Chapter 17 Electrochemistry

Tesla Motors

85 kWh battery rated to deliver 320 miles (265 by EPA)
Contains 7,104 lithium-ion battery cells in 16 modules wired in series.



Chemistry: OpenStax

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Electrochemistry

- Electrochemistry is the study of batteries and the conversion between chemical and electrical energy.
- Based on redox (oxidation-reduction) reactions in which one substance gains electrons and another loses electrons.
 - These two processes MUST happen together.
- Single replacement, combustion, combination and decomposition rxns are all examples of redox reactions.

Oxidation Numbers

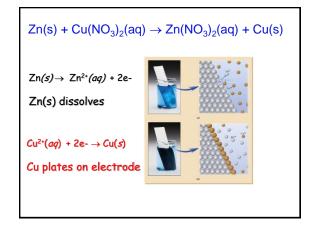
- Free elements: ox # = 0 (H₂(g), Hg(l), etc.)
- lons in binary ionic compounds: ox # = charge.
 Ex. For Al₂S₃, ox # for Al = +3, ox # for S = -2.
- H: ox # = +1, except when H is with alkali metals it is -1 (LiH, NaH, etc.)
- O: ox # = -2, except in peroxides it is -1 (H_2O_2 , K_2O_2)
- The sum of the oxidation numbers of all the atoms in a molecule = 0
- For polyatomic ions, the sum of the oxidation numbers must equal the charge on the ion.

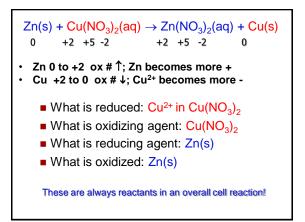
Ox # examples

- Find ox numbers for all the atoms in HCO₃⁻
 - H: ox # = +1 O: ox # = -2
- 1×H + 1×C + 3×O = -1
- + 1 + C + 3x(-2) = -1
 - Ox # for C = +4
- What is the ox # for Cr in Cr₂O₇²⁻?
 - 2Cr + 7O = -2
 - 2Cr + 7(-2) = -2
 - Cr = +6

Redox: LEO the lion goes GER

- Oxidation: loss of electrons; ox # ↑, more +
- **Reduction**: gain of electrons; ox $\# \downarrow$, more –
- oxidizing agent: substance that is reduced; it caused oxidization of other substace.
- reducing agent: substance that is oxidized; it caused reduction of other substance.
- $Zn(s) + Cu(NO_3)_2(aq) \rightarrow Zn(NO_3)_2(aq) + Cu(s)$
- Identify atom oxidized, atom reduced, oxidizing agent and reducing agent.





Redox Reactions

- What is oxidized/reduced, give the specific atom.
- Agents: give the whole substance as an answer.
- MnO₄⁻(aq) + 8H⁺(aq) + 5 Fe²⁺(aq) \rightarrow Mn²⁺(aq) + 5Fe³⁺(aq) + 4H₂O(I)
- For this reaction:
 - What is the ox # for Mn in MnO_4^- +7
 - What is oxidized? Fe²⁺
 - What is reduced? Mn in MnO₄-
 - What is the oxidizing agent? MnO₄
 - What is the reducing agent? Fe²⁺

Balancing Simple Redox Reactions

E.g. How do we balance the following reaction? $Cr^{3+}(aq) + Be(s) \rightarrow Cr(s) + Be^{2+}(aq)$

- 1) Break the redox rxn into two *half reactions*, the oxidation half reaction and reduction half reaction.
- 2) Balance charges by adding electrons (e-) to the more + side for each half reaction.
- Balance electrons by multiplying each half reaction by an integer so that the # electrons gained = # electrons lost.

