Week 7
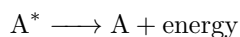
Electronic Relaxation

7.1   Office Hours (Moe)

2/13:
- Use chemical shift as your x-axis in NMR plots.

- Hexylamine is our substance.

- Interpreting NMR data files: Column E is chemical shift; column C is peak intensity. Column D is hertz (not chemical shift).

  - Chemical shift is in the rightmost column.

- Fitting tutorial: If solver still isn't helping (you get an error message and no convergence), divide the absolute intensities by a million. You can also do this from the get-go.

- M_z should be calculated for each carbon; it is the absolute integral value in the all-integrals spreadsheet.

- Don't let the peaks overlap in the plot of multiple vertically offset T_1 values.

  - Use 3 plots.

- R outputs standard error values automatically.

  - In Excel, it's much more difficult.
  - A residuals plot is a good thing to include, but there won't be points for it. Standard error also isn't worth points. Sarah will have them upload the rubric. Sarah opened the door to email her.
  - We need standard error for all 6 regressions.

- Sarah will send a source for literature values.

7.2   Lecture 12: Electronic Relaxation and Fluorescence Spectroscopy

2/14:
- Today: What happens after absorption (fluorescence and relaxation).

- Motivating question: What is the fate of electronic excitations?

  - Absorption to an electronic excited state takes a lot of energy.
  - This energy needs to be dissipated to return to equilibrium via

  $$\text{A}^* \longrightarrow \text{A} + \text{energy}$$

  - Many possible routes (radiative [releasing low-energy photons] and non-radiative [various]).

- Review: Electronic absorption leads to vibrational excitation which relaxes vibrationally.
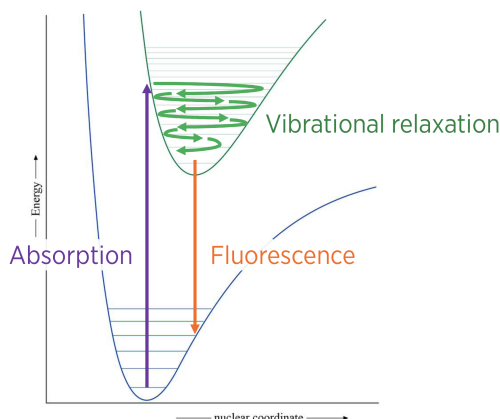

Figure 7.1: The photophysical excitation process.

  – Vibrational energy dissipates non-radiatively via intramolecular vibrational energy redistribution and intermolecular collisions.
    ■ No change in electronic state is involved.
  – The radiative path (fluorescence) is slower.
    ■ $k_{\mathrm{rad}} \ll k_{\mathrm{IVR}}$.
    ■ Most fluorescence occurs from $v' = 0$. Further relaxation requires a change of electronic state.
  – Time scale of relevant processes.
    ■ The vibrational period of a molecule is 10-100 fs.
    ■ Vibrational relaxation in solution takes 1-10 ps.
    ■ Fluorescence emission takes 1-10 ns.
  – Once you get into the ground state, you have further vibrational relaxation.

- k_{rad}: The radiative fluorescence emission rate.

- k_{nr}: The rate of all nonradiative processes leaving the flourescent state. *Given by*

$$k_{\mathrm{nr}} = \sum_i k_{\mathrm{nr},i}$$

- k_{IVR}: The intramolecular vibrational relaxation rate.

