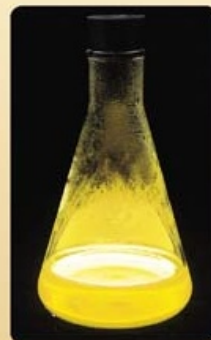Reduction of an ion containing vanadium(V) with zinc metal

The yellow color of the VO2+ ion in acid solution.

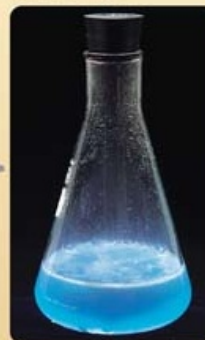Zn added. With time the yellow VO2+ ion is reduced to blue VO2+ ion.

With time the blue VO2+ ion is further reduced to green V3+ ion.

Finally, green V3+ ion is reduced to violet V2+ ion.

Add Zn

VO2+   VO2+   V3+   V2+
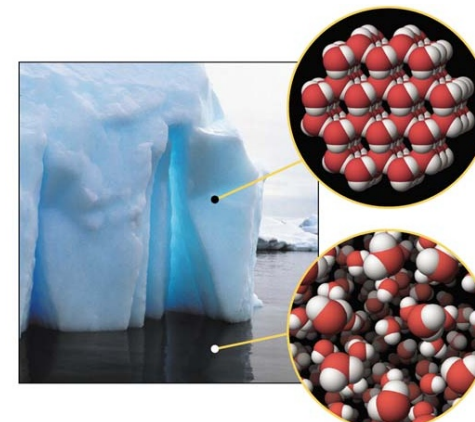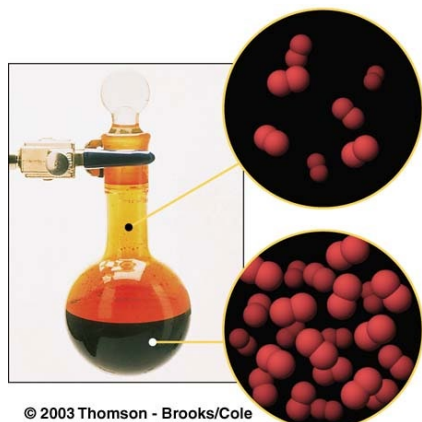
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CHEMISTRY 2000

Topic #2: Thermochemistry and Electrochemistry –
What Makes Reactions Go?
Fall 2020
Dr. Susan Findlay
See Exercises 9.3 to 9.5

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Electrochemical Cells

- An electrochemical cell consists of:
  - Two physically separated half-cells (one for each half-reaction),
  - An external circuit via which electrons generated by the oxidation half-cell can travel to the reduction half-cell,
  - A salt bridge (or equivalent) to allow ions to move between the two half-cells so that charge doesn't build up in them. (That would stop the flow of electrons, rendering the cell useless.)
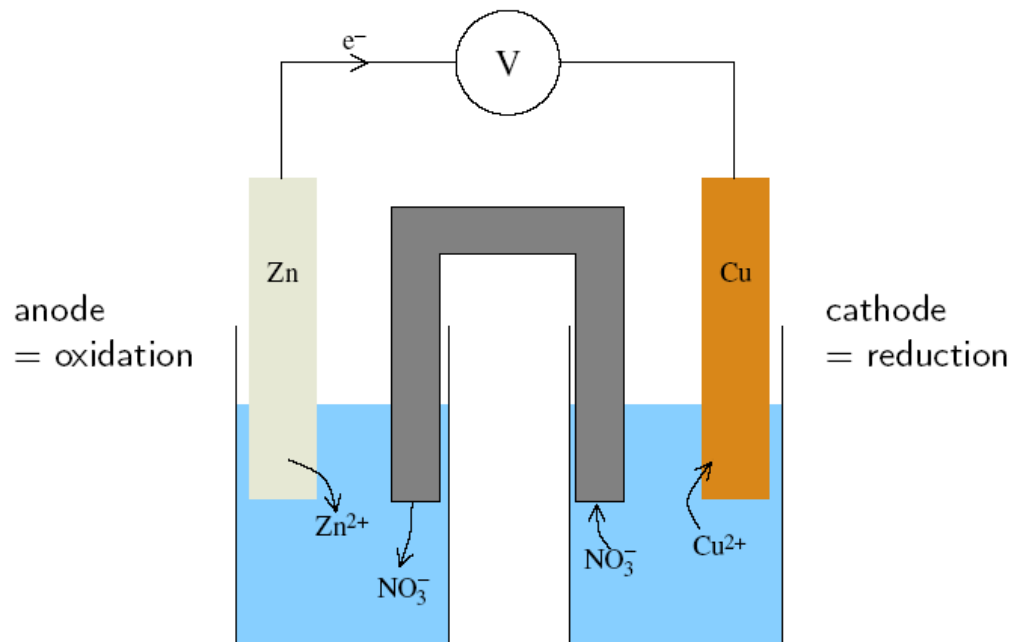
Electrochemical Cells

