

Chapter 20

Electrochemistry

Chapter 20 suggested problems

10th Ed. - 20.x: 17, 19, 23, 31, 33, 37, 39, 49, 51, 59, 61, 91, 95, 109

11th Ed. - 20.x: 19, 21, 25, 33, 35, 39, 41, 51, 53, 61, 63, 93, 97, 111

interesting links:

Battery Chemistry Tutorial at <http://www.powerstream.com/BatteryFAQ.html>

Duracell Procell: Battery Chemistry at <http://www.duracell.com/procell/chemistries/default.asp>

Class Notes

I. Oxidation states: a review (see **Ch. 4 notes** for review)

A. Terms

1. Oxidation-reduction reaction (redox reaction): a reaction in which electrons are transferred between spp. and/or in which atoms involved in the reaction change oxidation number
2. Oxidation number: a concept devised as way of keeping track of electrons in reactions: the actual charge on a monatomic ion, or the *hypothetical charge* assigned to an *uncharged* atom using a set of rules
3. Oxidation (oxidized): the loss of one or more electrons
4. Reduction (reduced): the gain of one or more electrons
5. Oxidizing agent: a chemical that oxidizes something else and reduces itself
6. Reducing agent: a chemical that reduces something else and oxidizes itself

B. Rules for determining oxidation numbers

1. Rule 1: the oxidation number of atoms in their elemental state is zero
2. Rule 2: the oxidation number of a monatomic ion is equal to its charge
3. Rule 3: the oxidation number of oxygen is always equal to -2 unless in a

peroxide (then -1)

4. Rule 4: the oxidation number of hydrogen is always +1 unless in a hydride (then -1)
5. Rule 5: Fluorine always has an oxidation number of -1. The other halogens always have an oxidation of -1 as anions in binary compounds. Halogens listed as the first member of a binary molecular compound or involved in oxyanions have positive oxidation numbers.
6. Rule 6: for either a neutral compound or for any polyatomic ion, the sum of the oxidation numbers of the atoms in the molecule is equal to the net charge on the specie

C. Examples of determining oxidation numbers:

1. NO_3^-
2. H_2SO_4
3. $\text{Fe}(\text{OH})_2$
4. Li_3PO_4
5. HClO_3
6. $\text{W}_2(\text{SO}_3)_3$

D. Balancing simple redox equations: rules

- a. Assign oxidation numbers to all atoms in all reactants and products
- b. Break the reaction down into oxidation and reduction half-reactions
- c. Multiply if necessary to get the number of electrons in each half-reaction to be equal
- d. Add the half-reactions together

II. Balancing redox equations

A. Simple half-reactions: breaking redox reactions down into half-reactions (see BLB Chapter 4)

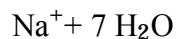
B. Acidic solution

1. Steps
 - a. Divide into half-reactions, including electrons and oxidation numbers
 - b. Balance all but O and H
 - c. Balance O by adding H_2O

- d. Balance H by adding H^+
- e. Multiply the half-reactions if necessary so that the electrons will cancel when the two half-reactions are added together
- f. Remember to always check both mass and charge balance for correctness

