Chemistry 2000 Slide Set 15: Electrochemistry
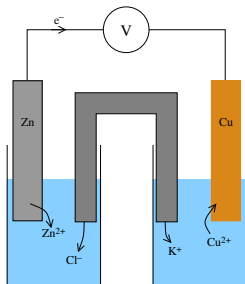
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March 5, 2020

Electrochemical cells
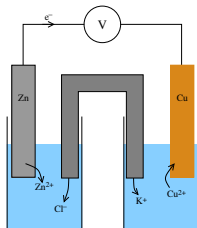

anode
= oxidation

cathode
= reduction
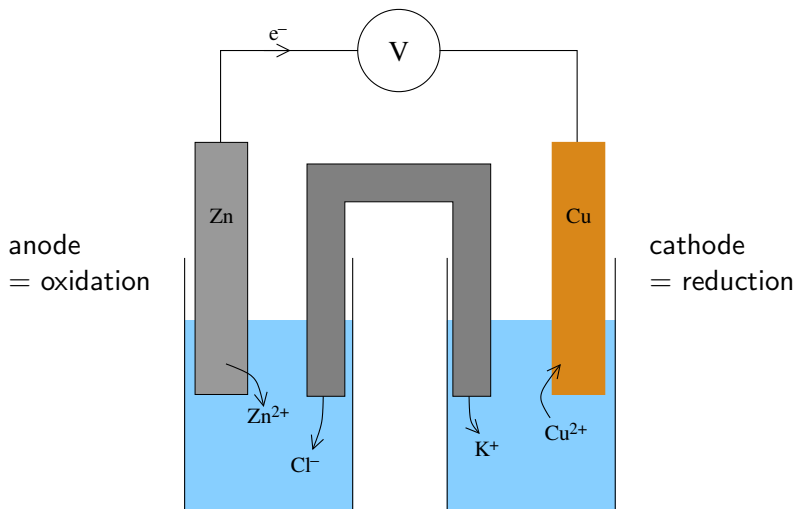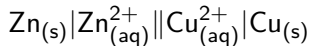
Key requirements for an electrochemical cell

- Spatial separation of half-reactions
- An external electrical circuit
- A means of maintaining electroneutrality

Cell diagrams

- There is an abbreviated notation to describe an electrochemical cell.
  Example:

$$Zn_{(s)}|Zn^{2+}_{(aq)}\|Cu^{2+}_{(aq)}|Cu_{(s)}$$

- A single bar represents direct contact between two phases.
- The double bar represents an indirect junction between two miscible phases (e.g. a salt bridge).
- When we know which is which, we put the anode on the left.

Reversible emf
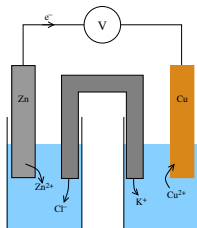
- Recall that reversibility of a process means that the system and surroundings are in equilibrium during the process.
- The voltage produced by the cell can be measured under reversible conditions by using a voltage source that opposes current flow.
- The externally applied voltage that just stops current flow is called the electromotive force or emf.

Some nearly synonymous words

- Voltage
- (Reversible) emf
- Electric potential difference

So why is G called the Gibbs free energy?

- We can show that ΔG is the non-pV reversible work in a process.

- If $w < 0$, work is done by the system. This could be used to, e.g., raise a weight.

- The maximum work that can be extracted from a system is $-w_{rev}$.

- This means that $-\Delta G$ is the maximum non-pV work that could be extracted from a process.

The Nernst equation

- For a chemical reaction, $\Delta_r G = w_{\text{rev,non-}pV}$
- Electrical work on a charge q moving through an electric potential difference (voltage) $\Delta\phi$:

$$w = q\Delta\phi$$

- If we measure the voltage under reversible conditions, $\Delta\phi$ is the emf E.

$$\Delta_r G = qE$$

- The charge carriers are electrons, so $q = -nF$, where n is the number of moles of electrons, and F is the charge of a mole of electrons, a quantity called Faraday's constant:

$$\Delta_r G = -nFE$$
$$F = eN_A = 96\,485.332\,123\,\text{C/mol}$$

$$\Delta_r G = -nFE$$

- It is generally more convenient to work in terms of the molar free energy $\Delta_r G_m$. To get this, divide both sides of the equation by the number of moles of a reactant or product involved in a particular reaction:

$$\Delta_r G_m = -\nu_e FE$$

where ν_e is the stoichiometric coefficient of the electrons in the overall redox reaction.