- So that we don't have to draw a picture every time we want to describe an electrochemical cell, there is a standard notation:
  - With the anode (where electrons are generated) at the left, we describe the relationships between each phase in the cell.
  - A single bar represents two phases in direct contact.
    e.g. an electrode immersed in a solution
  - A double bar represents two phases indirectly connected.
    e.g. two solutions connected by a salt bridge.

anode
= oxidation

cathode
= reduction
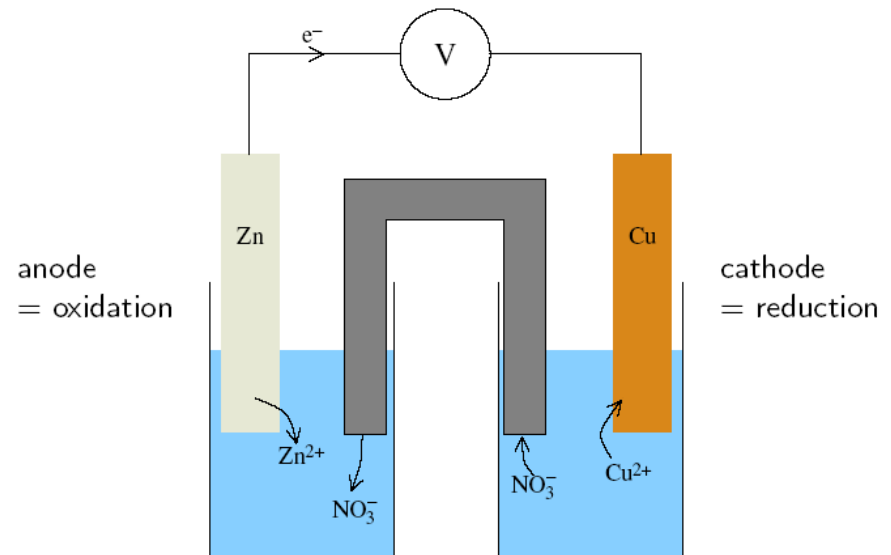
Cell Potential and Gibbs Free Energy

- If the overall reaction in an electrochemical cell is spontaneous, energy is released. This energy is measured in relation to the number of electrons involved in the reaction, giving a **potential**. When 1 Joule of energy is released by an electrochemical reaction involving electrons with 1 Coulombe of charge, the potential is 1 Volt:

$$1 \text{ V} = 1 \frac{\text{J}}{\text{C}} \qquad \text{where 1 electron has a charge of } -1.602176 \times 10^{-19} \text{ C}$$

- A cell's potential can be measured by applying an external voltage opposing the current flow. When the external voltage has exactly the right energy to stop the reaction but not reverse it (i.e. to make the system be at equilibrium), that external voltage is termed the **electromotive force (emf)**. Since the electromotive force must be exactly equal to the potential produced by the cell, the following terms are often used interchangeably:
  - Voltage (or potential)
  - Electromotive force (or emf)
  - Electric potential difference

Cell Potential and Gibbs Free Energy

- Changes to internal energy occur via heat and work (the first law of thermodynamics).

- The reaction in an electrochemical cell is a reversible process, so both the heat and work are reversible.

- As long as the electrochemical cell is operating at constant pressure and temperature, the heat will be equal to the enthalpy change.

- The work can be divided into two components: pressure-volume work (e.g. expansion of a balloon or pressure moving a piston) and non-pressure volume work (in this case, the work done on the electrons as they travel through a potential difference).

Cell Potential and Gibbs Free Energy

- It works out that the non-pressure-volume work for an electrochemical cell is equal to a familiar set of terms:

$$w_{rev,non-PV} = \Delta_r H - T\Delta_r S$$

- This should suggest that the work done on electrons in an electrochemical cell is directly related to the free energy change for the reaction!

- The maximum work that can be done <u>on the system</u> is $\Delta_r G$. Since $\Delta_r G < 0$ for a spontaneous reaction, a spontaneous reaction can do work <u>on the surroundings</u>.

- The maximum amount of non-PV work that can be done <u>on the surroundings</u> is therefore equal to $-\Delta_r G$!

