why worry about margins?
  - White space helps with clarity.
  - Don't just insert figures; make figures break text.
- Equations should be numbered.
- Color.
  - Don't let it distract; let it help you make a cleaner presentation.
  - Really bright colors draw the eye too much.
- Scientific figures.
  - Purpose: To convey quantitative information on the relationship between different physical variables with minimal effort.
  - Each figure should convey information on exactly one topic.
  - Again, know your audience, be aware of your medium (typed vs. oral), clarity, etc.
  - Additional consideration for scientific reports: Often the figure is the only documentation of the data.
    - If the reader wanted to analyze your data, can they read data values off the graph using the axis labels?
    - Raw Excel sheets, other records may not be saved, so the literature report may be the only way for future scientists to reanalyze your data.
- Examples of good and bad figures.
  - As you see scientific figures going forward, take note of what you like and what you don't like and learn.
  - Tokmakoff asks for the class's feedback on his examples.
- You should have 4-6 axis labels and 4-10 tick marks.
  - More tick marks than labels is a good idea!
- Make sure colors translate to black and white, so maybe I should vary both shapes and colors in my Birge-Sponer plot.
- Rowan is very picky about what Excel settings you use.
  - Don't cut and paste into word; stuff gets realigned.
- Tokmakoff doesn't look for units for unitless quantities (e.g., absorbance).
- Use a legend when there are two or more series being plotted.
- Caption.

- Use for report figures.
- It should describe what is plotted and is needed to interpret the data beyond what is in the figure.
- For data, typically quote specific experimental conditions.
- Titles are only for oral presentation graphics.
- Don't mislead! Rescaling your axes can mislead about growth.
- Make everything 300 dpi.
- Publishers use JPG in CMYK color profile.
  - Online: Use RGB color profile.
  - Everything else is up to us.
- Takeaways.
  - Clarity and conciseness.
  - White space is good!
  - Microsoft is (mostly) your friend.
    - Their templates, colors, and fonts have been professionally designed... with everyone in mind.
    - Use recommended formatting, but be aware it isn't for scientists.
  - There are no firm rules — just guidelines. It is an art.

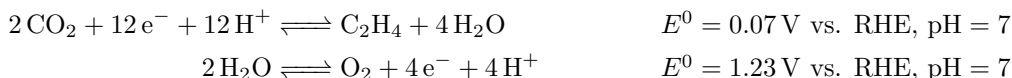
## 6.2 Lecture 11: Electrochemistry

2/9:

- Guest lecture by Anna Wuttig.
- Ben Masters (our TA) is one of her grad students.
- Electrochem can solve important problems, and we know the mechanisms in principle because we can measure the flow of electrons in it as current.
  - Thus, we can modify whatever we want and have an *in situ* handle on reaction rate.
  - This is why it's important for physical chemistry, which seeks to understand, predict, and rationally design future reactions.
- We will focus on CO<sub>2</sub>-reduction today.
  - Wuttig hopes to **upconvert** it to other things.
- We currently do this with the water-gas shift reaction and Fischer-Tropsch chemistry.
  - But this is both energy-intensive and has poor selectivity.
- Alternative: Electrochemistry.
- Example.

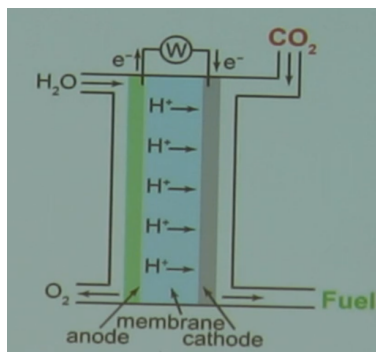


- Produces ethylene (used in a lot of things in industry) and O<sub>2</sub> (benign).
- Allows you to store  $\Delta G = 1343 \text{ kJ mol}^{-1}$  of energy, corresponding to  $\Delta E = -1.16 \text{ V}$ .
- This involves two electrochemical half-reactions (recall from gen-chem).



- The first one is kinetically very difficult, though — it requires you to input *twelve* electrons.

- In the EChem module, we'll study RHEs and other kinds of electrodes.
  - Essentially, these allow us to pin EChem reactions on a common axis.
  - The axis does move as a function of pH, though.
- We have no electrolyser or catalyst that can run the example reaction right now.
  - Thus, we so far have to put in more energy to store that energy.
  - A focus of the chemistry world: Find catalysts and conditions such that this is possible.
- CO<sub>2</sub> reduction as an energy storage scheme.