- We can apply the above equation under any conditions. In particular, under standard conditions,

$$\Delta_r G_m^\circ = -\nu_e FE^\circ$$

where E° is the emf under standard conditions.

$$\Delta_r G_m = -\nu_e FE \quad \text{and} \quad \Delta_r G_m^\circ = -\nu_e FE^\circ$$

- Since
$$\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q,$$

we get

$$
\begin{aligned}
-\nu_e FE &= -\nu_e FE^\circ + RT \ln Q, \\
\text{or} \quad E &= E^\circ - \frac{RT}{\nu_e F} \ln Q.
\end{aligned}
$$

The highlighted equation is known as the Nernst equation.

Some important relationships

$$K \xleftrightarrow{\Delta_r G_m^\circ = -RT \ln K} \Delta_r G_m^\circ \xleftrightarrow{\Delta_r G_m^\circ = -\nu_e F E^\circ} E^\circ$$

The emf is an intensive quantity

- Recall that free energy is an extensive quantity.

- In deriving the Nernst equation, we divided ΔG by n.

- This means that emf is an intensive property.

- The emf won't change if you multiply a reaction. Don't multiply the emf.

Thermodynamic feasibility and the emf

- $\Delta_r G_m < 0$ for a thermodynamically allowed reaction at constant temperature and pressure, and $\Delta_r G_m = -\nu_e F E$.
- We now have yet another way to decide if a reaction is thermodynamically allowed:

<div style="text-align:center; color:red;">

$E > 0$ for a thermodynamically allowed reaction at constant temperature and pressure.

</div>

- When we write a cell diagram, it is assumed that oxidation occurs at the electrode on the left.
  If this is wrong, the calculated emf will be negative, indicating that reduction occurs at the electrode on the left, or equivalently that the reaction occurs in the opposite direction to that implied by the diagram.
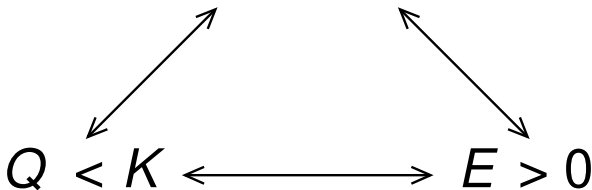
Criteria for thermodynamic feasibility

$$\Delta S_{\text{universe}} > 0$$

constant T, p

$$\Delta_r G < 0$$

$$Q < K \longleftrightarrow E > 0$$

Half cells

A half-cell consists of an electrode (possibly including a gas flowing over the electrode) and the necessary solution for one of the half-reactions in an electrochemical process.

Example: a zinc electrode bathing in a zinc nitrate solution

Half-cell potentials

- Suppose that we have three different half-cells, A, B and C.
- We measure the emfs of the following cells:

$$A\|B \quad B\|C \quad A\|C$$
$$E_{AB} \quad E_{BC} \quad E_{AC}$$

- Experimentally, we find the following:

$$E_{AB} + E_{BC} = E_{AC}$$

- This can be explained if each cell emf can be calculated as the difference of half-cell potentials:

$$
\begin{aligned}
E_{AB} &= E_B - E_A \\
E_{BC} &= E_C - E_B \\
E_{AC} &= E_C - E_A
\end{aligned}
$$

- By convention, we use reduction potentials as our half-cell potentials.