Cell Potential and Gibbs Free Energy

- So, the free energy change is equal to the work done on the electrons (charge = q) as they travel through a potential difference (cell potential = E):

$$w_{rev,non-PV} = \Delta_r G = q \cdot E$$

- The charge of the electrons will be negative with a magnitude equal to the # moles of electrons (n) multiplied by the charge of 1 mole of electrons (F = Faraday's constant = 96485 C/mol):

Cell Potential and Gibbs Free Energy

- Usually, we work in terms of **molar free energy change.** When we divide both sides of the equation by moles of a product (or reactant), n is converted to the stoichiometric coefficient of the electrons in the overall redox reaction (ν_e):

For a spontaneous reaction, $\Delta_r G < 0$ therefore $E > 0$!!!

The Nernst Equation

- This equation can, of course, be used under standard conditions (among others), so we can say:
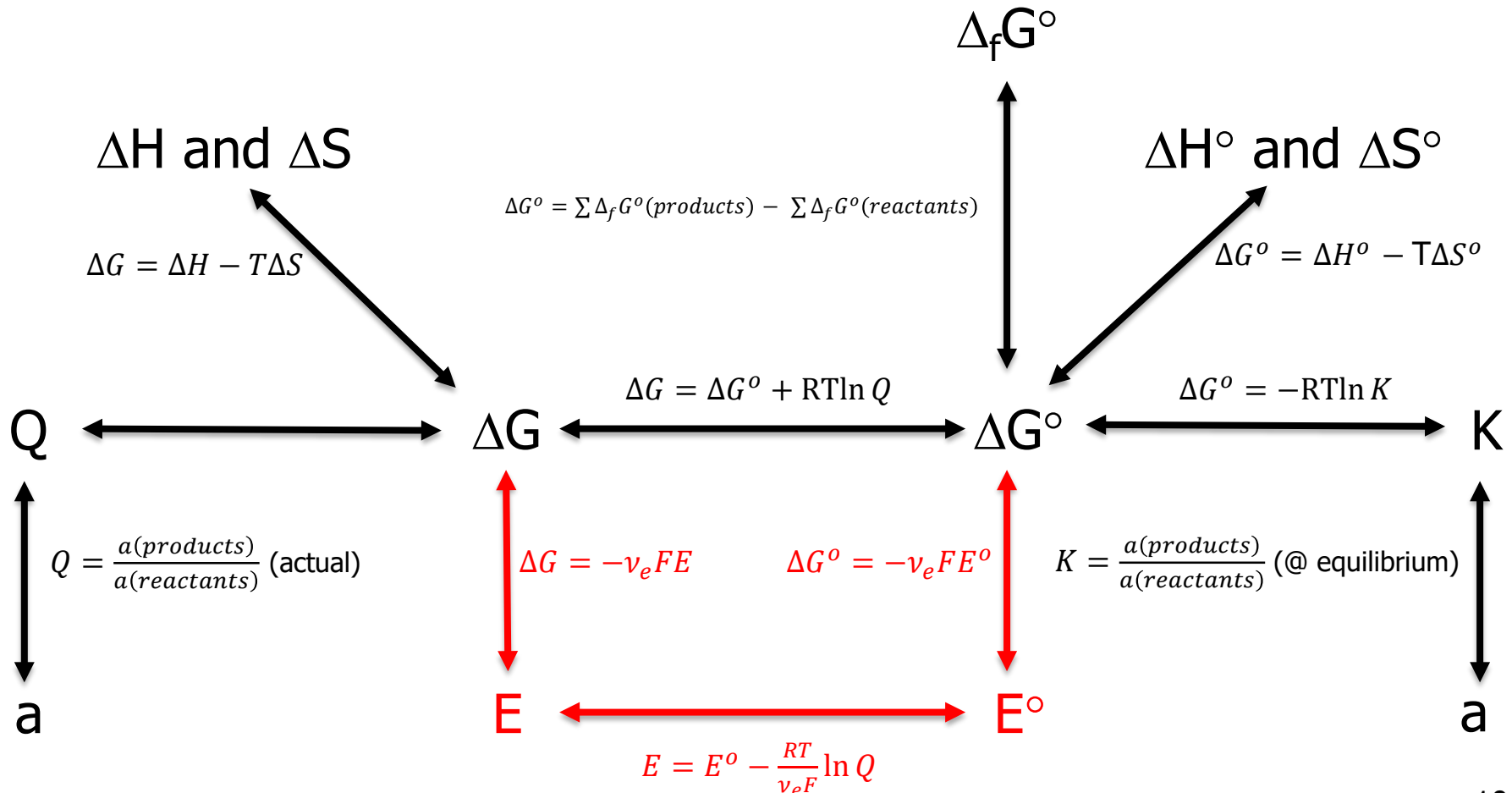
  and