Example Balancing Redox Rxn

E.g. $Cr^{3+}(aq) + Be(s) \rightarrow Cr(s) + Be^{2+}(aq)$

Write the Half reactions
 Oxidation: Be(s) →Be²⁺(aq) + 2e⁻ (e⁻ = product)
 Reduction: Cr³⁺(aq) + 3e⁻ → Cr(s) (e⁻ = reactant)
 Balance the electrons
 Oxidation: (Be(s) → Be²⁺(aq) + 2e⁻)x3
 Reduction: (Cr³⁺(aq) + 3e⁻ → Cr(s))x2

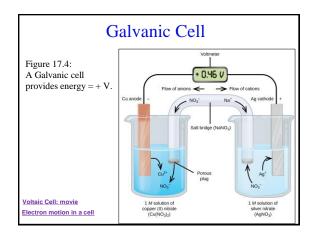
Add reactions and cancel common terms:

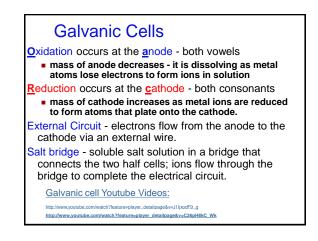
 $2Cr^{3+}(aq) + 3Be(s) \rightarrow 2Cr(s) + 3Be^{2+}(aq) \checkmark$

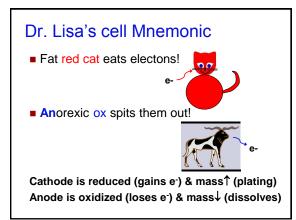
Types of Cells

- Galvanic cell (also called voltaic cell) Electrochemical cell in which a spontaneous reaction generates electricity. (Electric energy is produced.)
- Electrolytic cell

Electrochemical cell in which an electrical current is used to drive a nonspontaneous reaction. *(Electric energy is consumed.)*

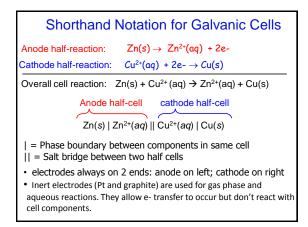






What happens in Salt Bridge?

- Migration of ions maintains charge neutrality in both compartments:
- Anions move into the anode where excess + charge builds up as metal cations are formed by oxidation.
- Cations move into the cathode where excess (-) charge builds up as the metal cations are reduced to form neutral metal atoms.



Electromotive Force

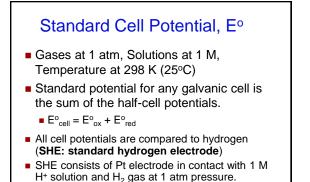
$emf = E_{cell} = cell voltage:$

Electromotive force is the cell potential measured in volts. This is the driving force that pushes electrons away from the anode and towards the cathode.

Joules = Coulombs x Volts

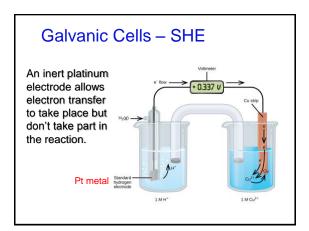
 E_{cell} is measured in volts: V = J/C

coulomb - the quantity of charge that passes a point in 1 sec when a current of 1 ampere flows.



 $E_{red}^{o} = 0 V$

■ $2H^+ + 2e^- \rightarrow H_2(g)^-$



Reduction Potentials

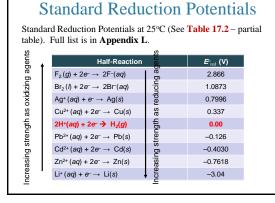
- We can use the table of Standard Reduction Potentials for reduction half reactions to determine the cell potential of a galvanic cell.
- Table 17.1: All potentials are listed as reduction potentials.
- Oxidation potentials: reverse the reaction

and
$$E_{or}^{\circ}(anode) = -E_{red}^{\circ}(cathode)$$

Calculating Cell potentials

 $E_{cell}^{\circ} = E_{red}^{\circ}(cathode) + E_{ox}^{\circ}(anode)$

- For the oxidation reaction at the anode, make sure you reverse the reaction and change the sign for E^o_{ox}, then add the reduction and oxidation potentials.
- E° is intensive; it does not depend on # of moles involved. Don't multiply E° by a factor if coefficients of reaction are changed.