- Since oxidation occurs at the anode and we use half-cell reduction potentials,

$$E_{\text{cell}} = E_{\text{cathode}} - E_{\text{anode}}$$

- Conceptually, it is often useful to think of this equation as an addition:

$$E_{\text{cell}} = E_{\text{cathode}}^{\text{red}} + E_{\text{anode}}^{\text{ox}}$$

 with

$$E_{\text{anode}}^{\text{ox}} = -E_{\text{anode}}^{\text{red}}$$

The negative sign is the result of reversing the reduction reaction to obtain the oxidation reaction that occurs at the anode.
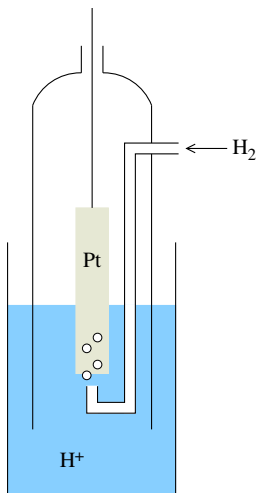
Standard reduction potentials

- Our tables will contain standard reduction potentials, i.e. reduction potentials under the usual thermodynamic standard conditions (unit activities of all reactants and products, etc.).
- Electric potential is a relative measurement, so there is no way to assign absolute values to the standard reduction potentials.
- We arbitrarily assign a standard reduction potential of zero to the half-reaction

$$H^+_{(aq)} + e^- \rightarrow \frac{1}{2}H_{2(g)}$$
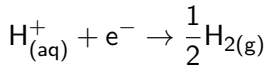
- This choice fixes all other reduction potentials, both under standard and nonstandard conditions.
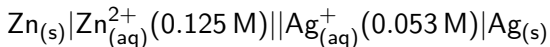
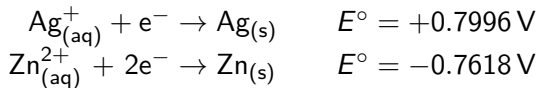# The (standard) hydrogen electrode

- We can use a hydrogen electrode to measure electrode potentials, then use the Nernst equation to calculate standard reduction potentials.
- We then build tables of standard reduction potentials.
- We can also use the hydrogen electrode to measure the reduction potentials of electrodes for some defined conditions in order to create reference electrodes that are easier to use than the hydrogen electrode.

Example: Calculating an emf with the Nernst equation
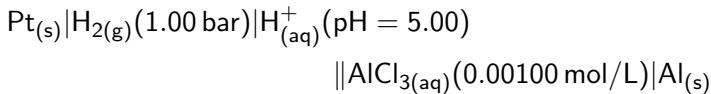
Calculate the emf generated by the following cell at $25\,^\circ$C:

$$Zn_{(s)}|Zn^{2+}_{(aq)}(0.125\,M)||Ag^{+}_{(aq)}(0.053\,M)|Ag_{(s)}$$

Data:

$$
\begin{aligned}
Ag^{+}_{(aq)} + e^{-} &\rightarrow Ag_{(s)} \qquad E^{\circ} = +0.7996\,V \\
Zn^{2+}_{(aq)} + 2e^{-} &\rightarrow Zn_{(s)} \qquad E^{\circ} = -0.7618\,V
\end{aligned}
$$

Answer: $1.5126\,V$

Example:
Obtaining the standard reduction potential of Al^{3+}

- The cell

$$Pt_{(s)}|H_{2(g)}(1.00\,bar)|H^+_{(aq)}(pH = 5.00)$$
$$\|AlCl_{3(aq)}(0.00100\,mol/L)|Al_{(s)}$$
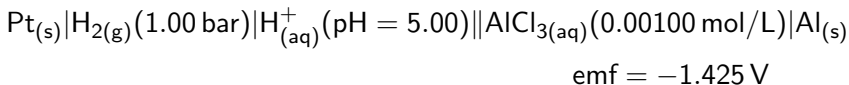
  has an emf of -1.425 V at $25°C$.

- We want to get the standard reduction potential of Al^{3+}, i.e. the standard half-cell potential for

$$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$$
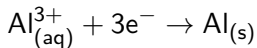
Example: standard reduction potential of Al^{3+}
(continued)

$$Pt_{(s)}|H_{2(g)}(1.00\,bar)|H^+_{(aq)}(pH = 5.00)\|AlCl_{3(aq)}(0.00100\,mol/L)|Al_{(s)}$$
$$emf = -1.425\,V$$

$$E = E^\circ - \frac{RT}{\nu_e F} \ln Q$$

Strategy:

- We know the cell emf, E in the Nernst equation.
- We first want to calculate the standard emf E° by rearranging the Nernst equation.
- Then we can relate E° to the standard reduction potentials of the two half cells, one of which is our unknown.