- Recall that:

$$\Delta_r G = \Delta_r G° + RT \ln Q$$

- Rearrangement gives us the **Nernst equation**:

$$E = E° - \frac{RT}{v_e F} \ln Q$$

Back to the Equation Map…

- Now we have even more equations and terms to add to our equation map:

$$\Delta_f G^\circ$$

$$\Delta H \text{ and } \Delta S$$

$$\Delta G^o = \sum \Delta_f G^o(products) - \sum \Delta_f G^o(reactants)$$

$$\Delta H^\circ \text{ and } \Delta S^\circ$$

$$\Delta G = \Delta H - T\Delta S$$

$$\Delta G^o = \Delta H^o - T\Delta S^o$$

$$\Delta G = \Delta G^o + RT\ln Q$$

$$\Delta G^o = -RT\ln K$$

$$Q \longleftrightarrow \Delta G \longleftrightarrow \Delta G^\circ \longleftrightarrow K$$

$$Q = \frac{a(products)}{a(reactants)} \text{ (actual)}$$

$$\Delta G = -\nu_e FE$$

$$\Delta G^o = -\nu_e FE^o$$

$$K = \frac{a(products)}{a(reactants)} \text{ (@ equilibrium)}$$

$$a \qquad E \longleftrightarrow E^\circ \qquad a$$

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

Half-cells and Standard Reduction Potentials

- It's impossible to directly measure the potential for a half-cell since there would be no current and therefore no voltage. Instead, cell potential is measured against an arbitrary zero reference point, the **standard hydrogen electrode (SHE)**.

- In the SHE, hydrogen gas is bubbled over a platinum electrode in the presence of $1 \text{ M } H^+_{(aq)}$.

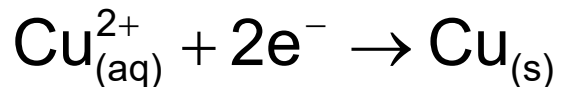- By definition, it has a standard reduction potential of zero:

$$2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad\qquad E° = 0 \, V$$
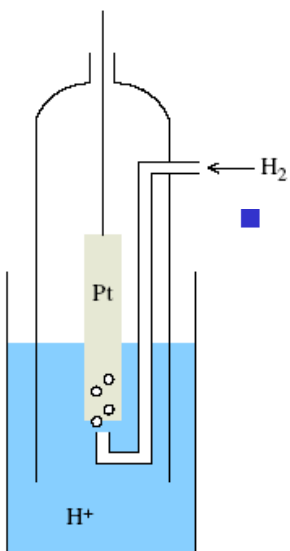
- As it does for ΔH, ΔS, and ΔG, reversing the reaction reverses the sign of $E°$, so we can also say that:
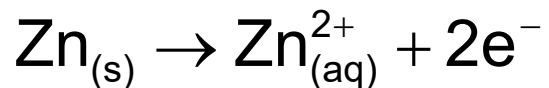
$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \qquad\qquad E° = 0 \, V$$
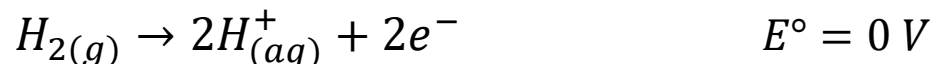
Half-cells and Standard Reduction Potentials

- Like enthalpies, entropies and free energies, cell potentials are additive:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E^o_{Cu^{2+}/Cu} = +0.340V$$

$$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- \qquad E^o_{Zn/Zn^{2+}} = +0.763V$$
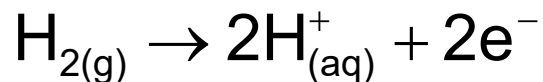
Half-cells and Standard Reduction Potentials

- As such, when a cell is constructed under standard conditions with a standard hydrogen electrode as the anode, the measured cell potential will be equal to the standard reduction potential for the other half-cell.
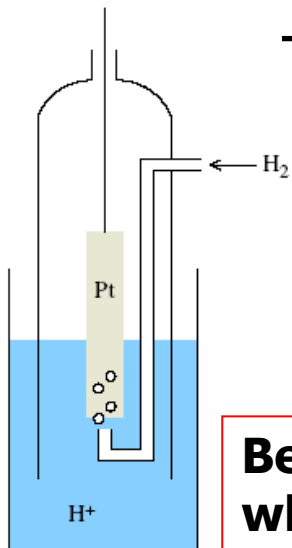
$$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)} \qquad E^o_{Ag^+/Ag} =$$

$$H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \qquad E^o_{H_2/H^+} = 0V$$

$$\overline{\phantom{H_{2(g)} \rightarrow 2H^+_{(aq)} + 2e^- \qquad E^o_{H_2/H^+} = 0V}}$$

$$E^\circ = +0.800V$$

Because E° is measured in J/C, it <u>DOES NOT CHANGE</u> when the reaction equation is multiplied by a coefficient!

