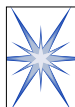


Class 10.2
Electrochemistry

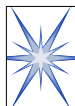
CHEM 102H
T. Hughbanks



Standard Reduction Potentials

<u>Reduction Half-reaction</u>	<u>E° (V)</u>
$\text{Ag}^+(aq) + e^- \rightarrow \text{Ag}(s)$	0.80
$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$	0.34
$2\text{H}^+(aq) + 2e^- \rightarrow \text{H}_2(g)$	0.00 (by defn.)
$\text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn}(s)$	-0.76

The choice of SHE sets the zero of the scale, but all the measurable cell potentials don't depend on that choice.



From Red. Potentials to Cell Potentials

<u>Reduction Half-reaction</u>	<u>E° (V)</u>
$\text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu}(s)$	0.34
<u>$\text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + 2e^-$</u>	<u>[-0.76]</u>
$\text{Cu}^{2+}(aq) + \text{Zn}(s) \rightarrow \text{Zn}^{2+}(aq) + \text{Cu}(s)$	1.10

The choice of SHE sets the zero of the scale, but all the measurable cell potentials don't depend on this choice.

Using the Electromotive Series -

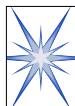
“Recipe” for Evaluating Redox Rxns’ Spontaneity

- ◆ Find the appropriate half-reactions
- ◆ Write the half-reactions with the most positive (or “least negative”) value first.
- ◆ Write the other half-rxn as an oxidation and write its oxidation potential ($= -$ reduction Potential)
- ◆ Balance the half-rxns. with respect to e^- transfer.
(Don’t multiply the potentials by the multiplicative constant used in balancing.)
- ◆ Add half-rxns and E° ’s to get E°_{cell} , if > 0 , it’s spontaneous.



Examples

- ◆ Can MnO_4^- oxidize Cl^- to Cl_2 to form Mn^{2+} in acidic solution (all species 1.0 M)?



Examples

- ◆ Can Ag(s) reduce $\text{Mg}^{2+}(\text{aq})$ to metallic Mg (with formation of $\text{Ag}^+(\text{aq})$)?





More Definitions and Concepts

- ◆ Faraday: the “amount of electricity” in one mole of electrons:

$$1 \text{ Faraday} = N_A e =$$

$$(6.022 \times 10^{23} \text{ mol}^{-1})(1.6022 \times 10^{-19} \text{ C})$$

$$1 F = 96,485 \text{ Coulombs/mol}$$

- ◆ Ampere: current flow equal to the passage of 1.0 C per second:

$$1 \text{ A} = 1 \text{ C/s}$$



More ...

- ◆ With the definitions above, we can quickly see that:

- ◆ If s amperes of current flow for t seconds, then st Coulombs of charge have passed through the circuit, and

$$(st)/96,485 = \# \text{ of moles of electrons that have passed through the circuit}$$

Key Relationship between ΔG_{rxn} and E

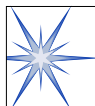
In Chap. 7 of your book, you will see that ΔG_{rxn} is equal to the maximum amount of nonexpansion work that a reaction can do at const. T and P. In an electrical cell, this is the electrical work, w_{elec} , that can be done:

$$\Delta G_{\text{rxn}} = w_{\text{elec}}$$

The electrical work to move a particle of charge q through a potential difference E is just qE . To move n moles of electrons (nN_A electrons, each with charge $-e$) through a potential difference E , $w_{\text{elec}} = nN_A(-eE) = -nFE$

$$\Delta G_{\text{rxn}} = -nFE$$

n is number of moles of electrons in the half-reactions of a cell reaction



Some checks on units

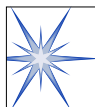
From electricity, we know Ohm's Law, $V = IR$

$J/s \sim \text{Power (Watts)} \sim I^2R = IV \sim \text{Amps} \cdot \text{Volts}$

$J/s = \text{Amps} \cdot \text{Volts} = C/s \cdot V \quad \therefore J = C \cdot V$
Joules = Coulombs \cdot Volts

$$\Delta G_{\text{rxn}} = -nFE$$

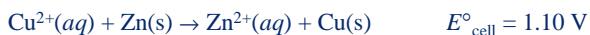
Check: Joules $\sim \text{mol} \cdot \text{Coulombs/mol} \cdot \text{Volts}$



E°_{cell} and $\Delta G^\circ_{\text{rxn}}$

Very often, we refer to standard conditions for a cell reaction:

$$\Delta G^\circ_{\text{rxn}} = -nFE^\circ_{\text{cell}}$$

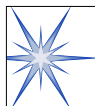


All conditions are standard:

$T = 298 \text{ K}$, $P = 1 \text{ atm}$, $[\text{Cu}^{2+}] = [\text{Zn}^{2+}] = 1.0 \text{ M}$

$$\Delta G^\circ_{\text{rxn}} = -nFE^\circ_{\text{cell}} =$$

$$(-2)(96,485 \text{ C})(1.10 \text{ V}) = -212.3 \text{ kJ}$$



Going to Equilibrium from Standard Conditions

$$\Delta G = \Delta G^\circ_{\text{rxn}} + RT \ln Q$$

(see Chap. 9) Starting at standard conditions,

$$Q = 1, \quad \Delta G = \Delta G^\circ_{\text{rxn}}$$

As we approach equil.,

$$Q \rightarrow K_{\text{eq}}, \quad \Delta G \rightarrow 0$$

we recover,

$$\Delta G^\circ_{\text{rxn}} = -RT \ln K_{\text{eq}}$$

$$\Delta G_{\text{rxn}} = -nFE_{\text{cell}}$$

Substitution gives the famous Nernst Eqn:

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{RT}{nF} \ln Q$$

as $Q \rightarrow K_{\text{eq}}$, $E_{\text{cell}} \rightarrow 0$

$$E^\circ_{\text{cell}} = \frac{RT}{nF} \ln K_{\text{eq}}$$



Nernst Equation

- ◆ The Nernst Eqn., using base 10 logarithm:

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - 2.303 \frac{RT}{nF} \log Q$$

Often, $\frac{2.303 RT}{F}$ is combined ($T = 298 \text{ K}$)

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{n} \log Q$$



Example 1

- ◆ What is the initial potential, E_{cell} ?
- ◆ What will happen as the cell goes to equilibrium?