- **Reorganization energy**: The amount of energy dissipated on one of the potential energy surfaces. *Denoted by λ.*

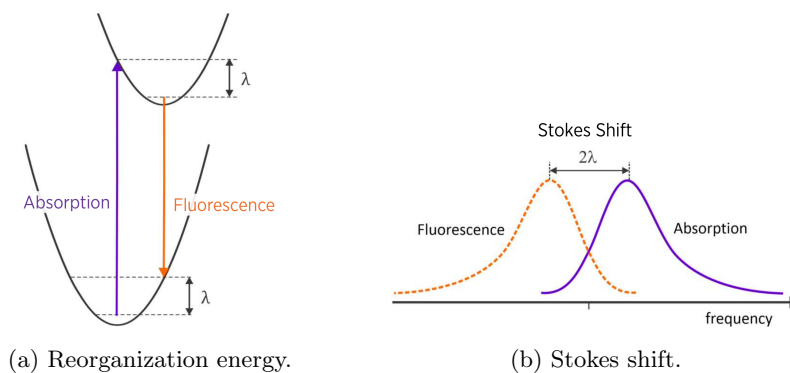
(a) Reorganization energy. (b) Stokes shift.

Figure 7.2: Quantifying photophysical reorganization.

- Per the above, some energy is dissipated in both the ground and excited states. The amount dissipated in both is (roughly??) the same and is denoted by λ.
  - The overall energy shift is known as the **Stokes shift** and is the sum of the two reorganizational energies.

- **Stokes shift**: The difference in energy absorbed vs. energy fluoresced. *Denoted by* $\mathbf{2\lambda}$.

- Other non-radiative intramolecular electronic relaxation process.
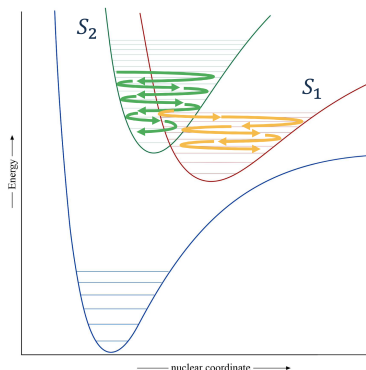
- Internal conversion.

Figure 7.3: Internal conversion.

- Essentially, exchange between higher lying excited singlet states can be very efficient.
  - We obey the **energy gap law**.

- **Energy gap law**: The non-radiative relaxation rate scales exponentially in the energy gap between the initial and final states. *Given by*
$$k_{\mathrm{nr}} \propto \exp(-\Delta E)$$

- Intersystem crossing.
  - Non-radiative singlet to triplet energy transfer.
  - We have to consider what happens when we change the spin angular momentum. Because this takes energy, this is quite improbable unless we have something like spin-orbit coupling present.
  - Nominally forbidden in closed shell molecules. Hence, it is slow.
    - ms in closed shell organics.
    - ps-ns in metal coordination compounds via SOC, MLCT.

- **Phosphorescence**: Luminescence from triplet states.
  - Occurs on a very slow microsecond to millisecond time scale.

- Intermolecular processes.

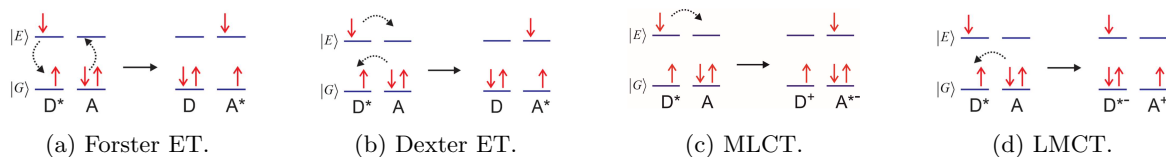(a) Forster ET.   (b) Dexter ET.   (c) MLCT.   (d) LMCT.

Figure 7.4: Intermolecular relaxation mechanisms.

- Forster energy transfer (through space), aka, electronic resonance energy transfer.
    - Two dipoles couple, and one drives the other.
- Dexter energy transfer.
    - Wavefunction overlap and electrons move.
- MLCT (electron transfer).
    - Donor gives a high energy electron to an acceptor.
- LMCT (hole transfer).
    - Donor gives a hole to the acceptor.
    - Electronic excitation brings electron density to the metal center.

