Electrochemistry

Half-cells, Cells, and the Nernst Equation

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Objective:

Examine electrical consequences of some chemical reactions and derive some chemically useful information from electrical measurements

Concepts:

Oxidation / Reduction	Electric potential
Cell/Half Cell	Nernst Equation
Concentration Cell	Reduction Potential
Solubility Product	Salt Bridge
Basic Electrical Units	Anode, Cathode

Techniques:

Constructing Cells — Measuring Voltage

Apparatus:

pH Meter — Salt Bridge

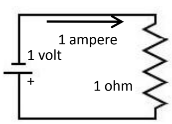
Basic Electrical Units & Concepts:

Units

Charge,	q:	coulomb	
Potential,	V:	volt	
Current,	i:	ampere	= coulomb/sec
Energy,	E:	joule	= watt-second = volt-coulomb
Power,	P:	watt	= volt-ampere
Resistance,	R:	ohm	= volt/ampere

Ohm's Law

$i = V / R$



1 volt of potential applied to a resistance of 1 ohm will cause 1 ampere to flow.
The resistor will give off energy at 1 watt and dissipate 1 joule of energy per second.

Michael Faraday defined the **cathode** as the electrode to which **cations flow** (positively charged ions, like silver ions Ag^+), to be reduced by reacting with (negatively-charged) electrons on the cathode.

which **anions flow** (negatively charged ions, like chloride ions Cl^-), to be oxidized by depositing electrons on the anode.

Thus, (positive) electric current flows from the cathode to the anode.

To an external wire connected to the electrodes of a battery, the cathode is positive and the anode is negative and:

electrons flow from the anode to the cathode.

One more unit - The Faraday - A Chemical unit

If we agree to include electrons in chemical equations, we need to be able to account for them stoichiometrically, just as we do with moles of other chemical substances.

To that end, we define the Faraday, $\mathcal{F}$, to be the (absolute value) of the charge on Avogadro's number (1 mole) of electrons:

$$1\ \mathcal{F} = Ne = 6.022141 \times 10^{23}\ mol^{-1} \times 1.6021765 \times 10^{-19}\ C = 96{,}485.3383\ C/mol$$

How many Faradays of charge must flow to keep a 100 watt bulb (@ 110 v) lit for 1 day?

(volt-coulomb/sec)

$$\frac{100 \text{ watt} \times 1 \text{ day} \times 86{,}400 \text{ sec/day}}{110 \text{ volts}} = 78.5 \times 10^3 \text{coulombs} = 0.814\ \mathcal{F}$$

Voltages, Equilibrium Constants and ΔG

$\mathbf{Cu}\ (s) + 2Ag^+\ (aq)$

$$\Delta G = \Delta G^0 + \mathcal{R}T \ln Q \qquad Q = \frac{[\mathbf{Cu^{2+}}]}{[Ag^+]^2}$$

$$\Delta G^0 = -\mathcal{R}T \ln \mathbf{K_{eq}} \qquad \Delta G^0 = -88.72 \text{ kJ/mol Cu}$$

Voltages, Equilibrium Constants and ΔG

Cu (s) + 2Ag$^+$ (aq) $\rightarrow$ 2Ag (s) + **Cu^{2+} (aq)**

$$\mathcal{E} = \mathcal{E}^0 - \frac{\mathcal{R}T}{n\mathcal{F}} \ln Q \qquad Q = \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$\Delta G^0 = -n\mathcal{F}\mathcal{E}^0$ $\quad$ $\Delta G^0 = -88.72$ kJ/mol Cu

$\Delta\mathcal{E}^0 = -(-88.72) / 2 \times 96485 =$ **0.4599 v**

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So, for the reaction:

Cu (s) + 2Ag$^+$ (aq) $\rightarrow$ 2Ag (s) + **Cu^{2+} (aq)**

$$\mathcal{E} = 0.462 - \frac{2.303\,\mathcal{R}T}{2\mathcal{F}} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$\mathcal{E} = 0.462 - 0.0295 \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

Can we conduct the reaction in such a way as to get electrical energy?

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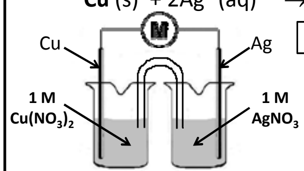
Cu (s) + 2Ag$^+$ (aq) $\rightarrow$ 2Ag (s) + **Cu^{2+} (aq)**



Cu | Cu $^{2+}$ (1 M) || Ag$^+$ (1M) | Ag

$$\mathcal{E} = 0.462 - 0.0295 \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

Initially, $\mathcal{E} = 0.462$ v

0.1 M	**1 M**
1 M	**0.1 M**
0.1 M	**5.3X10^{-9} M**

If we change the silver ELECTRODE to copper will the process change?

If we change the copper ELECTRODE to silver will the process change?