Strength of Oxidizing Agents F₂(g) + 2e⁻ → 2F⁻(aq) E^o_{red} = 2.866 V F₂ has the most positive E^o_{red} value. F₂ is the easiest to reduce. (It wants e-the most!) Thus F₂ is strongest oxidizing agent. Active nonmetals are good oxidizing agents. (ox agent = reduced = gain e-) As E^o_{red}↑, strength ox agent ↑

Strength of Reducing Agents

- $Li^+(aq) + e^- \rightarrow Li(s)$ $E^\circ_{red} = -3.04 \text{ V}$
- Li has the most negative E^o_{red} value, so it is the easiest to oxidize.
- Li(s) is strongest reducing agent.
- Li(s) wants to lose electrons, so reverse reaction occurs:
- Li(s) \rightarrow Li⁺(aq) + e⁻ E^o_{ox} = +3.04 V
- Active metals are good reducing agents. (red agent = oxidation = lose e-).

Cell Potentials

Based on their E_{red}° values, determine the best oxidizing agent, best reducing agent, worst oxidizing agent, and worst reducing agent. <u>Half-reaction</u> E_{red}° $Co^{2+}(aq) + 2e^{-} \rightarrow Co(s) -0.28 \text{ V} (most + E_{red}^{\circ})$ $Mn^{2+}(aq) + 2e^{-} \rightarrow Mn(s) -1.18 \text{ V} (most - E_{red}^{\circ})$ $Cd^{2+}(aq) + 2e^{-} \rightarrow Cd(s) -0.40 \text{ V}$

Best/worst agents

For reduction half rxns, oxidizing agents are reactants and reducing agents are products.

- Co²⁺ is the easiest to reduce = best oxidizing agent (most + E^o_{red} value).
- Mn²⁺ is the hardest to reduce = worst oxidizing agent. (most - E^o_{red} value).
- Mn(s) is the easiest to oxidize = best reducing agent. (most + E^o_{ox} value).
- Co(s) is the hardest to oxidize = worst reducing agent. (most - E^o_{red} value).

Cell Potentials

- Positive E^o_{cell} means the reaction is productfavored and spontaneous.
 - A negative E^o_{cell} means the reaction won't happen in the forward direction.
- Therefore, we want two half reactions that yield the <u>most positive</u> E^o_{cell} value.
- Assign rxn with more + E^o_{red} as cathode!
- $\bullet E^{\circ}_{cell} = E^{\circ}_{red} + E^{\circ}_{ox}$

Galvanic Cell Potentials

If we were to make a Galvanic cell from the following metals, which would act as the anode and which as the cathode? Refer to the standard reduction potential table.

- Write the half-cell reactions and the overall balanced reaction for each cell.
- Calculate E^o_{cell} for the Fe(s) Ni(s) cell

Example: Fe(s) + Ni(s)

 $\begin{array}{l} {\sf Fe} \ ^{2+}(aq)+2e^{\cdot}\rightarrow {\sf Fe}(s) \ {\sf Eo}_{\rm red}=-0.44 \ {\sf V} \\ {\sf Ni}^{2+}(aq)+2e^{\cdot}\rightarrow {\sf Ni}(s) \ \ {\sf Eo}_{\rm red}=-0.25 \ {\sf V} \end{array}$

- Assign more + one (Ni) as cathode: Cathode: Ni²⁺(aq) + 2e⁻ → Ni(s) E^o_{red} = -0.25 V
- For anode: reverse reaction and change sign Anode: $Fe(s) \rightarrow Fe^{2+}(aq) + 2e^{-} E^{o}_{ox} = +0.44 V$ Overall: $Ni^{2+}(aq) + Fe(s) \rightarrow Ni(s) + Fe^{2+}(aq)$ $E^{o}_{cell} = -0.25 + 0.44 = 0.19 V$

Cell Potentials

Use these values for problem 5 on worksheet.