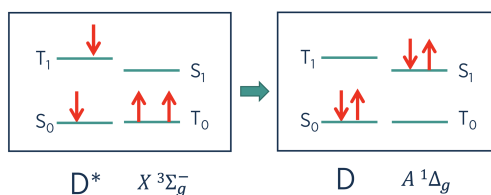- Triplet quenching by oxygen.

Figure 7.5: Triplet quenching by oxygen.

- Oxygen is a rare ground-state triplet compound.
- Thus, it can easily transfer electron density to other excited triplets, quenching them.
- Rate is partially determined by the proximity of oxygen to whatever it's quenching.

- Photochemistry summary.

- Light provides energy to surmount activation barriers (relevant to atmospheric chemistry, photosynthesis).
- Photodissociation (relevant to bond cleavage, ligand release, photoacids, photoionization, and radicals).
- Electron transfer and proton-coupled electron transfer.
- Photoisomerization (see below).

- Photoisomerization.

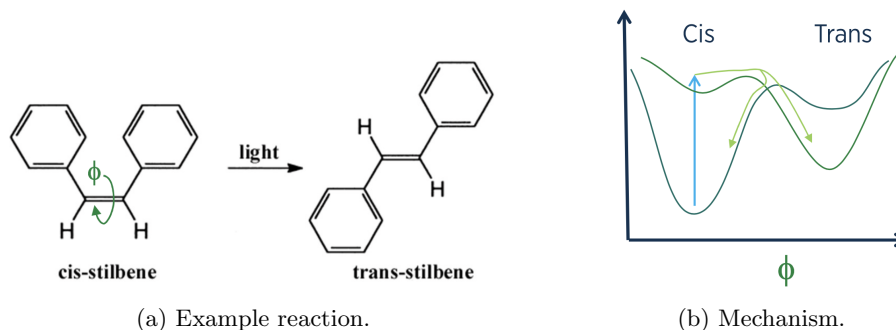
(a) Example reaction.

(b) Mechanism.

Figure 7.6: Photoisomerization.

- Stilbene possesses *cis/trans* photoisomerization.

- Quantities in fluorescence spectroscopy.

- **Fluorescence quantum yield**: The probability that an absorbed photon led to emission of a photon via fluorescence. *Denoted by* Φ. *Given by*

$$\Phi = \frac{\text{\# of fluorescence photons emitted}}{\text{\# of input photons absorbed}} = \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{nr}}}$$

  – Tells you how good of a fluorophore your molecule is, i.e., how good it is at absorbing light and turning it back into fluorescence.

- k_{f}: The rate constant for fluorescence emission. *Given by*

$$k_{\text{f}} = k_{\text{rad}} + k_{\text{nr}}$$

- **Fluorescence lifetime**: The time constant relating to the rate of fluorescence emission. *Denoted by* τ. *Given by*

$$\tau = \frac{1}{k_{\text{f}}}$$

- The underlying theory behind the fluorescence lifetime.

  – The measured fluorescence intensity $I(t)$ is proportional to the number of excited states, i.e.,

$$I(t) \propto A^*(t)$$

  – The rate law for fluorescence decay is

$$\frac{dA^*}{dt} = -k_{\text{f}}A^*$$
$$I(t) = I(0)\exp(-k_{\text{f}}t)$$

- Implication: We can use fluorescence to probe non-radiative processes.

- Example: Quenching experiments.

  – Object of study: Short-range interactions that lead to rapid non-radiative relaxation.
  – Background: The fluorescence lifetime in the absence of quencher is $\tau_0 = k_0^{-1}$. The quencher results in an additional route for non-radiative relaxation.

    ■ Implication: The fluorescence lifetime τ decreases: $\tau < \tau_0$.
    ■ If [Q] denotes the concentration of the quencher and k_q denotes the rate constant associated with quenching by the quencher, then we have

$$-\frac{dA^*}{dt} = k_0 A^* + k_q A^*[Q]$$
$$= (k_0 + k_q[Q])A^*$$

    so that

$$\frac{1}{\tau} = k_0 + k_q[Q] = \frac{1}{\tau_0} + k_q[Q]$$

  – Analysis: Use a **Stern–Volmer plot**.

