Unit 4: Electrochemistry

UNIFYING ELECTROCHEMISTRY, FREE ENERGY, & EQUILIBRIUM

Goals for Today

1. Describe fully the relationship between electrical potential (ε) and free energy (ΔG)

$$\Delta G = -nF\mathcal{E}$$

2. Describe fully the relationship between electrical potential (ε) and the equilibrium constant (K)

$$\mathcal{E}^{\circ} = \frac{0.05916}{n}\log K$$

3. Use these relationships to calculate the cell potential of a non-standard cell

$$\mathcal{E} = \mathcal{E}^{\circ} - \frac{0.05916}{n}\log Q$$

4. Use these relationships to fully explain the operation and purpose of a concentration cell

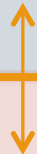5. Be able to explain the first principles of basically everything in the chemistry universe

Free Energy and Electrical Potential

Chemical Definition: The free energy of an electrochemical cell is proportional to the negative electrical potential and the number of electrons involved in the balanced redox reaction

$$\Delta G = -nF\mathcal{E}$$

Chemistry World

Physics World

$$w = -q \cdot \mathcal{E}$$

Physics Definition: The maximum electrical work that can be done on an electrochemical cell is proportional to the negative electrical potential and the charge the balanced redox reaction

Conceptual Summary

1. **There is a simple relationship between free energy and electrical potential:**

$$\Delta G = -nF\mathcal{E}$$

2. **This equation can be applied to tell us about the capacity for an electrochemical system to do work:**

$$w = -q \cdot \mathcal{E}$$

3. These values are ideal, meaning we are calculating the maximum electrical work, **or the maximum reversible non-expansion work.**

4. **This relationship provides an effective way of determining the capacity for a chemical system to do work when we do not have a change in gas moles (no change in volume)**

REEF Question

Suppose you are sitting in a test and completely blank on the formula that relates electrical potential and K (which we are about to discuss), and all you can remember is the equation from unit 2:

$$\Delta G^{\circ} = -RT \ln K$$

Can you derive the formula that you need?

A. $\mathcal{E}^{\circ} = -\dfrac{RT}{nF} \log K$

C. $\mathcal{E}^{\circ} = \dfrac{RT}{nF} \ln K$

E. None of the above

B. $\mathcal{E}^{\circ} = \dfrac{nF}{RT} \log K$

D. $\mathcal{E}^{\circ} = -\dfrac{RT}{nF} \ln K$

Electrical Potential and Equilibrium

Now that we know the relationship between electrical potential and free energy:

$$\Delta G^{\circ} = -nF\mathcal{E}^{\circ} \qquad\qquad \Delta G^{\circ} = -RT\ln K$$

We can very clearly connect the dots between free energy and the equilibrium constant, K:

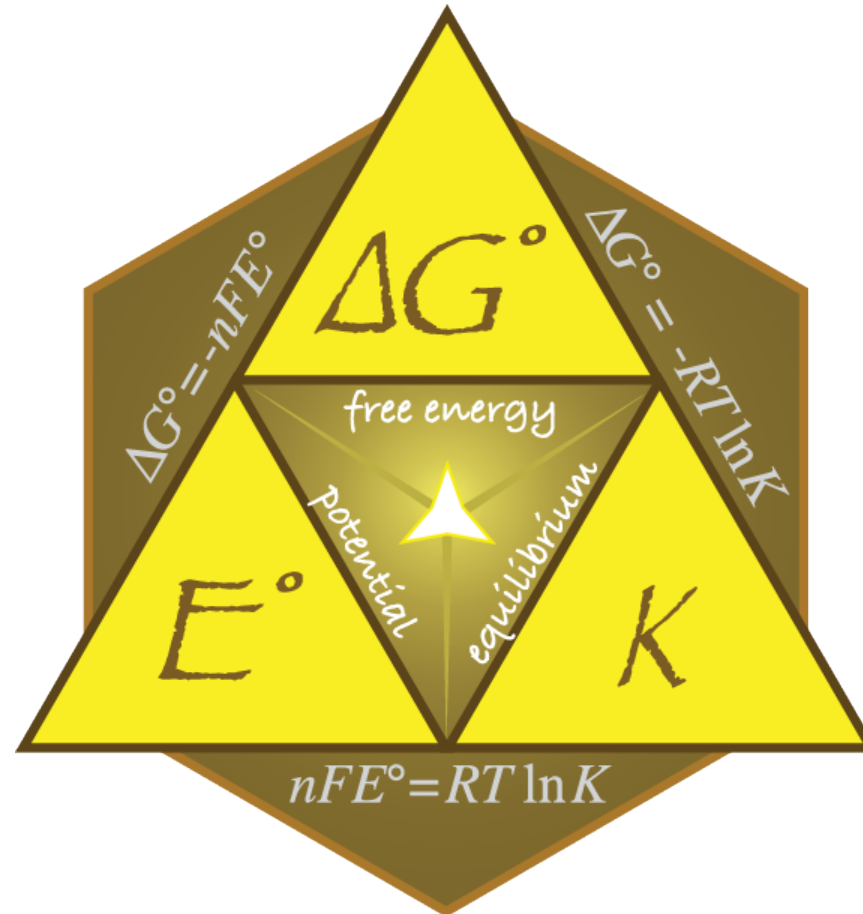$$\mathcal{E}^{\circ} = \frac{RT}{nF}\ln K \qquad\qquad \boxed{\mathcal{E}^{\circ} = \frac{0.05916}{n}\log K}$$

Conceptual Summary: Standard Cells

Electrical Potential $\varepsilon°$	Free Energy $\Delta G°$	Equilibrium Constant K	Spontaneous?
Positive	Negative	Greater than 1	Yes
Negative	Positive	Less than 1	No

Conceptual Summary: Standard Cells

REEF Question

What is the maximum non-expansion work that can be **done by the system** of the following cell at standard conditions?

$$Fe|Fe^{2+}||Fe^{3+}|\ Fe$$

Answer in units of kJ/mol. Round to the nearest whole number.

Answer = _ _ _ kJ/mol

Cl_2	+	$2e^-$	$\rightleftharpoons$	$2Cl^-$		+1.36 V
Ag^+	+	$1e^-$	$\rightleftharpoons$	Ag		+0.80 V
Fe^{3+}	+	$1e^-$	$\rightleftharpoons$	Fe^{2+}		+0.77 V
Cu^{2+}	+	$2e^-$	$\rightleftharpoons$	Cu		+0.34 V
$2H^+$	+	$2e^-$	$\rightleftharpoons$	H_2		0.00 V
Fe^{3+}	+	$3e^-$	$\rightleftharpoons$	Fe		−0.04 V
Pb^{2+}	+	$2e^-$	$\rightleftharpoons$	Pb		−0.13 V
Fe^{2+}	+	$2e^-$	$\rightleftharpoons$	Fe		−0.44 V
Zn^{2+}	+	$2e^-$	$\rightleftharpoons$	Zn		−0.76 V
Al^{3+}	+	$3e^-$	$\rightleftharpoons$	Al		−1.66 V

increasing strength as an reducing agent

REEF Question

At standard conditions, you can look up the half reactions of the following cell to get an electrical potential equal to -0.576V. What is the value of K?

$$Ag(s)|Ag^+ (aq)||Cl^-(aq)| AgCl(s) | Ag(s)$$
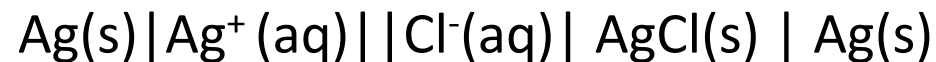
a. 2.8×10^8

b. 3.6×10^{-10}

c. 1.8×10^{-10}

d. 1.8×10^{10}

e. None of the above

Once you've answered, think about the meaning of this particular K value.

