

By measuring the change in current we gain these insights

1. **Reaction Kinetics:** We can understand the rate at which redox reactions are occurring. This helps us understand how quickly a substance is being Ox or red.
2. **Electroactive Species Concentration:** The magnitude of the current observed often relates to the concentration of electroactive species according to Faraday's Law. Allows quantitative analysis.
3. **Redox behavior and Reversibility:** The shape of the  $i-E$  curve tell us about the redox behavior of the analyte. A reversible reaction will produce a symmetric peak, while irreversible reactions will have asymmetric peaks.
4. **Electrochemical Mechanisms:** Current response can help infer the sequence of steps in a redox reaction. Gives insight into reaction intermediates and pathways.
5. **Diffusion Coefficients:** The current at the peak of a CV wave is proportional to the sqrt of the scan rate. Can be used to calculate the diffusion coefficient.  
Randles-Sevcik eq  
$$i_p = 0.446 n F A C \sqrt{\frac{n F v D}{RT}}$$
6. **Electrocatalytic Activity:** Identify potential windows where certain materials exhibit catalytic activity towards specific redox rxns.

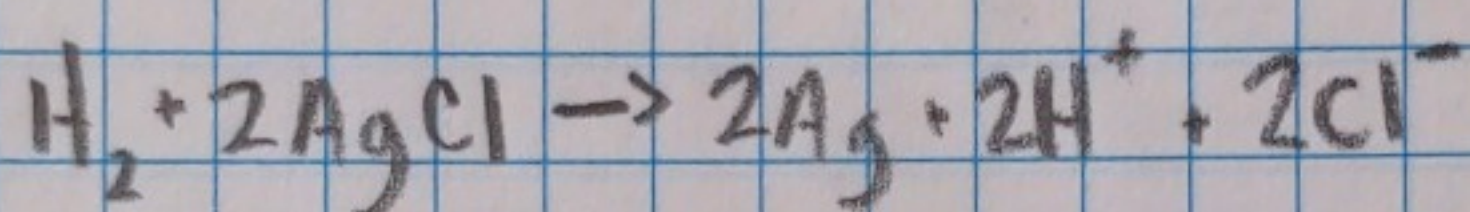


## 2 - Potentials and Thermodynamics of Cells

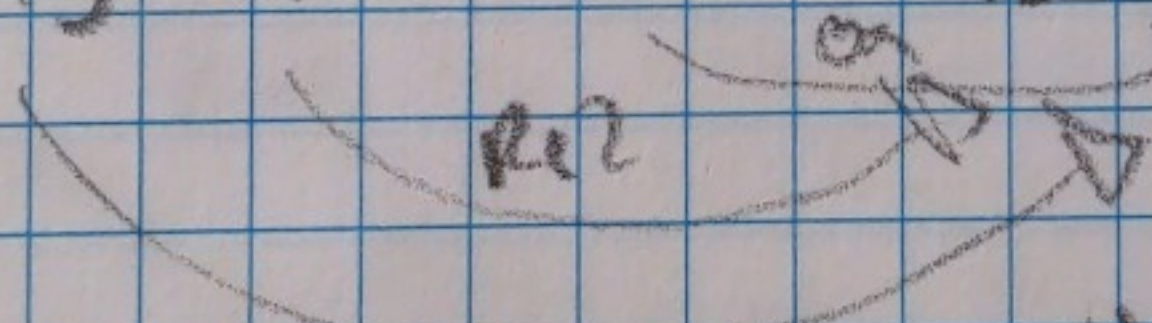
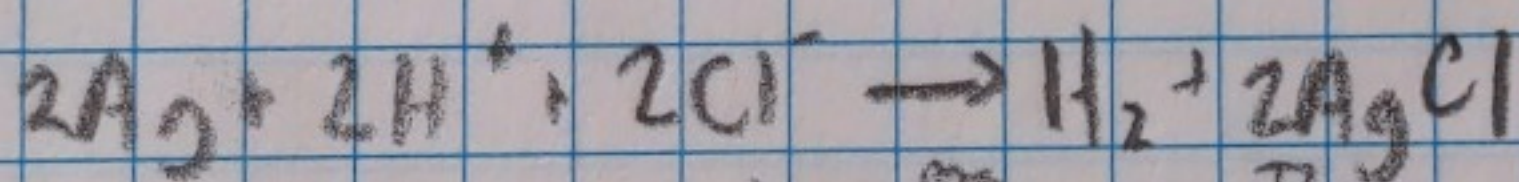
## • Reversibility:

Chemical - Consider the cell -  $\text{Pt}/\text{H}_2/\text{H}^+, \text{Cl}^-/\text{AgCl}/\text{Ag}$

When Pt electrode is shorted with Ag electrode  $e^-$  flows from Pt to Ag, the following rxn occurs



If a battery is connected such that an inverse current occurs we get



This is Chemical Reversibility

If a chem rxn has different net processes it is called chemically irreversible

Thermodynamic - A process is thermodynamically reversible if an infinitesimal reversal in a driving force causes it to reverse direction

- it must therefore always be at equilibrium

If a system follows the Nernst Eq, the electrode reaction is said to be thermodynamically or electrochemically reversible or  $\rightarrow$  Nernstian



## Reversibility and Gibbs Free Energy

Cell reaction emf,  $E_{\text{cell}}$  - the electrostatic potential of the electrode

$$\Delta G = -nFE_{\text{cell}}$$

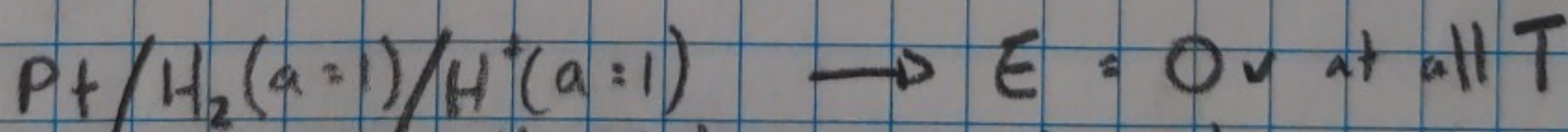
The negative sign indicates that a spontaneous reaction corresponds to a positive cell  $E$  ( $\Delta G < 0$  then  $E > 0$ )

This relationship is derived from thermodynamics. Gibbs Free energy is a measure of the max reversible work that a thermodynamic system can perform at constant pressure and temp. In an electrochemical cell this comes in the form of electrical work.

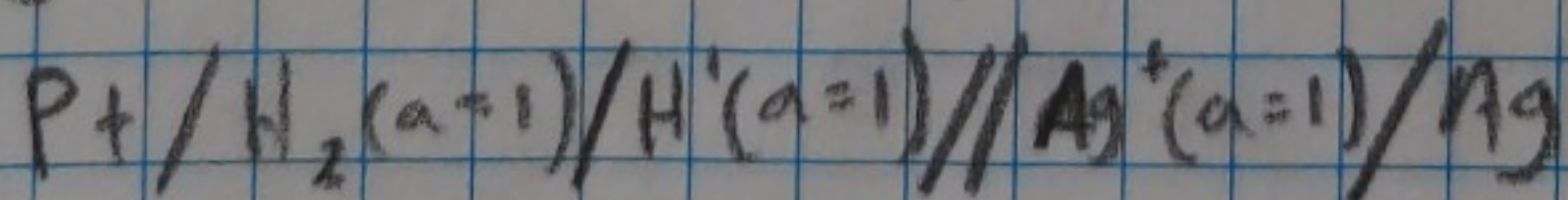
Utility in determining the spontaneity and direction of an EC rxn.

- Knowing the cell  $E$  can help in assessing the energy storage capacity of the battery. Knowing  $G$  can help in determining the applied potential needed to drive a non-spontaneous reaction.