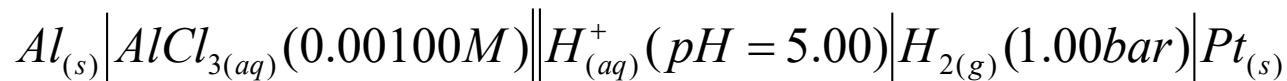# Electrochemical Cells Under Nonstandard Conditions

- A hydrogen electrode (standard or nonstandard) can also be used to measure reduction potentials of half-cells under nonstandard conditions.

- To do this, it's necessary to know the exact activities of each species in order to determine Q and use the Nernst equation:
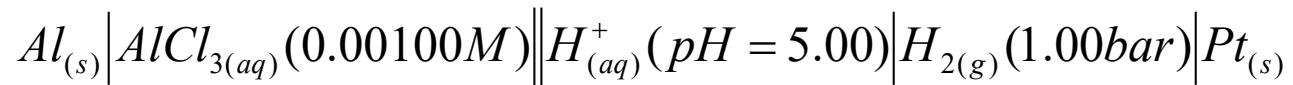
$$E = E° - \frac{RT}{v_e F} \ln Q$$

Electrochemical Cells Under Nonstandard Conditions

- The cell below has a potential of $+1.425\ V$ at 25 °C.

$$Al_{(s)}\left|AlCl_{3(aq)}(0.00100M)\right\|H^+_{(aq)}(pH=5.00)\left|H_{2(g)}(1.00bar)\right|Pt_{(s)}$$
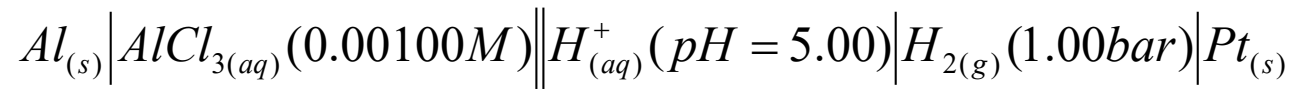
Write balanced equations for each half-cell and an overall chemical equation.

Electrochemical Cells Under Nonstandard Conditions

- Knowing that $E = +1.425\ V$, calculate $E°$ for this cell.

$$Al_{(s)} \left| AlCl_{3(aq)}(0.00100M) \right\| H^+_{(aq)}(pH = 5.00) \left| H_{2(g)}(1.00bar) \right| Pt_{(s)}$$
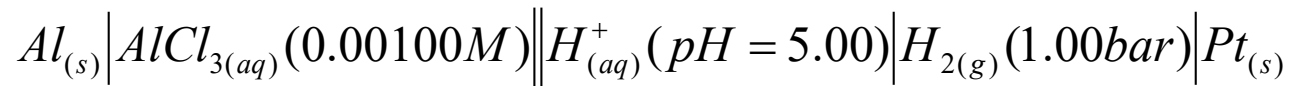
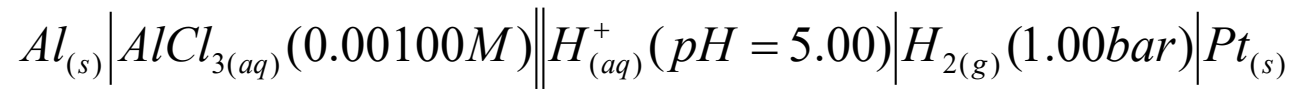# Electrochemical Cells Under Nonstandard Conditions
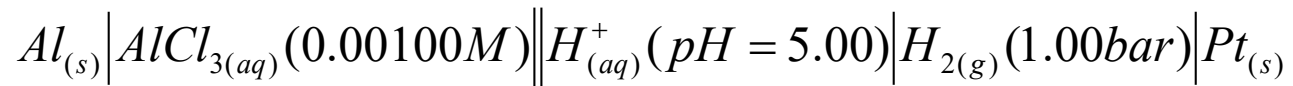
Electrochemical Cells Under Nonstandard Conditions

- Use $E°$ for the cell to determine the standard reduction potential of the Al/Al^{3+} half-cell.

Electrochemical Cells Under Nonstandard Conditions

- Finally, the standard potential for an electrochemical cell can be used to determine the standard free energy of formation for one of the reactants or products. This is a convenient method to measure $\Delta_f G^\circ$ for new compounds or ions.