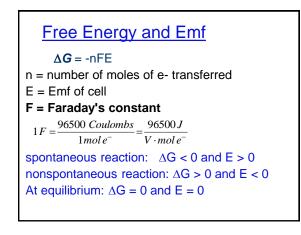
- $Au^{3+} + 3e^{-} \rightarrow Au(s)$
- $Br_2(I) + 2e^- \rightarrow 2Br^-(aq)$
- $Pb^{2+} + 2e^{-} \rightarrow Pb(s)$
- Ni²⁺ + 2e⁻ \rightarrow Ni(s)
- $E_{red}^{o} = 1.07 V$ $E_{red}^{o} = -0.13 V$

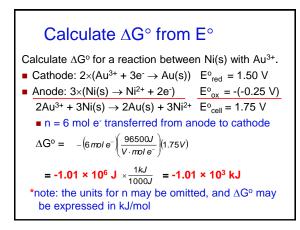
 $E_{red}^{o} = 1.50 V$

- $E_{red}^{o} = -0.25 V$

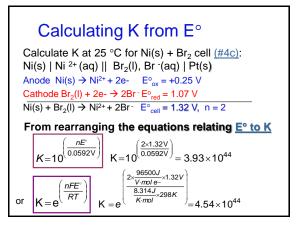
Cell Potentials in Reactions

5. b) What will E°_{cell} be if Pb²⁺ reacts with Br -? E^o_{red} Pt(s) = -0.13 V E^o_{ox} Br⁻(aq) = -1.07 V Sign changed for bromide since it is oxidized! E°_{cell} = -1.07 V + -0.13 V = -1.20 V c) Calculate Eocell for the following cell Ni(s) | Ni²⁺(aq) || Br₂(I), Br ⁻(aq) | Pt(s) Ni = oxbromine = red E^o_{cell} = 0.25 V + 1.07 V = <u>1.32 V</u> Reaction for part c is spontaneous (+ E)





Standard emf & K At equilibrium, E = 0 and Q = K (plug these) conditions into Nernst Equation) $0 = \mathbf{E}^{\circ} - \frac{\mathbf{RT}}{\mathbf{nF}} \mathbf{InK} \implies \mathbf{E}^{\circ} = \frac{\mathbf{RT}}{\mathbf{nF}} \mathbf{InK}$ $R = 8.314 \frac{J}{K \cdot mol}, F = 96500 \frac{J}{V \cdot mol e^{-1}}$ • At 298 K, $E^{\circ} = \frac{0.0592V}{n} \log K$



Cell Potentials Summary

- Positive E^o_{cell} value
 - Provides energy
 - △G° is negative
 - K is large
 - Reaction is product-favored
- Negative E^o_{cell} value
 - Consumes energy
 - <u>AG°</u> is positive
 - K is small
 - Reaction is reactant-favored

The Nernst Equation: Calculate emf for nonstandard conditions Recall: $\Delta G = \Delta G^{\circ} + RT \ln Q$ • Plugging in $\Delta G = - nFE$ and $\Delta G^{\circ} = - nFE^{\circ}$ $-nFE = -nFE^{\circ} + RT \ln Q$ Nernst Equation: $E = E^{\circ} - \frac{RT}{nF} \ln Q$ $E = E^{\circ} - \frac{2.303RT}{nF} \log Q$ $R = 8.314 \frac{J}{K \cdot mol}$, $F = 96500 \frac{J}{V \cdot mole^{-1}}$ At 298 K: $E = E^{\circ} - \frac{0.0592V}{n} \log Q$

Pb and Ag⁺ cell (worksheet)

