The Nernst Equation

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- **The Nernst equation is an equation that relates the reduction potential of a reaction (half-cell or full cell reaction) to the standard electrode potential, temperature, and activities (often approximated by concentrations) of the chemical species undergoing reduction and oxidation.**
- **It was named after Walther Nernst, a German physical chemist who formulated the equation.**

$E°_{cell}$ and ΔG (cont.)

$$E°_{cell} = \frac{(0.0257\ V)\ \ln(K)}{n} = \frac{(0.0591)\log(K)}{n}$$

- The above relationship states that by measuring $E°_{cell}$, we can determine K.

E°_{cell} and ΔG

$$\Delta G^\circ = -RT\ln(K)$$

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

$$E^\circ_{cell} = \frac{(0.0591\ V)}{n}\log(K)$$

An Example

- Balance, determine $E°_{cell}$ and K for the following:

$$S_4O_6^{2-}\,(aq) + Cr^{2+}(aq) \longrightarrow Cr^{3+}(aq) + S_2O_3^{2-}(aq)$$

$$\cancel{2e^-} + S_4O_6^{2-} \longrightarrow 2\ S_2O_3^{2-}$$

$$\boxed{Cr^{2+} \longrightarrow Cr^{3+} \cancel{+ e^-}} \quad x\ 2$$

$$S_4O_6^{2-} + 2Cr^{2+} \longrightarrow 2Cr^{3+} + 2S_2O_3^{2-}$$

An Example (cont.)

- Determining $E°_{cell}$

$$2e^- + S_4O_6^{2-} \longrightarrow 2\ S_2O_3^{2-} \qquad E°_{1/2} = 0.17\ V$$

$$2Cr^{2+} \longrightarrow 2Cr^{3+} + 2e^- \qquad E°_{1/2} = 0.50\ V$$

$$S_4O_6^{2-} + 2Cr^{2+} \longrightarrow 2Cr^{3+} + 2S_2O_3^{2-}$$

$$E°_{cell} = 0.67\ V$$

An Example (cont.)

- Determining K

$$S_4O_6^{2-} + 2Cr^{2+} \longrightarrow 2Cr^{3+} + 2S_2O_3^{2-}$$

$$E°_{cell} = 0.67\ V$$

$$E°_{cell} = \frac{(0.0257\ V)}{n}\ \ln(K) = \frac{(0.059\ V)}{n} \log K$$

$$\frac{n(E°_{cell})}{(0.059\ V)} = \frac{2\ (0.67\ V)}{(0.059\ V)} = 22.7 = \log K$$

$$K = 10^{22.7} = 5 \times 10^{22}$$

Concentration and E_{cell}

- Consider the following redox reaction:

$$Zn(s) + 2H^+(aq) \longrightarrow Zn^{2+}(aq) + H_2(g) \qquad E^\circ_{cell} = 0.76\ V$$

$$\Delta G^\circ = -nFE^\circ_{cell} < 0 \qquad \text{(spontaneous)}$$

- What if $[H^+] = 2$ M?

Expect shift of equilibrium to products.

Therefore ΔG decreases, and E_{cell} increases

How does E_{cell} dependend on concentration?

Concentration and E_{cell} (cont.)

- Recall, in general:

$$\Delta G = \Delta G° + RT\ln(Q)$$

- However:

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

$$-nFE_{cell} = -nFE°_{cell} + RT\ln(Q)$$

$$E_{cell} = E°_{cell} - (RT/nF)\ln(Q)$$

$$\boxed{E_{cell} = E°_{cell} - (0.0591/n)\log(Q)}$$

The Nernst Equation

Concentration and E_{cell} (cont.)

- With the Nernst Eq., we can determine the effect of concentration on cell potentials.

$$E_{cell} = E°_{cell} - (0.0591/n)\log(Q)$$

- Example. Calculate the cell potential for the following:

$$Fe(s) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s)$$

Where $[Cu^{2+}] = 0.3$ M and $[Fe^{2+}] = 0.1$ M

Concentration and E_{cell} (cont.)