- Use the information from the previous example to calculate $\Delta_f G^\circ$ for $Al^{3+}_{(aq)}$.

$$Al_{(s)} \left| AlCl_{3(aq)}(0.00100M) \right\| H^+_{(aq)}(pH = 5.00) \left| H_{2(g)}(1.00bar) \right| Pt_{(s)}$$
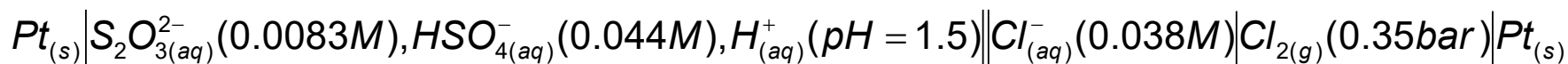
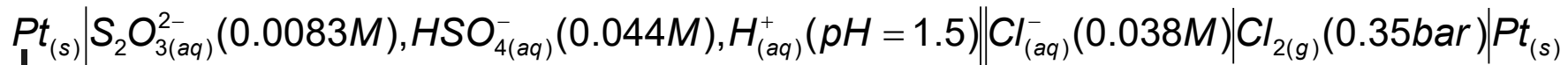# Electrochemical Cells Under Nonstandard Conditions

Electrochemical Cells Under Nonstandard Conditions

- If we can use cell potentials to determine free energies then, logically, we can use free energies to determine cell potentials.

- Let's say we wish to know whether the reaction described by the cell below is spontaneous and, if so, what is its potential.

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

- The standard reduction potential for the $Cl_{2(g)}/Cl_{(aq)}^-$ half-cell can be found in most tables of standard reduction potentials, but the standard reduction potential for the $S_2O_3^{2-}/HSO_{4(aq)}^-$ half-cell won't be listed. We can, however, look up standard free energies of formation for each species in the reaction…

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

Electrochemical Cells Under Nonstandard Conditions

- Start by writing balanced half-reactions and a balanced overall reaction:
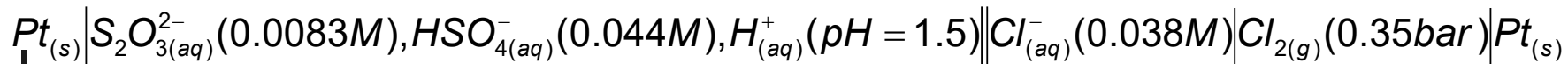
Electrochemical Cells Under Nonstandard Conditions
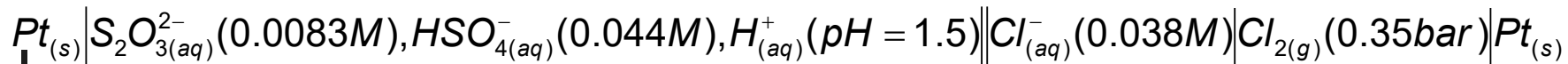
- Then calculate $\Delta_r G°$ for the overall reaction.

$$\Delta_f G°(S_2O_{3(aq)}^{2-}) = -522.5\frac{kJ}{mol}$$

$$\Delta_f G°(H_2O_{(l)}) = -237.1\frac{kJ}{mol}$$

$$\Delta_f G°(HSO_{4(aq)}^-) = -755.7\frac{kJ}{mol}$$

$$\Delta_f G°(Cl_{(aq)}^-) = -131.2\frac{kJ}{mol}$$

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

Electrochemical Cells Under Nonstandard Conditions

- At this point, there are two equally valid paths from $\Delta_r G°$ to E:
  - Calculate $E°$ from $\Delta_r G°$ then use the Nernst equation to find E.
  - Calculate $\Delta_r G$ from $\Delta_r G°$ then use $\Delta_r G = -\nu_e FE$ to find E.

  Either way, the answer is the same and, either way, you need to **find Q** to get from standard conditions to actual conditions…
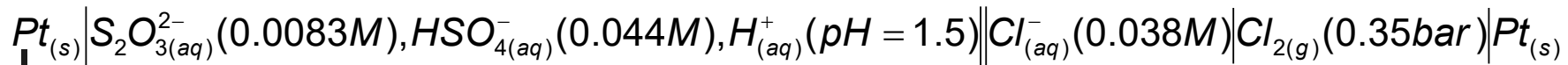
Electrochemical Cells Under Nonstandard Conditions

- Finally, calculate E. Is this reaction spontaneous at $25\ °C$?