#8. A galvanic cell utilizes the reaction: $2Ag^{+} + Pb(s) \rightarrow Pb^{2+} + 2Ag(s)$ a) Write the half reactions and calculate E^{o}_{cell} . b) Write the short-hand notation for this cell. a) Look up reduction potentials Cat: Ag^{+}(aq) + e^{-} \rightarrow Ag(s) E^{\circ}_{red} = 0.80 V An: Pb(s) \rightarrow Pb^{+2}(aq) + 2e^{-} E^{\circ}_{ox} = -(-0.13) V $E^{\circ}_{cell} = 0.80 V + 0.13 V = 0.93 V$ b) Pb(s)|Pb^{+2}(aq)||Ag^{+}(aq)|Ag(s)

Nernst Equation: Pb/Ag⁺ cell 8c) Calculate the cell potential if [Pb²⁺] = 0.88 M and

Both []'s & P's can be plugged into Q; V = volts (unit)

8c) Calculate the cell potential if $[Pb^{-+}] = 0.88$ M and $[Ag^+] = 0.14$ M. $2Ag^+(aq) + Pb(s) \rightarrow 2Ag(s) + Pb^{2+}(aq)$ $E^{\circ}_{cell} = 0.93$ V, n = 2 Q = (0.88 M) / (0.14 M)² = 44.9 E = E^o - (0.0592 V/n) log Q E = 0.93 V - (0.0592 V/2)×log 44.9 E = 0.93 V - (0.0296 V)(1.65) = 0.93 - 0.049 = 0.88 V E = 0.88 V (E↓ because Q > 1) Do Worksheet problem #9

Electrolysis

Electrolytic Cell: Electrical energy from an external source (outlet or a battery) is used to force a nonspontaneous redox reaction to proceed.

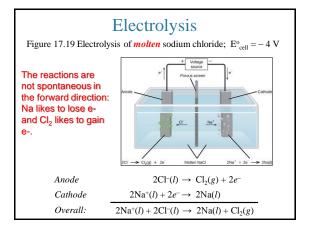
 Water doesn't naturally decompose into H₂ and O₂. A battery must supply energy to drive this reaction forward.

■
$$2H_2O(I) \rightarrow 2H_2(g) + O_2(g)$$
 $E_{cell} = -1.23 V$

Anode: $2H_2O(I) \rightarrow O_2(g) + 4H^+(aq) + 4e^-$

Cathode: $4H_2O(I) + 4e^- \rightarrow 2H_2(g) + 4OH^-(aq)$

• The electrodes are the still the same for electrolysis: (oxidation at anode, reduction at cathode).



Electrolysis Calcs

Used to find mass or volume of product produced by passing current through cell.

Current and time

Charge

Moles of e

Moles o

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se coefficients in le balanced equa find mole ratios

se molar mass or andard molar volum

a conversion fa

- Current: measured in Amps A = C/s
- **ampere:** unit of electric current; rate of flow of e-.
- charge = current x time
- coulombs = amps x seconds

Electrolysis Calculations How many grams of Cu can be collected in 1.00 hour by a current of 1.62 A from a CuSO₄ solution? • Reduction reaction: $Cu^{2+} + 2e^{-} \rightarrow Cu(s)$ Calculate coulombs: Current (C/s) x time (s) = C • C \rightarrow mol e \rightarrow mol solid \rightarrow g solid convert time to secs: 1 hr = 3600 secs $3600s \times \frac{1.62C}{s} \times \frac{1 \text{mol e}^-}{96,500C} \times \frac{1 \text{molCu}}{2 \text{mol e}^-} \times \frac{63.55g}{\text{mol}} = \textbf{1.92 g Cu}$

Batteries

- Batteries are examples of Galvanic cells we use in everyday life.
- For a Galvanic cell the voltage keeps dropping as the spontaneous reaction proceeds right.
- Battery is dead when E_{cell} = 0 (at equilibrium) the rxn no longer proceeds forward; this is minimum pt on free energy curve).
- Bigger batteries only last longer, they don't have more volts. Volts are determined by the chemical reaction that occurs.