Figure 6.1: CO<sub>2</sub> reduction as an energy storage scheme.

- Use renewable energy sources like wind and solar to drive electrochemical reactions. Specifically, driving the transfer of electrons may facilitate oxidation of water to O<sub>2</sub> at the anode reduction of CO<sub>2</sub> to fuels (such as ethylene) at the cathode. Note that the water's protons will theoretically diffuse through a proton exchange membrane.
- Big idea: Store renewable intermittent electricity in energy-dense chemical bonds.
- Selectivity challenges in CO<sub>2</sub> reduction.
  - One reason we don't know how to do this yet: CO<sub>2</sub> can be reduced to myriad products.
  - A competitive side reaction: Hydrogen evolution.
  - Other carbonaceous products include methanol, ethanol, etc. Some of these may be good, but we don't want to produce all of them at once!
  - Though it might be theoretically possible to pin the  $\Delta E$  thermodynamically, it's practically virtually impossible.
  - Consequently, selective CO<sub>2</sub>RR requires control over the relative rates (kinetics) of competing reactions.
- Understanding of interfacial proton coupling is poor.
  - $\text{CO}_2 + 2\text{e}^- + 2\text{H}^+ \longrightarrow \text{CO} + \text{H}_2\text{O}$  is possible.
  - Things like molecular electrocatalysts allow us to access this at a high rate and selectivity.
    - We can boost the rate even further with *intramolecular* proton donors (esp. phenolic groups).
    - *Intermolecular* proton donors can help, too, but make sure not to make it too acidic, or you'll favor hydrogen evolution!
    - Thus, what you really need is precise proton delivery.
  - These homogeneous catalysts are nice and pretty, but in a functional device, we'll need heterogeneous catalysis.

- Possible example: Au catalyst.
  - Mathematical models suggest that the concentration profiles at the interface of the solid are higher. Essentially, the pH near the surface becomes much more alkaline very quickly.
  - We don't have control over the proton coordinate here, and we don't actually know what the proton donor is (could be water, hydronium, carbonic acid, etc.).
  - Thus, we need to understand the role of PCET in dictating CO<sub>2</sub>RR vs. HER selectivity.
  - This is what Wuttig did her PhD on!
- Electrochemistry is nice because you always know the rate.
  - The velocity  $v$  of the reaction is related to the current  $i$ , the number of electrons  $n$ , and Faraday's constant  $F = 96\,485\text{ C/mol e}^-$  via
 
$$i = nFv$$
  - You can also measure how many product you're forming either by assuming that all current is going to your reaction, or by using in-line gas chromatography.
    - In the EChem module, we'll assume that everything is going to hydrogen evolution.
  - Knowing how much current is going to hydrogen and CO, we can construct a **Tafel plot**.
- **Tafel plot**: The relationship that describes the log-linear dependence of the reaction rate as a function of the applied potential.
  - We will take the partial current going to CO and plot it vs. the applied potential.
  - This yields direct mechanistic insight: Increasing the overpotential decreases the  $\Delta G^\ddagger$ .
- Example of using a Tafel plot.
  - Assume CO<sub>2</sub> is reduced in a rate limiting step by combining with an electron.
  - Using kinetics, we would have
 
$$R_{\text{CO}} = k_1(\theta^*)(a_{\text{CO}_2}) \exp\left(\frac{\beta nF}{RT}\right)$$
    - $\theta^*$  is the concentration of the active sites on the gold surface; not every atom on the surface is active, as can be shown via fancy microscopy techniques.
    - $a_{\text{CO}_2}$  is the **activity** of CO<sub>2</sub> dissolved in solution.
    - $\beta$  is the symmetry factor: For reactions in which there is a high reorganizational potential energy, we can take  $\beta \approx 1/2$ .
  - This yields info on the Tafel slope:
 
$$\frac{\partial \eta}{\partial \log(j)} = \frac{60\text{ mV}}{\beta} = 120 - 150\text{ mV}$$
  - Thus, we check the data: At all potentials in the linear range, check for linear dependence.
  - Tafel data implies ET RLS with slope about 1.
- What if instead, we couple adsorption with proton transfer from?
  - Look at the rate of CO formation vs. the bicarbonate concentration.
    - Nothing here, so it's not this.
    - Moreover, because it's not this charged species, it's not any acidic species (because changes in one would change the pH of all).
  - Nothing for water, too.
  - Thus, the data suggests that there's no proton transfer in the initial step, so it must happen afterwards.