Using Electrochemistry to Measure K_{sp} Values

- K_{sp} are equilibrium constants for dissolving ionic solids in water:

- K_{sp} values for relatively insoluble solids are tiny!

  - Iron(III) hydroxide has a K_{sp} of 4×10^{-38}.

  - At pH 7, you could only dissolve 4 fg ($4 \times 10^{-15} g$) of $Fe(OH)3$ in 1 L of water.

To analyze a solution this dilute, you can't just titrate it!

Using Electrochemistry to Measure K_{sp} Values

- Electrochemistry to the rescue! If we can set up an electrochemical cell such that the two half reactions add up to the desired reaction equation, we can:

  - Measure cell potential

  - Use cell potential to find standard cell potential

  - Use standard cell potential to find standard free energy change

  - Use standard free energy change to find equilibrium constant

- Let's say that we can't find the K_{sp} value for silver(I) iodide:

We can obtain this net reaction using a Ag/Ag^+ anode and a AgI cathode:

$$Ag_{(s)} \rightarrow Ag^+_{(aq)} + e^- \qquad\qquad E° = -0.7991\,V$$

$$AgI_{(s)} + e^- \rightarrow Ag_{(s)} + I^-_{(aq)} \qquad\qquad E° = -0.1518\,V$$

The value for the electron coefficient (v_e) is _____ and the standard cell potential ($E°$) is _____.

Most tabulated half-cell potentials are for reduction half reactions. The standard reduction potential for Ag^+ is +0.7991 V. To find the standard potential for the <u>reverse reaction</u> (oxidation of Ag to Ag^+), <u>reverse the sign</u>.

# Using Electrochemistry to Measure K_{sp} Values

- This allows calculation of the K_{sp} for AgI at 25 ℃.

Batteries

- Electrochemical cells produce a voltage, so they can be used to power electrical devices. The voltage produced depends on:
    - Standard cell potential (due to half-cells)
    - Concentrations of reactants and products (Q in Nernst equation)
    - Temperature (T in Nernst equation)

  The voltage **<u>does not</u>** depend on the size of the cell – that just determines the quantity of available reactants (i.e. how long the cell can run before the concentration of reactants is too low for the reaction to be spontaneous).

- Typical cell potentials are ~1V. If we want/need a larger potential, we must connect multiple cells in series, producing a **battery**:

$$\boxed{- \qquad +} \ \boxed{- \qquad +} \ \boxed{- \qquad +} \ \boxed{- \qquad +}$$
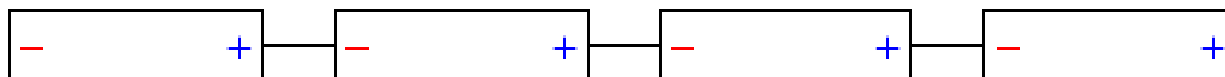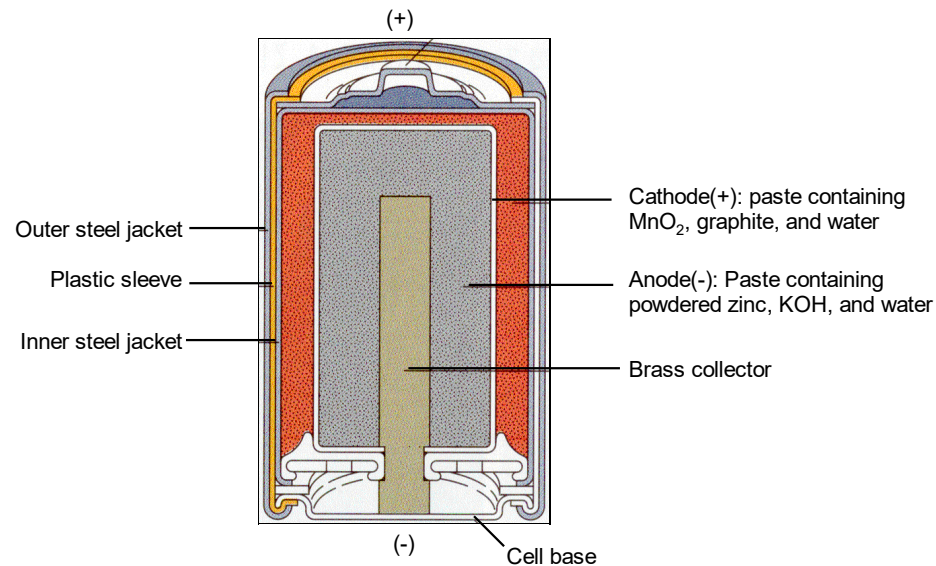
Batteries

- In theory, any battery can be recharged – just apply an external potential to force the reverse reaction to occur, "pushing the electrons backwards".