- First, need to identify the 1/2 cells

$$Fe(s) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s)$$

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \qquad E°_{1/2} = 0.34\ V$$

$$Fe^{2+}(aq) + e^- \longrightarrow Fe(s) \qquad E°_{1/2} = -0.44\ V$$

$$Fe(s) \longrightarrow Fe^{2+}(aq) + 2e^- \qquad E°_{1/2} = +0.44\ V$$

$$Fe(s) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s) \qquad E°_{cell} = +0.78\ V$$

Concentration and E_{cell} (cont.)

- Now, calculate E_{cell}

$Fe(s) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s)$ $E°_{cell} = +0.78$ V

$$E_{cell} = E°_{cell} - (0.0591/n)\log(Q)$$

$$Q = \frac{[Fe^{2+}]}{[Cu^{2+}]} = \frac{(0.1)}{(0.3)} = 0.33$$

$$E_{cell} = 0.78\text{ V} - (0.0591\ /2)\log(0.33)$$

$$E_{cell} = 0.78\text{ V} - (-0.014\text{ V}) = 0.794\text{ V}$$

Concentration and E_{cell} (cont.)

- If $[Cu^{2+}] = 0.3$ M, what $[Fe^{2+}]$ is needed so that $E_{cell} = 0.76$ V?

$$Fe(s) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s) \quad E^{\circ}_{cell} = +0.78\text{ V}$$

$$E_{cell} = E^{\circ}_{cell} - (0.0591/n)\log(Q)$$

$$0.76\text{ V} = 0.78\text{ V} - (0.0591/2)\log(Q)$$

$$0.02\text{ V} = (0.0591/2)\log(Q)$$

$$0.676 = \log(Q)$$

$$4.7 = Q$$

Concentration and E_{cell} (cont.)