Example: Standard free energy of formation of $Al^{3+}_{(aq)}$

- Emf measurements are an important source of standard free energies of formation.
- In the last example, we found that $E^{\circ} = -1.662\,\text{V}$ and $\nu_e = 6$ for the reaction

$$3H_{2(g)} + 2Al^{3+}_{(aq)} \rightarrow 6H^{+}_{(aq)} + 2Al_{(s)}$$
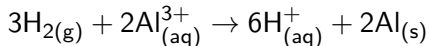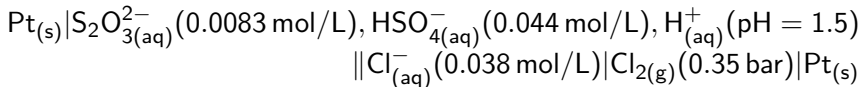
- Now we want to calculate the standard free energy of formation of the aluminium ion.

Answer: $-481.1\,\text{kJ/mol}$

Example: A thiosulfate/chlorine cell

- Consider the following cell:

$$Pt_{(s)}|S_2O_{3(aq)}^{2-}(0.0083 \, mol/L), HSO_{4(aq)}^{-}(0.044 \, mol/L), H_{(aq)}^{+}(pH = 1.5)$$
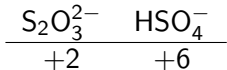$$\|Cl_{(aq)}^{-}(0.038 \, mol/L)|Cl_{2(g)}(0.35 \, bar)|Pt_{(s)}$$

- We want to know the emf generated by this cell.

  Problem: There are no appropriate half-reactions in our
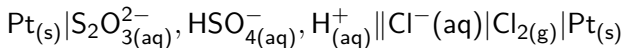 electrochemical table.

- We should start by balancing the reaction.
- We need to know which of the materials at the anode will be oxidized.
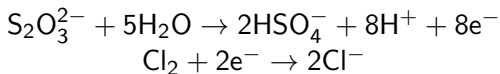 Oxidation state of S in chemical species at anode:

$$\frac{S_2O_3^{2-} \qquad HSO_4^-}{+2 \qquad\quad +6}$$
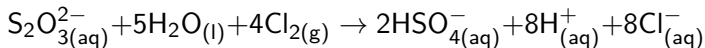
$\implies$ $S_2O_3^{2-}$ will be oxidized.

- Now balance those half reactions!

$$Pt_{(s)}|S_2O_{3(aq)}^{2-}, HSO_{4(aq)}^-, H_{(aq)}^+\|Cl^-(aq)|Cl_{2(g)}|Pt_{(s)}$$

Half-reactions:

$$S_2O_3^{2-} + 5H_2O \rightarrow 2HSO_4^- + 8H^+ + 8e^-$$
$$Cl_2 + 2e^- \rightarrow 2Cl^-$$

Overall reaction:

$$S_2O_{3(aq)}^{2-} + 5H_2O_{(l)} + 4Cl_{2(g)} \rightarrow 2HSO_{4(aq)}^- + 8H_{(aq)}^+ + 8Cl_{(aq)}^-$$

$$\nu_e = 8$$

Standard free energy change:

$$
\begin{aligned}
\Delta_r G_m^\circ &= 2\Delta_f G^\circ(HSO_4^-) + 8\Delta_f G^\circ(Cl^-) \\
&\quad - \left[\Delta_f G^\circ(S_2O_3^{2-}) + 5\Delta_f G^\circ(H_2O) \right] \\
&= 2(-755.7) + 8(-131.0) \\
&\quad - [-522.5 + 5(-237.1)] \text{ kJ/mol} \\
&= -851.4 \text{ kJ/mol}
\end{aligned}
$$

- We can now proceed in either of two ways:
  1. Calculate $\Delta_r G_m = \Delta_r G_m^\circ + RT \ln Q$, then use $E = -\Delta_r G_m/(\nu_e F)$.
  2. Calculate $E^\circ = -\Delta_r G_m^\circ/(\nu_e F)$, then use the Nernst equation to get E.
- Both ways will of course give the same answer. (Try it!)
- Answer: $E = 1.267\,\text{V}$