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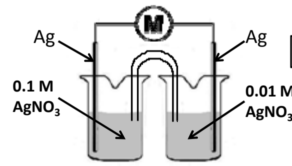
Must the two half cells involve different substances?

Ag(s) + Ag$^+$(0.1) $\rightarrow$ Ag(s) + Ag$^+$ (0.01)



Ag | Ag$^+$ (M$_1$) || Ag$^+$ (M$_2$) | Ag

$\Delta\mathcal{E}^0 =$ **0 v,** $\Delta G^0 = -n\mathcal{F}\Delta\mathcal{E}^0 = 0$

$$\mathcal{E} = \mathbf{0.000} - \frac{\mathcal{R}T}{\mathcal{F}} \ln \frac{[Ag^+]_1}{[Ag^+]_2}$$

A concentration difference suffices to produce a potential. E.g., for a 1 electron change, a factor of 10 in concentration produces:

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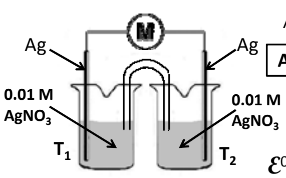
How Important is Temperature Control?

Ag(s) + Ag$^+$(0.01) $\rightarrow$ Ag(s) + Ag$^+$ (0.01)



Ag | Ag$^+$ (M$_1$),T$_1$ || Ag$^+$ (M$_1$),T$_2$ | Ag

Is $\Delta\mathcal{E}^0 =$ **0V ?** **Not necessarily!**

$\mathcal{E}^0$ values are tabulated at 25^{o}C!

$$\mathcal{E} = \mathcal{E}^0(\mathbf{T_2}) - \frac{\mathcal{R}\mathbf{T_2}}{\mathcal{F}} \ln [Ag^+] - \mathcal{E}^0(\mathbf{T_1}) + \frac{\mathcal{R}\mathbf{T_1}}{\mathcal{F}} \ln [Ag^+]$$

$$\mathcal{E} = \Delta\mathcal{E}^0 - \frac{\mathcal{R}(\mathbf{T_2 - T_1})}{\mathcal{F}} \ln [Ag^+]$$

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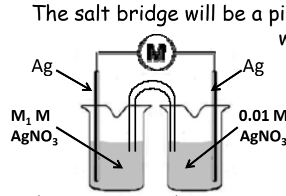
In part 1, you prepare, in **groups of two**, a series of concentration cells based on the half reaction:

Ag$^+$ (aq) + e- $\rightarrow$ Ag (s)

Ag | Ag$^+$ (M$_1$) || Ag$^+$ (0.01 M) | Ag

The reference electrode throughout will be the one with [Ag$^+$] = 0.01 M.

The salt bridge will be a piece of filter paper moistened with NH_4NO_3



You are required to plot the voltage measured *vs* the log of the varying concentration.

Silver nitrate solutions at concentrations 10^{-5}, 10^{-4}, 10^{-3}, 10^{-2} and 10^{-1} M will be available. **Take only what you need!**

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We have seen that temperature effects are expected to be small. Nevertheless, you should confirm that the temperature is sufficiently close to the standard temperature so that correction is not necessary.

If you have conducted this part of the exercise correctly, the plot should produce a straight line which provides qualitative confirmation of the Nernst equation for concentration cells. The slope of the straight line should confirm the law quantitatively.

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In the Cu/Ag+ example, you have seen that the logarithmic nature of the Nernst relationship means that cell potentials can be a way of measuring very small concentrations

In part 2, **WORKING ALONE**, you will prepare an assigned silver halide and measure its solubility product electrochemically.

For sparingly soluble salts, a common measure of their solubilities* is the solubility product. It is the equilibrium constant for the solubility reaction.

$M_p X_q\,(s) \rightarrow p\,M^{m+}\,(aq) + q\,X^{n-}\,(aq) \qquad K_{sp} = [M^{m+}]^p\,[X^{n-}]^q$

e.g.,

The silver halides (excluding AgF) are examples of such slightly soluble substances.

Each student will prepare a sample of an unknown silver halide by reaction of a measured volume of a solution of potassium halide , KX, of known concentration with a measured volume of 0.0100 M silver nitrate.

$Ag^+\,(aq) \quad + \quad X^-\,(aq) \quad \rightarrow \quad AgX\,(s)$

	Ag+	X-	AgX
Initial	5.00 mL X 0.0100 M = **0.0500 mmol**	5.00 mL X 0.0500 M = **0.250 mmol**	0
Final	?	0.250 – 0.050 = **0.200 mmol**	**0.05 mmol**

The final volume is 10.00 mL, so the final concentration of X^- is 0.200 mmol/10.00 mL = 0.0200 M

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Measure Ag^+ concentration by letting this solution be a half cell with a Ag/Ag^+ 0.01 M reference cell.