    ■ Acquire fluorescence lifetime as a function of the quencher concentration using the last equation above.
    ■ This gives us the rate constant k_q as the slope and $1/\tau_0$ as the y-intercept.
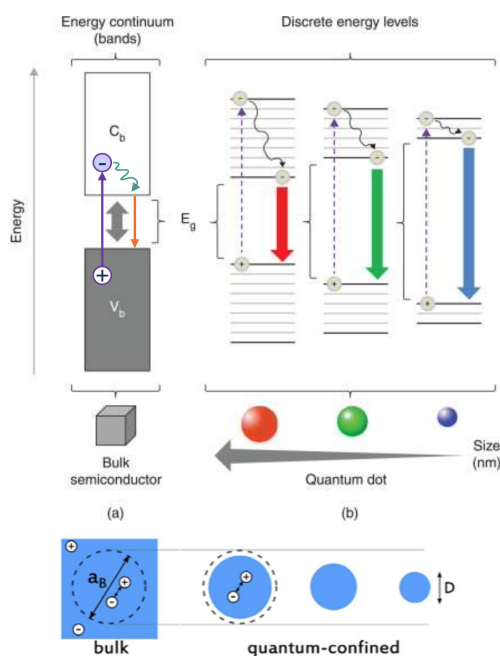
- Quantum dots: Electrons in confinement.


Figure 7.7: Quantum confinement effects in QDots.

  - Nanomaterials: Size-dependent optical properties.
  - The color changes from blue to red as the size of CdSe nanodots grows from $2\,\text{nm}$ to $8\,\text{nm}$.
  - Why?
      - In a bulk semiconductor, excitation creates an **exciton**.
      - Excited electron and hole can diffuse.
      - Dissipation of heat to lattice (via **phonons**).
      - Emission of light at the bandgap E_g.
      - The electron and hole attract coulombically, but there is a length scale in bulk; this is why size affects color.
  - Confinement: We confine the exciton to tiny sphere (like the particle in a box), but then only certain energy levels (corresponding to colors based on size) can be taken on.
  - The Coulomb potential leads to hydrogen-like energies and wavefunctions.

- **Exciton**: An electron-hole pair.

7.3 Lab 5: ECHEM

2/16:
- **Hydrogen evolution reaction**: The synthesis of non-carbon-containing fuel (H_2) from protons (water or hydronium) and electrons. *Also known as* **HER**. *Given by*

$$2\,\text{H}^+ + 2\,\text{e}^- \rightleftharpoons \text{H}_2$$
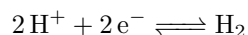
- Developing a rate law for the HER allows us to extract molecular-level insight into the chemistry of the catalyst active site.

- Thus, the goal of this lab is to: Develop a rate law for the HER consistent with experimental observations using physical electrochemistry techniques, and use it to further optimize key binding energetics of relevant intermediates.

- **Water-splitting**: The following reaction. *Given by*

$$2\,H_2O \rightleftharpoons 2\,H_2 + O_2$$
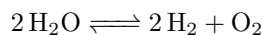
  – Stores $1.23\,V$ energy in chemical fuels.

- Water-splitting electrochemical half-reactions.

$$2\,H^+ + 2\,e^- \rightleftharpoons H_2 \qquad\qquad 2\,H_2O \rightleftharpoons 4\,H^+ + 4\,e^- + O_2$$
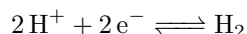
  – The left one is the HER!

- **Reduction potential**: The tendency of a chemical species to be reduced by gaining an electron. *Also known as* **thermodynamic potential**.