- In practice, this isn't always easy (or safe!)
    - In some batteries, the electrodes can be damaged during discharge
    - In some batteries, the electrodes get coated with resistive products which cause heating when current is passed through them.
    - In some batteries, the desired "reverse reaction" is not the one that occurs when recharging is attempted – generally because there is something else that is more easily oxidized or reduced. A common example is the electrolysis of water – used to make pastes in many batteries.

- A reliable battery is a good battery. Many batteries contain a paste so that the solutes are always saturated in the small amount of water available. This keeps the solute concentration constant – thereby keeping Q and E constant.
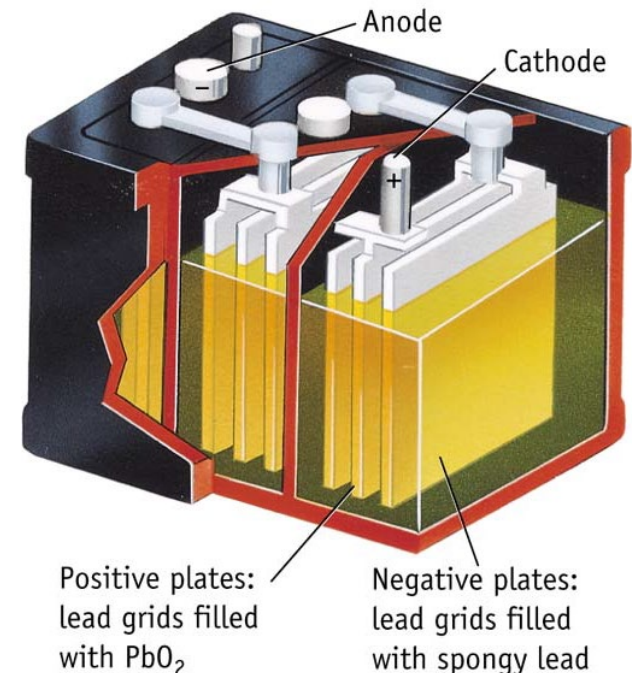
Alkaline Batteries

- An alkaline battery has a zinc anode and a manganese(IV) oxide cathode. As the name implies, it operates at high pH:

(+)

Outer steel jacket

Plastic sleeve

Inner steel jacket

Cathode(+): paste containing MnO_2, graphite, and water

Anode(-): Paste containing powdered zinc, KOH, and water

Brass collector

(-)   Cell base

Because there are no solutes in the overall reaction equation, $Q \approx 1$ and $E \approx E^\circ$, giving a constant voltage.

Lead-Acid Batteries

- An lead-acid battery has a lead anode and a lead(IV) oxide cathode. As the name implies, it operates at low pH:

Anode

Cathode

Positive plates: lead grids filled with PbO_2

Negative plates: lead grids filled with spongy lead

The cell potential is ~2 V. To get a 12 V car battery, six cells are connected in series.

Fuel Cells

- We know that burning a fuel releases energy as heat. This energy is more efficiently harnessed if it is produced by oxidizing the fuel electrochemically – as in a fuel cell. It also causes less pollution!
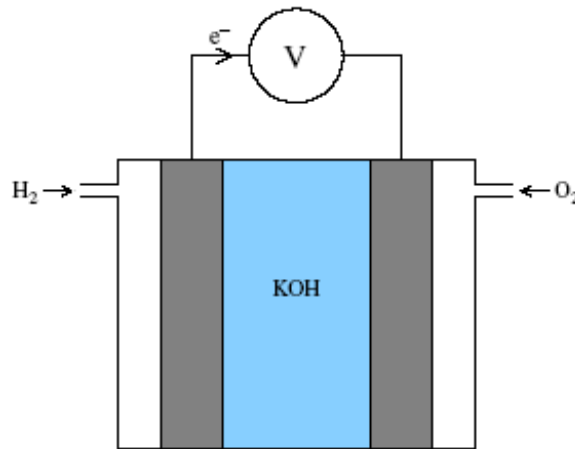
- A lot of research is currently being done to develop a practical hydrogen fuel cell – which would be a very environmentally friendly power source as the only waste product would be water:

Fuel Cells

- Since fuel cells always involved oxidation of a fuel (hydrogen, methane, methanol, etc.), the reaction at the cathode is always the same: reduction of oxygen to either water or hydroxide:

- What is the reaction at the anode in a hydrogen fuel cell? *Assume basic conditions.*

- The major difference between a battery and a fuel cell is that the reactions in a fuel cell cannot be reversed, so it cannot be recharged. Instead, the fuel must be replenished.