- Note that changing the partial pressure of CO also doesn't change anything, suggesting that as soon as CO is created, it is released and future adsorption is not inhibited.
- Other data complete the mechanism.

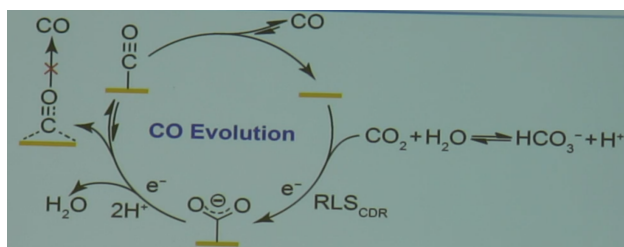
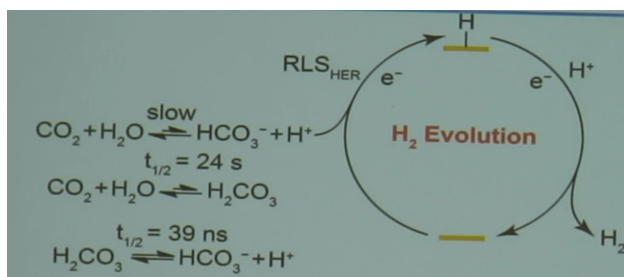
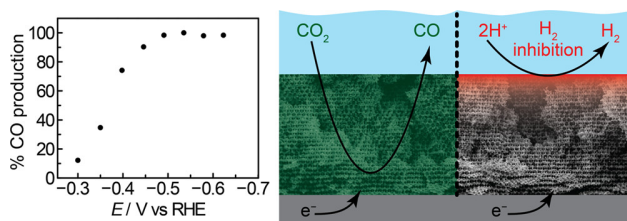


Figure 6.2: CO evolution mechanism.

- Simultaneous hydrogen evolution is dependent on the proton donor environment.

Figure 6.3: H<sub>2</sub> evolution mechanism.

- Mechanism is deceptively simple, but profound all the same.
- We first get adsorption of a proton to a hydride.
  - But Tafel slope is super high, so you may be being limited by the ability of the protons to get to the surface in the first place.
  - Suppose that the protons are special, i.e., donated by the relatively slow dissociation of H<sub>2</sub>CO<sub>3</sub>.
    - Note that H<sub>2</sub>CO<sub>3</sub> dissociates with  $t_{1/2} = 24\text{ s}$  in real life; it is only super fast in our body because of an enzyme we have that takes it to  $t_{1/2} = 39\text{ ns}$ .
  - Changing the concentration of H<sub>2</sub>CO<sub>3</sub> and rerunning the experiment confirms this.
- We do observe an explicit change in the rate of hydrogen evolution based on the concentration of H<sub>2</sub>CO<sub>3</sub>, but the relationship is complex and potential dependent.
- This is an independently occurring catalytic reaction on *some* catalytic site (maybe one that was occupied by CO, maybe not, we don't know).
- Utilizing this mechanism to design a better, more selective reaction.

Figure 6.4: Enhancing heterogeneous CO<sub>2</sub>RR with mesoporous membranes.

- If we couple the two reactions, because they both depend on  $\text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+$ , we can increase selectivity by slowing down this equilibration even further.
  - We make the environment at the gold catalysis further out of equilibrium with the bulk.
  - Wuttig teamed up with other scientists to develop a mesoporous gold structure, forcing everything that wants to touch the gold to go through the structure.
  - The  $\text{CO}_2$  reaction does not care how thick the structure is, but  $\text{H}_2$  does! This leads to near-selective CO formation.
- In our module, however, we need to *increase*  $\text{H}_2$  evolution, though!
    - We'll use all the same principles Wuttig just discussed, but it'll be simpler.
    - $\text{H}_2$  evolution is also an important reaction.