- **Standard Hydrogen Electrode**: The reduction potential of the HER in $1\,M$ acid conditions and at one atmosphere of H_2. *Also known as* **SHE**. *Given by*

$$E_{H^+/H_2} = 0.00$$

- **Nernst equation**: The relationship between the standard reduction potential and the reduction potential at nonstandard conditions. *Given by*

$$E = E^\circ - \frac{RT}{nF}\ln Q$$

- **Nerstian** (response): A response in line with the Nernst equation.

- The reduction potential for any electrochemical reaction involving the consumption or production of protons will exhibit a **Nerstian** response due to changes in pH conditions.

  – It follows that
  $$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{RT}{nF}\ln\left(\frac{P_{H_2}}{[H^+]^2}\right)$$

  – Under our conditions of $25\,°C$ and unit P_{H_2}, we obtain the following equation.

$$
\begin{aligned}
E_{H^+/H_2} &= E_{SHE} - \frac{\left(8.31\,\frac{J}{mol\,K}\right)(298\,K)}{(2)\left(96\,485\,C\,mol^{-1}\right)}\ln\left(\frac{1}{[H^+]^2}\right)\\
&= E_{SHE} - \frac{\left(8.31\,\frac{J}{mol\,K}\right)(298\,K)}{(2)\left(96\,485\,C\,mol^{-1}\right)}\cdot\frac{\log_{10}([H^+]^{-2})}{\log_{10}(e)}\\
&= E_{SHE} - \frac{\left(8.31\,\frac{J}{mol\,K}\right)(298\,K)}{(2)\left(96\,485\,C\,mol^{-1}\right)(\log_{10}(e))}\cdot 2\cdot-\log_{10}([H^+])\\
&= E_{SHE} - \frac{\left(8.31\,\frac{J}{mol\,K}\right)(298\,K)}{\left(96\,485\,C\,mol^{-1}\right)(\log_{10}(e))}\cdot pH\\
&\approx E_{SHE} - 0.059\cdot pH
\end{aligned}
$$

- To account for the affect of pH, we often reference the potential for the HER against the **Reversible Hydrogen Electrode** instead of the SHE.

- **Reversible hydrogen electrode**: The electrode with potential defined as follows. *Also known as* **RHE**. *Given by*
$$E_{RHE} = E_{SHE} - 0.059\cdot pH$$

- **Water oxidation reaction**: The other half-reaction involved in water-splitting. *Given by*
$$2\,H_2O \rightleftharpoons 4\,H^+ + 4\,e^- + O_2$$

- The reduction potential for the water oxidation reaction is 1.23 V vs. SHE.

  - In other words, at potentials below 1.23 V, water will be favored, and vice versa at potentials above 1.23 V.
  - Also Nerstian.

- **Pourbaix diagram**: A diagram depicting the thermodynamic scaling of reduction potential as a function of pH.

  - Alternative definition: A phase diagram of sorts that indicates the thermodynamically stable phase of an electrochemical system.

- Example: Pourbaix diagram for H_2O.
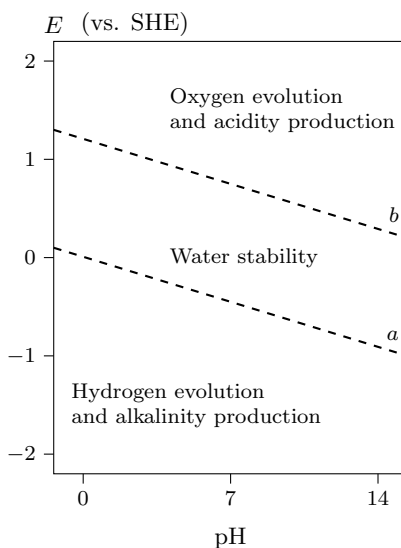
Figure 7.8: Pourbaix diagram for H_2O.

  - Line a corresponds to hydrogen evolution. It has y-intercept $(0, 0)$.
  - Line b corresponds to oxygen reduction. It has y-intercept $(0, 1.23)$.
  - Both lines have a slope of $-0.059 \, \text{V/pH}$.