$$Fe(s) + Cu^{2+}(aq) \longrightarrow Fe^{2+}(aq) + Cu(s)$$

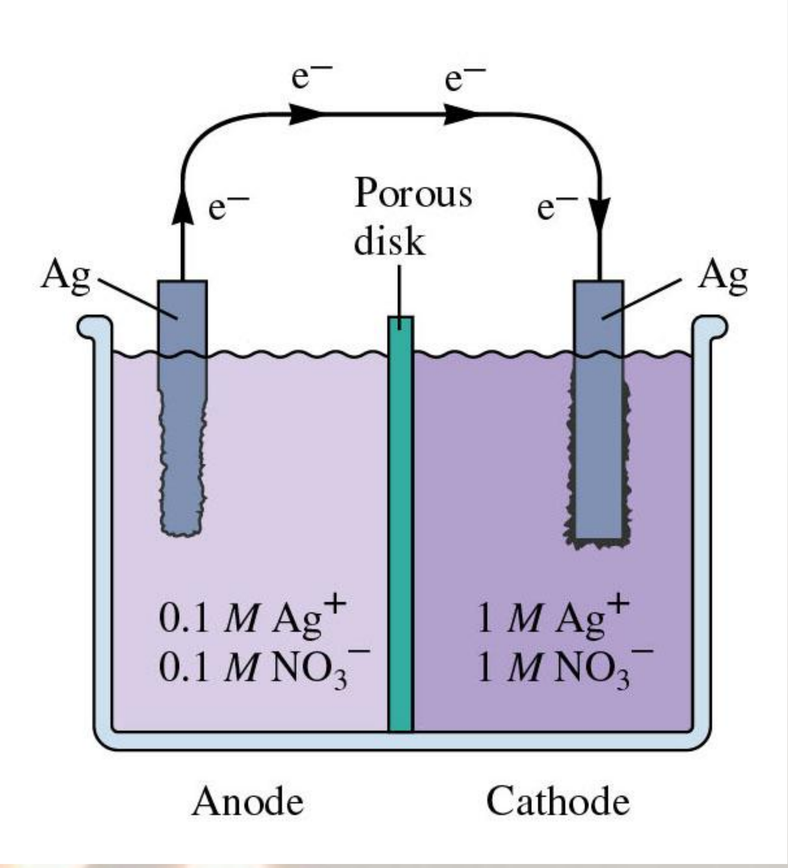
$$4.7 = Q$$

$$Q = \frac{\left[Fe^{2+}\right]}{\left[Cu^{2+}\right]} = 4.7$$

$$Q = \frac{\left[Fe^{2+}\right]}{[0.3]} = 4.7$$

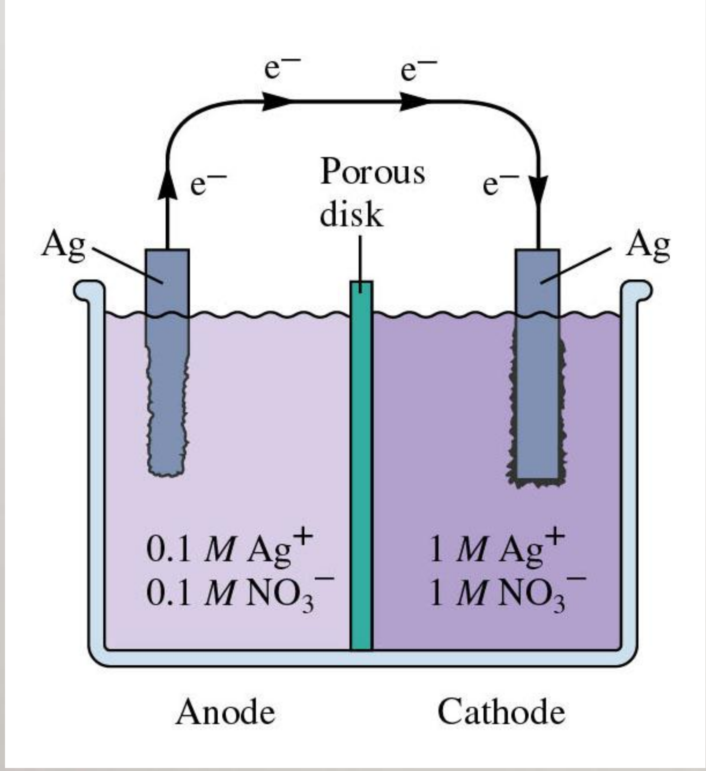
$$[Fe^{2+}] = 1.4 \text{ M}$$

Concentration Cells



- Consider the cell presented on the left.
- The 1/2 cell reactions are the same, it is just the concentrations that differ.
- Will there be electron flow?

Concentration Cells (cont.)

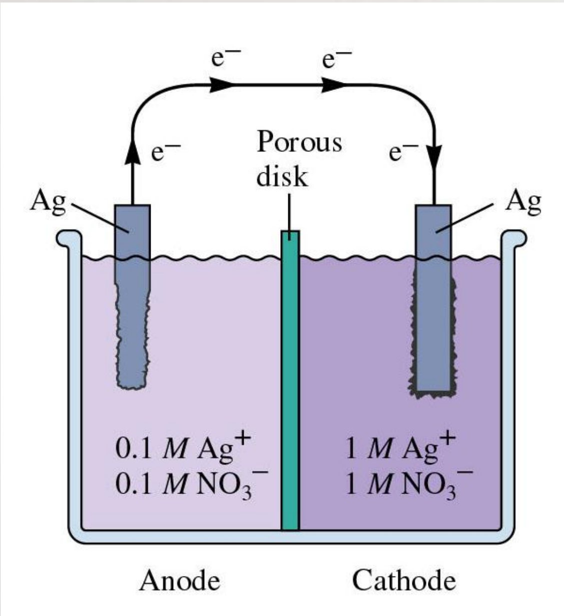


$Ag^{+} + e^{-} \longrightarrow Ag \quad E°_{1/2} = 0.80\ V$

- What if both sides had 1 M concentrations of Ag^{+}?

