

Admin:

Test #2 scheduled week 8, Fri Aug 10 . Test guide is posted online.

Last time:

- 1) Electrochemical Cells
- 2) Voltaic Cells , Line notation
- 3) Electrolytic cells - sample calculations

Today:

- 1) Nernst Equation
- 2) Voltaic Cells: calculations
- 3) Applications: batteries?

Lecture:

1) Nonstandard cells : Nernst Equation

What is the potential for a nonstandard cell?

Recall :

$$\Delta G = \Delta G^\circ + RT \ln Q \quad \text{and} \quad \Delta G = -nFE ; \Delta G^\circ = -nFE^\circ$$

$$\Delta G = \Delta G^\circ + RT \ln Q \Rightarrow -nFE = -nFE^\circ + RT \ln Q$$

$$\mathbf{E = E^\circ - (RT/nF) \ln Q}$$

(Nernst Equation)

If assume $T = 25^\circ\text{C}$, $R = 8.314\text{J/molK}$, $F = \text{Faraday's const}$, and use Log_{10} instead of \ln :

$$\mathbf{E = E^\circ - 0.06/n \text{ V } \log Q}$$

So if we have $[\text{Cu}^{2+}] = 0.010 \text{ M}$ & $[\text{Zn}^{2+}] = 1.00 \text{ M}$

$$\text{Then } E = 1.10 - 0.06/2 \log \{[\text{Zn}^{2+}]/[\text{Cu}^{2+}]\} = 1.10 - .03(\log(1.00/.01)) = 1.04 \text{ V}$$

note that as rxn proceeds, $[\text{Zn}^{2+}]$ increases and E_{cell} decreases until it reaches 0. (example: that's how a battery runs down, potential (volts) drops it gets used up)

Flow of electrons measured as current, (in Amperes, A). It can do work – such running a motor...

Practice:

Say that a Cu-Zn cell has a potential of 1.10 V. A Cu-Pb cell has a potential of 0.46 V. What is the potential of a Zn-Pb cell? Prove it by deriving the E° .

Concentration cells

Consider a galvanic cell with Cu half cells on both sides. Consider the left side being 1.00 M and the right 0.001M Cu^{2+} .

Draw the cell.

Draw the line diagram.

High conc side (i): $\text{Cu}^{2+} + 2\text{e}^- \rightarrow \text{Cu(s)}$
reduction, (+), cathode

Low conc side (ii): $\text{Cu} \rightarrow \text{Cu}^{2+} + 2\text{e}^-$
Oxidation (-), anode

What is the potential?

$$E_{\text{cell}} = E_{\text{cath}} - E_{\text{anode}} = E^\circ - .06/2 \log(1/[\text{Cu}^{2+}]_i) - E^\circ - .06/2 \log(1/[\text{Cu}^{2+}]_{ii})$$

$$= 0 + .03 \log \{ [\text{Cu}^{2+}]_i / [\text{Cu}^{2+}]_{ii} \} = .03 \log (.1 / .001) = +0.06 \text{ V} = +60 \text{ mV}.$$

Note how concentration of one half cell can be monitored by means of measuring the voltage. The other half cell can be "fixed" and be the reference. Potentiometry.

How useful is it?

A potentiometer like pH meter.