- Note that for practical reasons (side reactions, voltage lost as heat, etc.), application of a substantially higher voltage is necessary for the HER to proceed at a practical rate.

- **Overpotential**: The extra potential needed to overcome the kinetic barriers inherent to the half reactions.

- "The central challenge for chemistry is to develop catalysts to bring the operational potential as close to the thermodynamic potential as possible."

- Choosing catalysts.

  - The catalytic activity of solid electrodes toward the HER correlates with their surface metal hydride bond strength.
  - The correlation forms a volcano plot: When the metal hydride bond is too weak, there is not enough driving force to initiate the reaction; when it is too strong, the reaction is inhibited.
  - Takeaway: Pt is best (by this **descriptor**).
  - Other concerns include oxidation/corrosion of the metal surface.

- **Descriptor**: A (possibly incomplete) measure of something.

- Three materials we'll be working with: TiO_x, SnO_x, and PtO_x.

- **Working electrode**: The electrode material of interest. *Also known as* **w.e.**

- **Reference electrode**: The electrode of known potential. *Also known as* **r.e.**

- Such a **two-electrode cell** can determine the *i-E* curve.

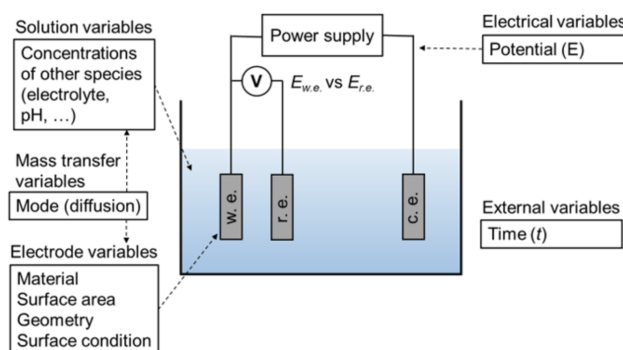- With more highly resistive solutions, a **three-electrode cell** is preferable.

Figure 7.9: Schematic three-electrode cell with variables affecting the rate of reaction.

  – Such a setup involves an additional **counter electrode**, or **c.e.**
  – The material of the c.e. does not matter since it won't affect the behavior of the w.e.

- Steps on the first day.

  – For each electrocatalyst, we'll take a CV first to figure out where the overpotential is.
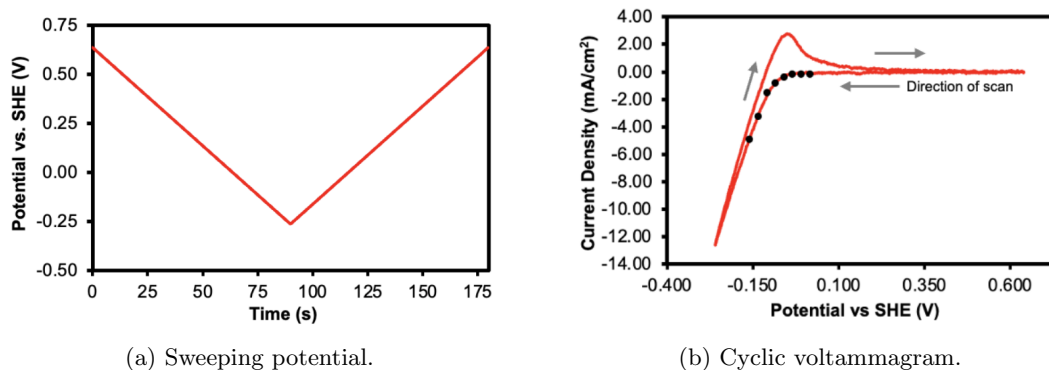 – We'll then identify points along the foot of the wave at which to collect **chronoamperograms**.

- CV.

