Electrochemistry

- Goal: Understand basic electrochemical reactions
- Concepts: Electrochemical Cell
  Half Cell Reactions
  Nernst Equation
  Pourbaix Diagrams
- Homework:
- Applications
  Battery potential calculation
  Fuel cell potential calculations
  Oxygen sensors

Application: Potato Battery

- Why is current generated?
  - Electrochemical reaction

  Can we calculate the voltage?
  - Yes, if we know the reactions

  What does it depend on?
  - Size of potato (no)
  - Placement of electrodes (no, if ideal)
  - Time (no until depletion)
  - Potato variety (no, only electrode material unless overpot. Δ)
  - Metals (yes)

  Which side will be positive, copper or aluminum?
  - Copper, it is the anode where reduction occurs (electron gain)

  Is this the potential that will be calculated from table values?
  - No, overpotential robs potential when current flows

Electrochemistry

- Electricity can be generated by burning a fuel, using the heat to run a heat engine, and using the heat engine to run a generator
- The efficiency of this process is limited by the second law of thermodynamics (33% is typical for a modern plant)
- Fuel cells (electrochemical cells) are not limited by the second law
- Efficiency can be much higher
- Note: Our book writes everything in terms of oxidation potentials, but the standard in metallurgy and electrochemistry is to write them as reduction potentials.
- Note: Cell voltage is an intensive property and does not vary with the size of the electrode or number of electrons transferred, only with the potential difference among metals

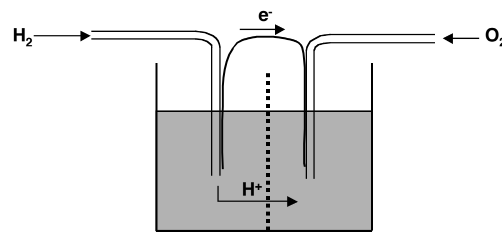
Electrochemical Cells

- Consider the reaction of H_2 and O_2 $$H_2 + \tfrac{1}{2}O_2 \Rightarrow H_2O$$
- During this reaction, electrons are transferred from hydrogen to oxygen
- As the reaction proceeds, hydrogen is oxidized producing free electrons $$H_2 \Rightarrow 2H^+ + 2e^-$$
- Oxygen is reduced, consuming the electrons $$\tfrac{1}{2}O_2 + 2e^- \Rightarrow O^{2-}$$
- More specifically, the reaction at the oxygen electrode is $$\tfrac{1}{2}O_2 + 2e^- + 2H^+ \Rightarrow H_2O$$

Electrochemical Cells

- If ions and electrons are transferred along separate paths, the spontaneous reaction can be used to generate current
- The potential generated by the oxidation of hydrogen is defined as 0 volts

$$H_2 \Rightarrow 2H^+ + 2e^- \quad 0V$$



- The potential due to the reduction of oxygen is 1.229 volts

$$O_2 + 2e^- \Rightarrow 2O^- \quad 1.229V$$

- The reaction can be operated in reverse. If 1.229 volts is applied to the cell, hydrogen and oxygen will be generated (electrolysis)

Nomenclature

- **Oxidation is an increase in the charge on an atom (electron loss)**
  Occurs at the anode of an electrochemical cell

$$Al^{o} \Rightarrow Al^{3+} + 3e^{-}$$
$$O^{2-} \Rightarrow O^{o} + 2e^{-}$$

- **Reduction is a decrease in the charge on an atom (electron gain)**
  Occurs at the cathode of an electrochemical cell

$$Al^{3+} + 3e^{-} \Rightarrow Al^{0}$$
$$O^{0} + 2e^{-} \Rightarrow O^{2-}$$

- **In a fuel cell, the hydrogen electrode is the anode**
  H_2 is supplied and H^+ and electrons are produced
- **In an electrolysis cell, the hydrogen electrode is the cathode**
  Electrons and H^+ ions are supplied, H_2 is produced

Cell Voltage

- From Chapter 5, $\Delta G = \Delta G° + RT \ln K_a$
- Equilibrium was a special case where $\Delta G = 0$ or $G_{products} = G_{reactants}$
- Using an applied potential, a non-equilibrium state can be stabilized

$$\begin{aligned}
&\Delta G = W_{rev} \\
&dW_{rev} = -(\text{quantity of charge})(\text{potential difference}) \\
&dW_{rev} = -dQ(E) \\
&Q = ne = (\text{number of electrons})(\text{charge per electron}) \\
&Q = zN_A e = zF \\
&\Delta G = W_{rev} = -EzF
\end{aligned}$$