The value of the solubility product, K_{sp}, is the product of the X^- concentration calculated above and the measured Ag^+ concentration.

Cell voltages are also a way of measuring other chemical equilibrium constants, particularly those involving redox reactions.

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In part 3, **working in pairs**, you will determine the standard reduction potentials of zinc and copper and establish the relative oxidation/reduction potentials of Zn, Cu and Pb. We will assume that the reduction potential for lead is known and is - 0.13 V.

$Zn \mid Zn^{2+}\,(0.050\ M) \mid\mid Pb^{2+}\,(0.050\ M) \mid Pb$

$Pb \mid Pb^{2+}\,(0.050\ M) \mid\mid Cu^{2+}\,(0.050\ M) \mid Cu$

$Zn \mid Zn^{2+}\,(0.050\ M) \mid\mid Cu^{2+}\,(0.050\ M) \mid Cu$

The logic in this part of the exercise is demonstrated in the following example:

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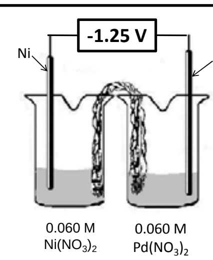

$Ni \mid Ni^{2+}\ 0.060\ M \mid\mid Pd^{2+}\ 0.60\ M \mid Pd$

$Pd\,(s) + Ni^{2+}\,(aq) \rightarrow Pd^{2+}\,(aq) + Ni\,(s)$

$$\mathcal{E} = \mathcal{E}^0(Ni/Ni^{2+}) - \frac{\mathcal{R}T}{2\mathcal{F}} \ln \frac{1}{[Ni^{+2+}]} - \mathcal{E}^0(Pd/Pd^{2+}) + \frac{\mathcal{R}T}{2\mathcal{F}} \ln \frac{1}{[Pd^{2+}]}$$

$$\mathcal{E} = \mathcal{E}^0(Ni/Ni^{2+}) - \mathcal{E}^0(Pd/Pd^{2+}) - \frac{\mathcal{R}T}{2\mathcal{F}} \ln \frac{[Pd^{2+}]}{[Ni^{2+}]}$$

$$\mathcal{E} = \mathcal{E}^0(Ni/Ni^{2+}) - \mathcal{E}^0(Pd/Pd^{2+}) = \mathbf{-1.25\ V}$$

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$\mathcal{E}^0(Ni/Ni^{2+})$ -- $\mathcal{E}^0(Pd/Pd^{2+})$ = **-1.25 V**

$\mathcal{E}^0(Cd/Cd^{2+})$ -- $\mathcal{E}^0(Pd/Pd^{2+})$ = **-1.39 V**

$\mathcal{E}^0(Cd/Cd^{2+})$ -- $\mathcal{E}^0(Ni/Ni^{2+})$ = **-0.15 V**

We appear to have 3 equations in 3 unknowns. Can we solve for all three unknowns?

However, if we knew $\mathcal{E}^0$ of one of the metals (relative to the standard hydrogen electrode), We could determine the actual values of the other two.

Suppose $\mathcal{E}^0$ for Pd/Pd^{2+} = + 0.99 V

$\mathcal{E}^0(Ni/Ni^{2+})$ -- 0.99 = **-1.25 V** $\mathcal{E}^0(Ni/Ni^{2+})$ = **- 0.26 V**

$\mathcal{E}^0(Cd/Cd^{2+})$ -- 0.99 = **-1.39 V** $\mathcal{E}^0(Cd/Cd^{2+})$ = **- 0.40 V**

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Be sure to dispose of all metal solutions in the waste containers provided.

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There are a number of misprints in the written procedure and on the data sheet.

On First page sentence should read:

Would be $E_{obs} = E_A - E_B$ (we don't multiply E's by n or m)

Computations for Part 2 should show:

[m] = antilog$_{10}$ (E_{obs}+0.118)/-0.0592) = $10^{-(E_{obs}+0.118)/0.0592}$

Beginning of Part 3, sentence should read.

Take 5.00 mL of $Cu(NO_3)_2$ solution in a 10 mL beaker and 5.00 mL of $Zn(NO_3)_2$ in another 10 mL beaker.

On the datasheet, the part 2 datasheet should read

E_{obs} of the cell:
Ag| AgX(s) | Ag^+ (m) ‖ Ag^+(0.010 M)| Ag ________________ V
Molarity (m) of (Ag^+) in the above cell ________________ M
Molarity of X^- in the cell ________________ M
K_{sp} of unknown halide (AgX) ________________ M^2

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CHE 134 Make-up Laboratory Session

Students who have excused absences for

1 or more Final Exercises, *or* Preliminary Exercises

are eligible to sign up for a Make-up Laboratory Session on

Monday, May 4 at 5:00 PM

You must sign up with Dr. Akhtar by April 30
He will give you the exercise at that time.

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Next Week's pre-lab lecture is a review.

Attendance is optional

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