(a) Sweeping potential.

(b) Cyclic voltammagram.

Figure 7.10: Cyclic voltammetry.

  – Figure 7.10a shows the potentials we sweep over, first negative and then positive, as time progresses. Notice that this change in potential is mirrored by the grey arrows in Figure 7.10b.
  – Figure 7.10b shows the cyclic voltammagram. The black points lie along the foot of the wave and are where we want to collect CA data. They correspond to overpotentials that induce catalysis.

- **Chronoamperometry**: The measure of the current (or current density, when normalized to the surface area of the working electrode) that flows as a function of time when a working electrode is poised at a specific potential. *Also known as* **CA**.
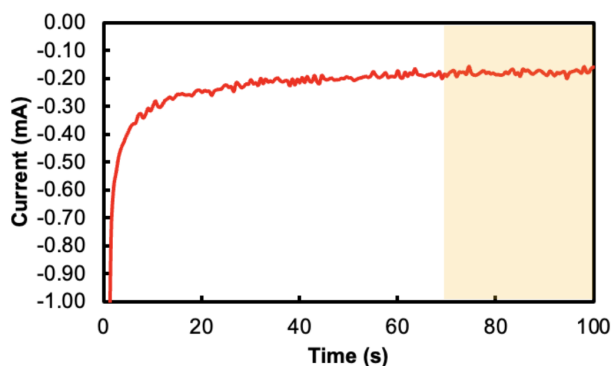

Figure 7.11: Chronoamperometry.

- We have an initially high charging current which decays exponentially with time, after which **Faradiac current** flows.

- **Faradaic current**: The current attributed to electron transfer events.

- In this case, this is the current attributed to H_2 evolution.

- Creating a Tafel plot.

- To extract kinetic and thermodynamic parameters and investigate the mechanism, we'll construct a Tafel plot for each electrode under each pH fo interest.

- Average the current density that flows over the last 30 seconds of the 100 second CA experiment (the yellow region in Figure 7.11).

- Plot the log of the negative of this value against the overpotential at which it was collected.

- We will be using a $Hg/HgSO_4$ (saturated K_2SO_4) electrode, which has a potential of $0.650\,\text{V}$ vs. SHE.

- Thus, I should (where asked) convert any measured potentials to SHE via

$$E_{\text{SHE}}(\text{V}) = E_{\text{Hg}/\text{Hg}_2\text{SO}_4}(\text{V}) + 0.650\,\text{V}$$

and then to RHE via its definition.

- **Overpotential** (for a reductive process): The quantity defined as follows. *Denoted by* $\boldsymbol{\eta}$. *Given by*

$$\eta(\text{V}) = E_{2\,\text{H}^+/\text{H}_2} - E_{\text{app}}$$

- Steps on the second day.

- Measure the pH dependence of the HER on Pt by collecting the same set of CVs and CAs over a range of pH values.
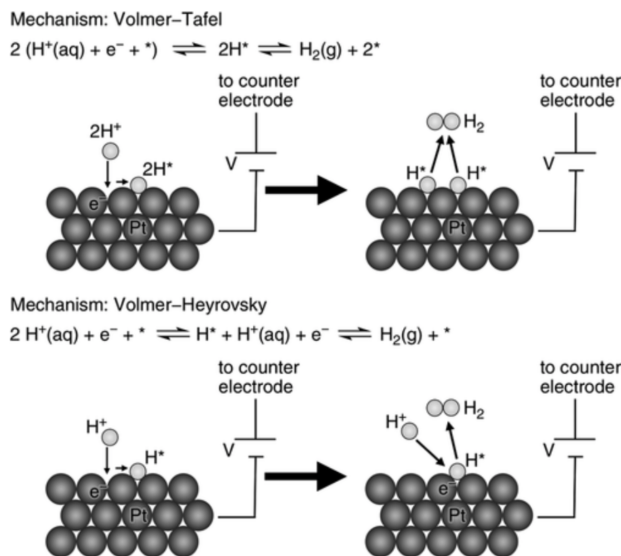
- Mechanisms of HER.