- F is the Faraday constant, 96,400 coulomb/mole
  z is the number of electrons transferred
  E is the cell voltage
- At standard state, $\Delta G° = -E°zF$
- Cell voltage is an intensive property, does not vary with size of the system or the number of electrons transferred

Cell Voltage Example

- Calculate the standard potential of the hydrogen-oxygen fuel cell at 298 K
- ΔG° = -237,191 J/mole at 298 K
- Half cell reactions so z = 2

$$H_2 \Rightarrow 2H^+ + 2e^-$$

$$\tfrac{1}{2}O_2 + 2e^- + 2H^+ \Rightarrow H_2O$$

$$\Delta G^\circ = -E^\circ zF$$
$$-237{,}191\ \mathrm{J/mole} = -E^\circ(2)(96{,}400\ \mathrm{Coulomb/mole})$$
$$E^\circ = 1.229\ \mathrm{J/coulomb}$$
$$E^\circ = 1.229\mathrm{V}$$

- From Coulomb's law, 1J/C = 1 V. Has to do with force between charged particles and charge separation

Direction of Reaction

- If E is greater than zero, then $\Delta G°$ is less than zero
  The reaction is spontaneous and will proceed forward
  If connected to a circuit, current can be generated
- If E is less than zero, then $\Delta G°$ is greater than zero
  The reaction won't proceed spontaneously
- Applied potential greater than the magnitude and opposite in direction can drive the reverse reaction (charge battery)

Half Cell Reactions

- Used to determine the potential of a process
- Potato battery example
  Copper electrode $Cu \Rightarrow Cu^{2+} + 2e^{-} \qquad E° = -0.337V$
  Aluminum Electrode $Al° \Rightarrow Al^{3+} + 3e^{-} \qquad E° = 1.66V$
- To generate current, find spontaneous direction, calculate potential
  remember, cell voltage is an intensive property
- In the potato battery, the reactions will proceed in the spontaneous direction. For the overall reaction to balance (stoichiometry and charge), the spontaneous direction is:

$$3Cu^{2+} + 2Al \Rightarrow 3Cu + 2Al^{3+} \qquad E° = 2.003V$$

Nernst Equation

- **For a chemical reaction:** $\mathbf{bB + cC \Rightarrow dD + eE}$
- **We stated that at equilibrium:** $\Delta G^\circ = -RT\ln K_a$
- **If we are not at equilibrium:** $\Delta G = \Delta G^\circ + RT\ln J_a$

$$\text{where } J_a = \frac{(a_C)^c (a_D)^d}{(a_A)^a (a_B)^b}$$

- **If we substitute $\Delta G° = -E°zF$ and $\Delta G = -EzF$, we get**

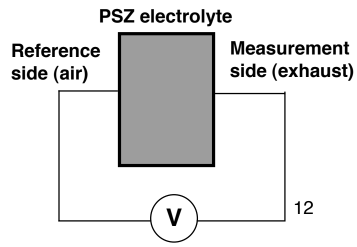
$$-EzF = -E^\circ zF + RT\ln J_a$$

$$E = E^\circ - \frac{RT}{zF}\ln J_a$$

At 298 K $$E = E^\circ - \frac{0.02570}{z}\ln J_a$$

Oxygen Pressure Determination

- How does a zirconia sensor measure the oxygen content in exhaust?
  pp. 1131-1140 in BOB
- Ion conductor that separates gases with different oxygen activities!
- Assumptions
  Steady state operation at equilibrium ($\Delta G° = 0$)
  Oxygen diffusion through cell does not affect a_{O2} in cell
  Typical operation temperature 250°C, pO_2 air = 0.2 atm
- Which side will have higher potential?



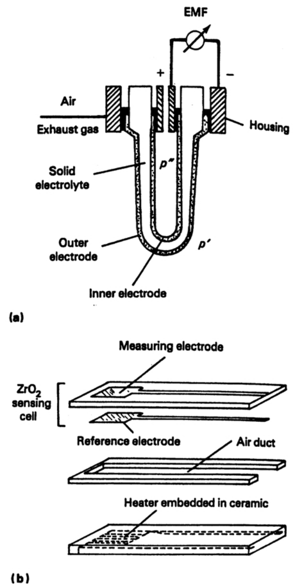


Fig 1 Examples of potentiometric sensors. (a) Automobile sensor. (b) Heated thin-film sensor. Partial oxygen pressures at the sensing and reference electrodes are shown as p' and p'', respectively. Source: Ref 48, 49