## 6.3 Lab 4: GCMS

### Lab Manual

2/9:

- Goal.
  - Use GCMS to quantify how much benzene there is in 87 gasoline.
  - We will use a **standard addition method** with respect to an internal standard reference.
- Why we are interested.
  - Gasoline is a complex mixture of hydrocarbons, and refineries are known to include aromatics such as benzene, toluene, and xylenes to increase the octane rating.
  - However, there is increasing concern about the hazards associated with these compounds.
- **Standard addition method:** The quantitation of a substance of interest in a complex mixture performed by spiking in increasing known amounts of that substance and plotting the resulting signal from this series of samples to determine the original amount.
- Description of how gas chromatography works.
- **Electron ionization** (mass spectrometry): A “hard ionization” source that results in a charged ion likely to fragment into a characteristic fragmentation pattern. *Also known as EI.*
  - As discussed in Labalme [1], electrons are generated via thermionic emission from a hot tungsten filament and then accelerated by applying a large potential between the filament and anode.
- **Chemical ionization** (mass spectrometry): A “soft ionization” source through which the major product is the molecular ion and very little fragmentation occurs. *Also known as CI.*
- EI is more useful for molecular identification against a library of known fragmentation patterns; CI is more useful for calculating the molecular weight of an unknown or newly synthesized compound.
- Common MS peaks in EI spectra.
  - Molecular ion at  $m/z = \text{MW}$ .
  - $[\text{C}_4\text{H}_3]^+$  at  $m/z = 51$ , which is often a tell-tale sign that the analyte is an aromatic.
  - $[\text{C}_7\text{H}_7]^+$  at  $m/z = 91$ , which often arises from the rearrangement of a benzyl fragment and suggests that the analyte contains a benzyl moiety.
- Mass analyzers.
- Methods of mass analysis: Quadrupole, time of flight, ion trap, ion cyclotron, etc.



- Our setup has both a quadrupole and time-of-flight mass analyzer.
- **Quadrupole:** A device that filters out ions with very low or very high  $m/z$  ratios.

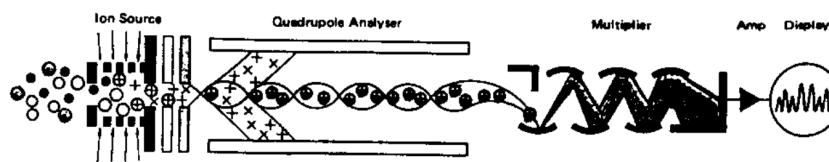


Figure 6.5: Quadrupole mass spectrometer.

- In our setup, it allows ions of our desired  $m/z$  range to pass into the time-of-flight tube where they are ultimately detected.
- Can be tuned to scan the atomic mass range or pass only a particular mass/charge of interest.
- Setup: Each parallel plate contains a dc voltage as well as a radiofrequency oscillation with frequency  $f$ . How much something moves correlates with its mass. We use one set of plates in the  $xz$ -plane, and one in the  $yz$ -plane, each meant to filter out an extreme of mass.
- **Time of flight:** A device that accelerates charged particles along a path and measures how long they are in the tube before they crash into a detector. *Also known as TOF.*

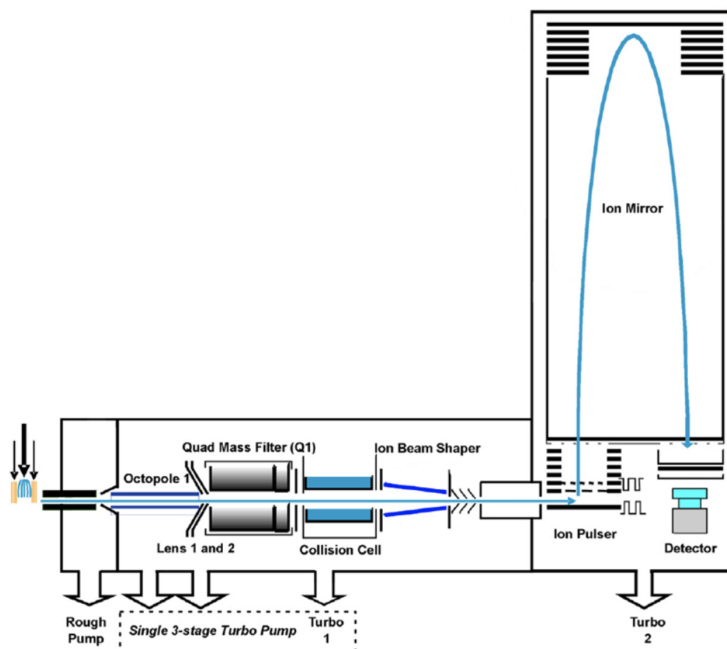


Figure 6.6: Time of flight mass spectrometer.

- We rearrange  $E = (1/2)mv^2$  to

$$m = \left( \frac{2E}{d^2} \right) t^2$$

- Smaller ions are accelerated to a higher total velocity and arrive at the detector first.
- Standard addition analysis: Largely to be discussed in lab.
- Error analysis discussed.