- $E°_{1/2}$ would be the same; therefore, $E°_{cell} = 0$.

Concentration Cells (cont.)



Anode: $Ag \longrightarrow Ag^{+} + e^{-}$ $E_{1/2} = ?\ V$

Cathode: $Ag^{+} + e^{-} \longrightarrow Ag$ $E_{1/2} = 0.80\ V$

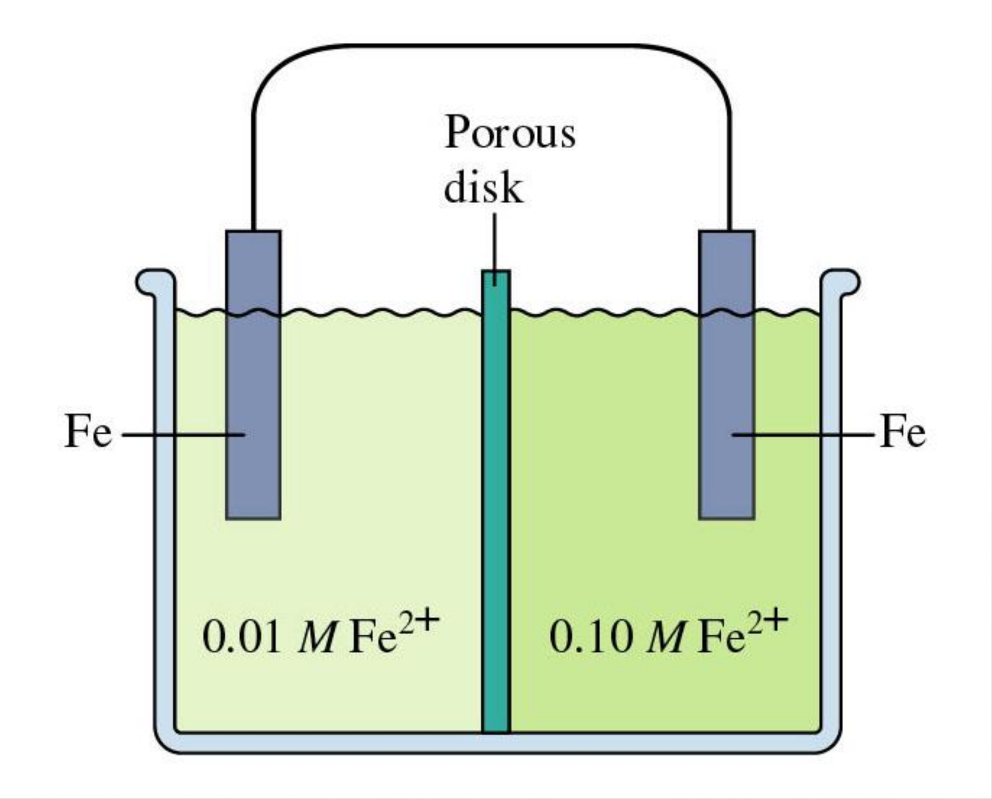
$$Q = \frac{[Ag^{+}]_{anode}}{[Ag^{+}]_{cathode}} = \frac{0.1}{1} = 0.1$$

$$E_{cell} = \underbrace{\cancel{E°_{cell}}}_{0\ V} - (0.0591/\underbrace{\cancel{n}}_{1})\log(Q)$$

$$E_{cell} = -\ (0.0591)\log(0.1) = 0.0591\ V$$

Concentration Cells (cont.)