Non-Standard Cells Electrical Potential

You can use Q to determine the non-standard potential with the Nernst Equation:

$$\mathcal{E} = \mathcal{E}^\circ - \frac{RT}{nF} \ln Q \qquad \text{OR:} \qquad \mathcal{E} = \mathcal{E}^\circ - \frac{0.05916}{n} \log Q$$

What is the non-standard potential of the AgCl, H_2 cell when we change
ONLY the chloride concentration to 8M?

a. 0.22V
b. -0.22V
c. 0.27V
d. 0.17V
e. None of these

HINT: remember how Q works:

Q is the given concentrations (or pressures) of the products raised to the power of their coefficients divided by the reactants raised to the power of their coefficients.

Non-Standard Cells Electrical Potential

Let's go back to our original cell at standard conditions. Now we modify only the [H$^+$] to get a voltage reading of 0.5454V. What is the pH of the anode compartment?

Answer using the following format: _ . _ _

The Concentration Cell

A concentration cell is simply a cell that has identical half-reactions and achieves a positive cell potential by having a favorable Q-value in the Nernst Equation.

$$reduction: Cu^{2+} + 2e^- \rightarrow Cu \ (0.34V)$$

$$oxidation: Cu \rightarrow Cu^{2+} + 2e^- \ (-0.34V)$$
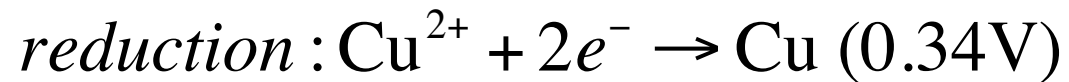
$$\varepsilon°_{cell} = \varepsilon°_{reduction} + \varepsilon°_{oxidation}$$

$$\varepsilon°_{cell} = 0V$$

$$\varepsilon = \cancel{\varepsilon°} - \frac{0.05916}{n} \log Q$$
$$= 0V$$

You can maximize ε by minimizing Q:
1. Increase the concentration of Cu^{2+} in the cathode compartment
2. Decreasing the concentration of Cu^{2+} in the anode compartment

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$$\mathcal{E}^{\circ} = \frac{RT}{nF}\ln K \qquad\qquad \mathcal{E}^{\circ} = \frac{0.05916}{n}\log K$$

3. Use these relationships to calculate the cell potential of a non-standard cell

$$\mathcal{E} = \mathcal{E}^{\circ} - \frac{RT}{nF}\ln Q \qquad\qquad \mathcal{E} = \mathcal{E}^{\circ} - \frac{0.05916}{n}\log Q$$

4. Use these relationships to fully explain the operation and purpose of a concentration cell: we can change the concentrations of a standard cell to create a cell potential when we have identical species in the half reactions

5. Be able to explain the first principles of basically everything in the chemistry universe: use the triforce

$$\boxed{W = -q \cdot \mathcal{E}^{\circ}} \implies \text{conceptual}$$

$\downarrow$

yes, these are "ideal"
- friction • Energy loss
- 2nd Law of thermo

$$\Delta G^{\circ} = -nF\mathcal{E}^{\circ}$$

$$\frac{J}{\text{mol rxn}} = (\text{moles } e^-)\left(\frac{C}{\text{mol } e^-}\right)\left(\frac{J}{C}\right)$$

"maximum" electrical work possible

provided
(96,485)

mol rxn

$\sqsupset \mathcal{E}^{\circ}_{cell} = \mathcal{E}^{\circ}_{cathode}$

$- \mathcal{E}^{\circ}_{anode}$

Remember: $W = -P\Delta V = -\Delta nRT = -nR\Delta T$

$\sqsupset$ needed gas moles, now we don't

non-expansion work

$$\Delta G^\circ = -nF\mathcal{E}^\circ$$

$$\Delta G = -RT \ln K$$

$$-nF\mathcal{E}^\circ = -RT \ln K$$

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

$$\mathcal{E}^\circ = \frac{RT}{nF} \ln K$$

$$\boxed{\mathcal{E}^\circ = \frac{0.05916}{n} \log K}$$

$n \rightarrow$ moles e^-

Conclusions:

1) $(+)$ $\mathcal{E}^\circ$, $K > 1$

2) $(-)$ $\mathcal{E}^\circ$, $K < 1$

$\rightarrow$ Voltaic Cell

$\rightarrow$ Electrolytic Cell

Anode: $Ag(s) \rightarrow Ag^+ + e^-$

Cathode: $AgCl(s) \xrightarrow{+e^-} Ag(s) + Cl^-$

Overall: $AgCl \rightarrow Ag^+ + Cl^-$

$$\mathcal{E}^\circ = -0.576 V$$

$$\mathcal{E}^\circ = \frac{RT}{nF} \ln K \quad \text{OR} \quad \mathcal{E}^\circ = \frac{0.05916}{n} \log K$$

$$K = e^{\frac{\mathcal{E}^\circ nF}{RT}} \quad \text{OR} \quad K = 10^{\frac{\mathcal{E}^\circ \cdot n}{0.05916}}$$

$n = 1, \ R = 8.314, \ T = 298K$

$\rightarrow MX \rightarrow M^+ + X^- \quad \underline{\underline{K_{sp}}}$

$K_A, \ K_w, \ K_B$

$-0.44V$ OX: $\left(Fe \rightarrow Fe^{2+} + 2e^- \right) \times 3$

$-0.04V$ Red: $\left(Fe^{3+} + 3e^- \rightarrow Fe \right) \times 2$
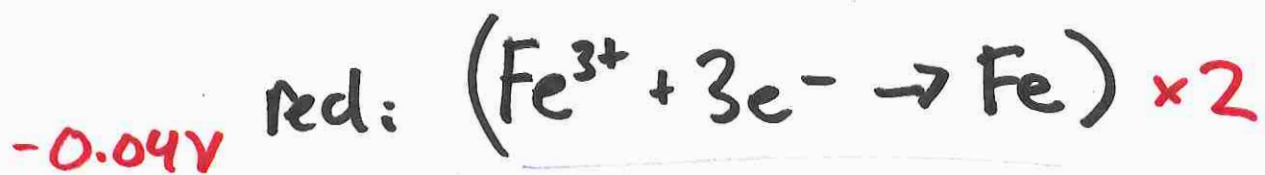
$\underline{6\ e^-\ total}$

$$\mathcal{E}°_{cell} = \mathcal{E}°_{cathode} - \mathcal{E}°_{anode}$$

$$0.40V = -0.04V - (-0.44V)$$

$$W = \Delta G° = -nF\mathcal{E}°$$

$$= -\frac{6 \quad 96,485 \quad 0.40V}{1000}$$

$$= -232\ \frac{KJ}{mol\ Rxn}$$

$$\overbrace{Pt \mid H_2 (g) \mid H^+ (1M) \| Cl^- (1M) \mid AgCl(s) \mid Ag(s)}^{+0.22V}$$

$$\underbrace{Pt \mid H_2 (g) \mid H^+ (1M)}_{\text{anode, } 0V} \| \underbrace{Cl^- (1M) \mid AgCl(s) \mid Ag(s)}_{\text{cathode, } +0.22V}$$

Overall reaction:

$$2 \, AgCl(s) + H_2(g) \xrightleftharpoons{2e^-} 2Ag(s) + 2Cl^-_{(aq)} + 2H^+_{(aq)}$$
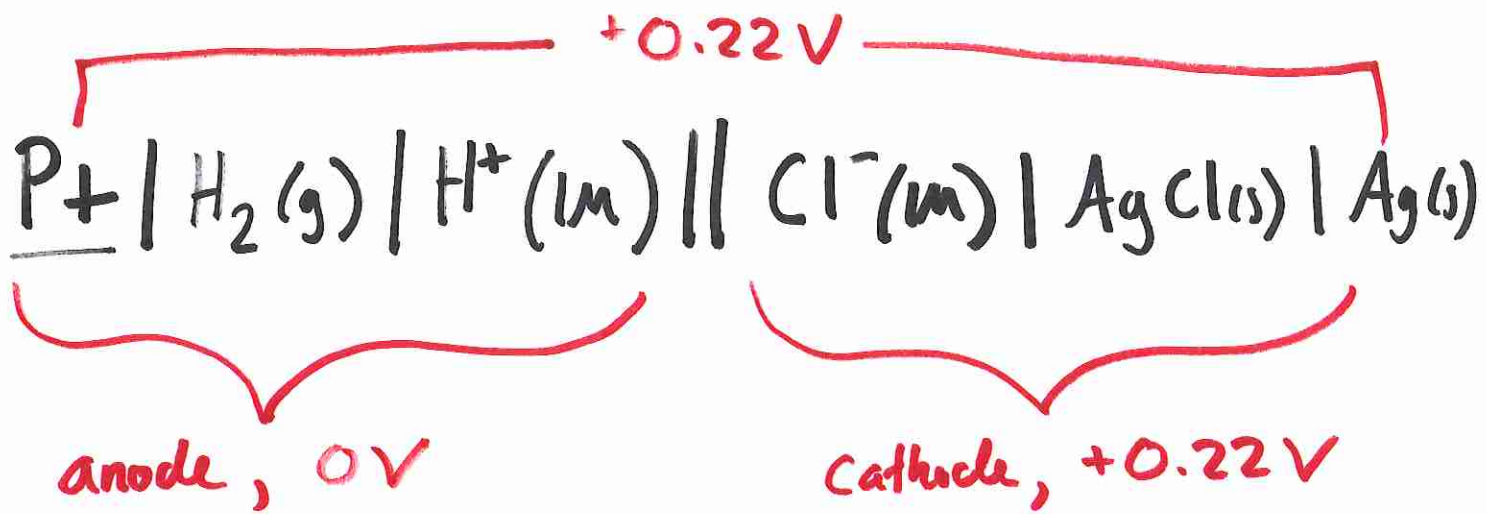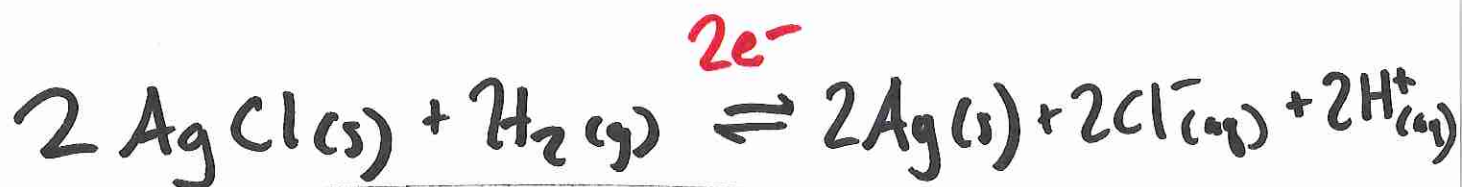
$$\mathcal{E}° = 0.22V \leftarrow \text{everything is std.}$$

How does $\mathcal{E}$ change when:

(1) Increase $[Cl^-]$ to 8M $\quad \mathcal{E} \downarrow$

(2) Increase amount of $Ag(s)$ $\quad \mathcal{E}$ same

(3) Increase P_{H_2} to 8atm $\quad \mathcal{E} \uparrow$

(4) Run battery/cell for 24 hours $\quad \mathcal{E} \downarrow$

$$Q = \frac{[Cl^-]^2 [H^+]^2}{P_{H_2}}$$

$\mathcal{E}$?

$$\mathcal{E} = 0.22V - \left(\frac{0.05916}{2}\right) \log \frac{(8)^2 \cdot 1^2}{1}$$

$$= 0.166 V$$

$$\approx 0.17V$$

pH?

$$0.5454 = 0.22 - \left(\frac{0.05916}{2}\right) \log \frac{[H^+]^2 \cdot 1^2}{1}$$

$$\left(\frac{0.5454 - 0.22}{0.05916}\right) = -\frac{1}{2} \log [H^+]^2$$

$$\Downarrow$$

$$5.50 = -\log [H^+] = pH$$