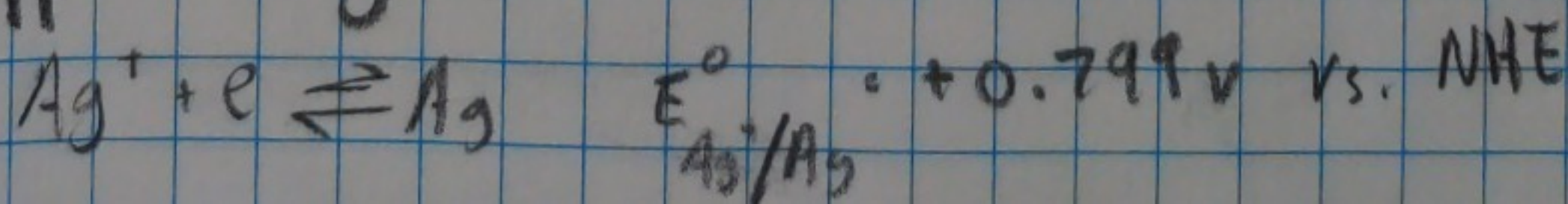
To measure a half cell's potential we must always have some reference cell. Consider NHE:



We can record half-cell  $E$  by measuring them in whole cells against the NHE



The cell  $E$  is 0.799 V,  $\text{Ag}$  is + so we say the standard potential of the  $\text{Ag}^+/\text{Ag}$  couple is +0.799 V vs. NHE or is opposite sign. reduction  $\downarrow$





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## Electrochemical Methods

Standard thermodynamic or potential values written with a 0 superscript

$$\Delta G^{\circ} \quad \text{or} \quad E^{\circ}$$

Debye-Hückel theory - Predicts that the activity coefficient of a given ionic species depends on its charge and size, the charges and concentrations of all other ions and the dielectric constant of the solvent

$$\log \gamma_i = \frac{-Az^2 I^{1/2}}{1 + B a_i I^{1/2}}$$

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emf and Concentration I'm not sure...



# ~~Experiment~~ + Electrochemical Methods

Formal Potential<sup>o</sup> Measured Potential of a half-cell (vs. NHE)  
when:

- Species  $O + R$  are present at concentrations such that  $[O]_0/[R]_0$  is unity - total unitless molar concentrations of species  $O + R$  in all equilibrated chemical forms
- Other substances are present at designated concentrations

Reference Electrodes:

## ● NHE / Hydrogen Electrodes

A real H electrode can be constructed by immersing a Pt electrode in an aq electrolyte with a known concentration of  $H^+$ , then  $H_2$  is bubbled through the solution near Pt

- Ag/AgCl - Fig. 1.5.4a

Contact between Reference electrolyte and working electrolyte is established via a Frit

- Ag/AgCl/KCl  $E_{ref} = 0.197 \text{ V vs. NHE at } 25^\circ\text{C}$

- Saturated Calomel Electrode (SCE)

Hg/Hg<sub>2</sub>Cl<sub>2</sub>/KCl  $E_{ref} = 0.244 \text{ V vs. NHE at } 25^\circ\text{C}$

Reversible Hydrogen Electrode

Buffering - helps maintain constant pH



## 2.2.1) The Physics of Phase Potentials

Electric Potential:  $\phi(x, y, z) = \int_{\infty}^{x, y, z} -E \cdot dl$

$$\phi(x, y, z) = \int_{\infty} -E \cdot dr$$

Gauss' Law:  $\frac{q}{\epsilon_0} = \oint E \cdot ds$

$\hat{n} dA$   
 $dr \times dr = dA$

Ferrocyanide is reduced,

Ferrocyanide is oxidized.

## 2.2.5) Fermi energy and Absolute potential

- a) absolute scale - define a redox couple at equilibrium in terms of half-reactions where  $e^-$  are in vacuo  
 redox couple at equilibrium: rate of Red and rate of Ox are equal. Concentrations of Ox/Red do not change.  $\Delta G$  net potential. Max entropy min  $\Delta G$

- b) equivalence of Fermi level

Fermi level  $\rightarrow$  highest energy level that an  $e^-$  can have

WRT EC  $\rightarrow$  Diff between 2 species in contact is what drives  $e^-$  transfer

Redox  $\rightarrow$  movement of  $e^-$  from higher Fermi level to a species with lower Fermi level



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## Electrochemical Methods

Liquid junction Potential - potential difference between two electrolytes. Caused by different diffusion rates

To minimize this a salt bridge or porous frit is used - allows passage of ions but limits the mixing of the two solutions

Lab note:

Leakage at reference tip - A double junction can be helpful toward preventing leakage