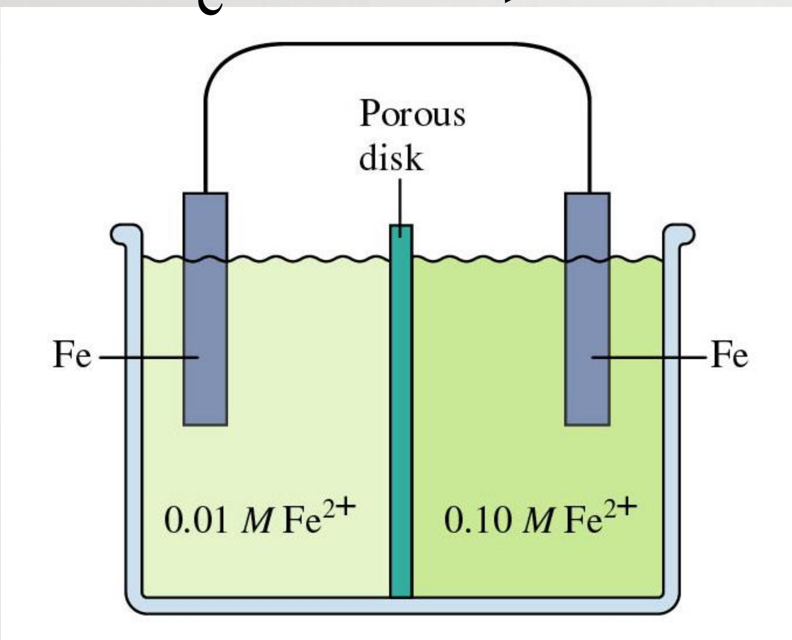
Another Example:



What is E_{cell}?

Concentration Cells (cont.)

e^- $\longrightarrow$



anode cathode

$$E_{cell} = \underset{0}{\cancel{E^{\circ}_{cell}}} - (0.0591/\underset{2}{\cancel{n}})\log(Q)$$

$$Fe^{2+} + 2e^- \longrightarrow Fe$$

2 e^- transferred…n = 2

$$Q = \frac{\left[Fe^{2+}\right]_{anode}}{\left[Fe^{2+}\right]_{cathode}} = \frac{0.01}{.1} = 0.1$$

$$E_{cell} = -(0.0296)\log(.1) = 0.0296\ V$$

Measurement of pH

- pH meters use electrochemical reactions.
- Ion selective probes: respond to the presence of a specific ion. pH probes are sensitive to H_3O^+.
- Specific reactions:

$$Hg_2Cl_2(s) + 2e^- \longrightarrow 2Hg(l) + 2Cl^-(aq) \quad E°_{1/2} = 0.27\ V$$

$$H_2(g) \longrightarrow 2H^+(aq) + 2e^- \quad E°_{1/2} = 0.0\ V$$

$$Hg_2Cl_2(s) + H_2(g) \longrightarrow 2Hg(l) + 2H^+(aq) + 2Cl^-(aq)$$

Measurement of pH (cont.)

$$Hg_2Cl_2(s) + H_2(g) \longrightarrow 2Hg(l) + 2H^+(aq) + 2Cl^-(aq)$$

- What if we let $[H^+]$ vary?

$$Q = [H^+]^2[Cl^-]^2$$

$$E_{cell} = E^\circ_{cell} - (0.0591/2)\log(Q)$$

$$E_{cell} = E^\circ_{cell} - (0.0591/\cancel{2})(\cancel{2}\log[H^+] + \cancel{2}\log[Cl^-])$$

$$E_{cell} = E^\circ_{cell} - (0.0591)(\log[H^+] + \log[\cancel{Cl^-}])$$

constant

saturate

Measurement of pH (cont.)

$$E_{cell} = E°_{cell} - (0.0591)\log[H^+] + \text{constant}$$

- E_{cell} is directly proportional to log $[H^+]$

REFERENCES

- Atkins’Physical Chemistry by James Keeler & Peter Atkins’(2002)
- Modern Physical Organic Chemistry by Dannis A. Dougherty& Eric V. Anslyn (2005)
- Physical chemistry by I.N. Levin (1990)