Figure 7.12: HER mechanisms.

- **Volmer-Tafel** (mechanism of HER): Both proton and electron are used to make a surface-bound H, and then two surface bound hydrogen atoms recombine to form H_2.

- **Volmer-Heyrovsky** (mechanism of HER): Only one pair of proton and electron forms a surface-bound hydrogen, which is then protonated and reduced in a single step to form H_2.

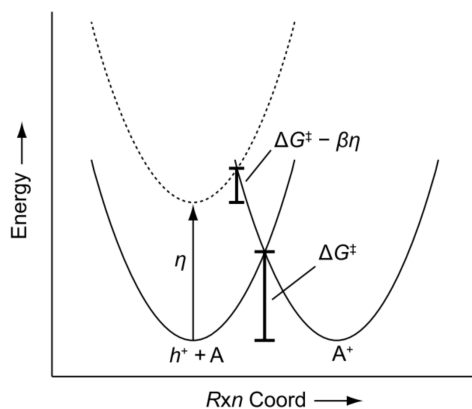- Distinguishing between the two mechanisms.

Figure 7.13: Reaction coordinate diagram.

- Quantities in Figure 7.13.
  - h^+ is a hole with chemical potential equal to the Fermi level of the poised electrode.
  - $\Delta G^{\ddagger}$ is the activation battier.
  - η is the overpotential.
  - β is the **symmetry factor**.
  - The reaction under study is single-electron oxidation of A.
- Assume that the total current we measure goes toward the HER.
  - Formally, we say that the Faradaic efficiency is 100%.

■ This assumption is experimentally supported
- We monitor and control reaction rate via

$$j = nFv$$

where j is current density, n is the equivalents of electrons, F is Faraday's constants, and v is the velocity of the reaction ($\mathrm{mol\,e^-/s}$).
- We tune the potentials in Figure 7.13 by adjusting the potential (which directly alters the energy of the electron).
- By the **Eyring equation**, there is an exponential relationship between activation barrier and reaction rate. In this case, this means that tuning the overpotential will lead to an exponential increase in activation-controlled current density, i.e.,

$$j = j_0 e^{\beta\eta F/RT}$$

- Rearranging the above and taking the base 10 logarithm yields

$$\text{Tafel slope} = \frac{2.3RT}{\beta F}$$

- We take $\beta = 0.5$ for processes such as this one with high **reorganizational energy**.
- Derivation that Volmer-Tafel has a slope of 30 mV/log j and Volmer Heyrovsky has a slope of 120 mV/log j.

- **Symmetry factor**: The fraction of the overpotential that goes toward lowering the activation of the electron transfer process. *Denoted by β*.

- **Reorganizational energy**: The energy required to rearrange the solvent after a redox reaction.

In Lab

Day 1

- Pt.

- Open circuit potential: $234.1\,\mathrm{mV}$.

- Ru: $51.888\,\Omega$.

- CV plot: Scanning right to left, we eventually induce the HER. Then on the way back, we oxidize leftover hydrides off of the catalyst surface.

  - This comes from previous literature; we can't derive that just from the CV.

- Ti electrode area: $9\,\mathrm{mm} \times 7\,\mathrm{mm}$.

- Sn electrode area: $8\,\mathrm{mm} \times 6\,\mathrm{mm}$.

- Pt electrode area: diameter $2\,\mathrm{mm}$.

- Sn.

- OCP: $-928.2\,\mathrm{mV}$.

- Ru: $9.508\,\Omega$.

- We have an oxide forming in solution; this means that the electrolyte will need to be switched out before our next run.

- Huge corrosion.

- Ti.

- OCP: $-227.5\,\mathrm{mV}$.

- Ru: $2.11\,\Omega$.