2. Examples

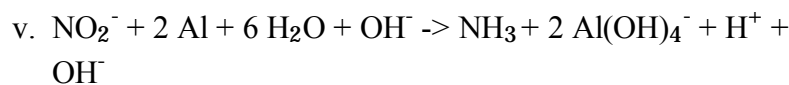
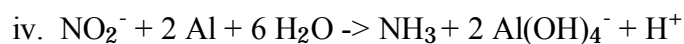
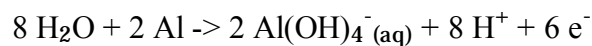
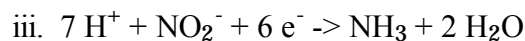
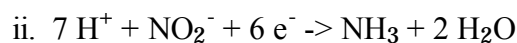
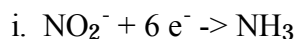
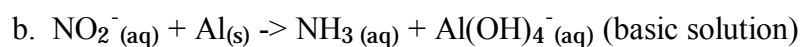
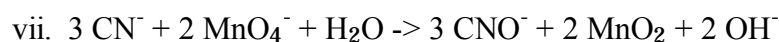
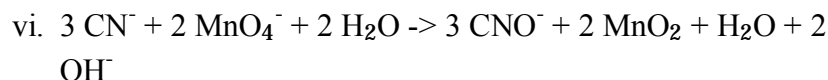
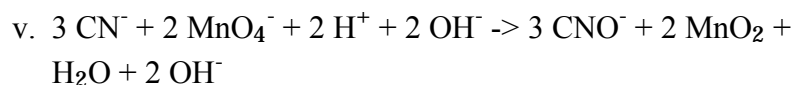
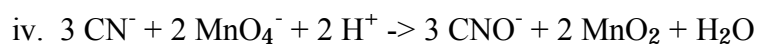
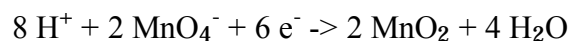
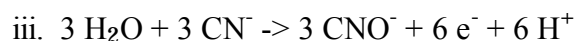
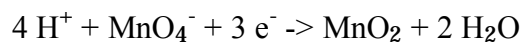
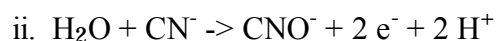
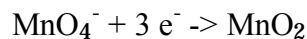
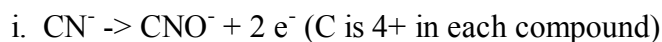
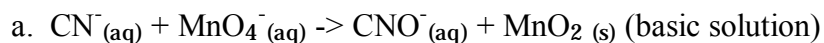
- a. $Cr_2O_7^{2-}(aq) + Cl^-(aq) \rightarrow Cr^{3+}(aq) + Cl_2(g)$ (acidic solution)
 - i. $Cr_2O_7^{2-} + 6 e^- \rightarrow 2 Cr^{3+}$
 $2 Cl^- \rightarrow Cl_2(g) + 2 e^-$
 - ii. $14 H^+ + Cr_2O_7^{2-} + 6 e^- \rightarrow 2 Cr^{3+} + 7 H_2O$
 $2 Cl^- \rightarrow Cl_2(g) + 2 e^-$
 - iii. $14 H^+ + Cr_2O_7^{2-} + 6 e^- \rightarrow 2 Cr^{3+} + 7 H_2O$
 $6 Cl^- \rightarrow 3 Cl_2(g) + 6 e^-$
 - iv. $14 H^+ + Cr_2O_7^{2-} + 6 Cl^- \rightarrow 2 Cr^{3+} + 3 Cl_2(g) + 7 H_2O$
- b. $Cu(s) + NO_3^-(aq) \rightarrow Cu^{2+}(aq) + NO_2(g)$ (acidic solution)
 - i. $Cu \rightarrow Cu^{2+} + 2 e^-$
 $NO_3^-(aq) + e^- \rightarrow NO_2$
 - ii. $Cu \rightarrow Cu^{2+} + 2 e^-$
 $2 H^+ + NO_3^-(aq) + e^- \rightarrow NO_2 + H_2O$
 - iii. $Cu \rightarrow Cu^{2+} + 2 e^-$
 $4 H^+ + 2 NO_3^-(aq) + 2 e^- \rightarrow 2 NO_2 + 2 H_2O$
 - iv. $4 H^+ + Cu + 2 NO_3^-(aq) \rightarrow Cu^{2+} + 2 NO_2 + 2 H_2O$
- c. $Mn^{2+}(aq) + NaBiO_3(s) \rightarrow Bi^{3+}(aq) + MnO_4^-(aq)$ (acidic solution)
 - i. $Mn^{2+}(aq) \rightarrow MnO_4^- + 5 e^-$
 $NaBiO_3(s) + 2 e^- \rightarrow Bi^{3+}$
 - ii. $4 H_2O + Mn^{2+}(aq) \rightarrow MnO_4^- + 5 e^- + 8 H^+$
 $6 H^+ + NaBiO_3(s) + 2 e^- \rightarrow Bi^{3+} + 3 H_2O + Na^+$
 - iii. $8 H_2O + 2 Mn^{2+}(aq) \rightarrow 2 MnO_4^- + 10 e^- + 16 H^+$
 $30 H^+ + 5 NaBiO_3(s) + 10 e^- \rightarrow 5 Bi^{3+} + 15 H_2O + 5 Na^+$
 - iv. $2 Mn^{2+}(aq) + 5 NaBiO_3(s) + 14 H^+ \rightarrow 2 MnO_4^- + 5 Bi^{3+} + 5$

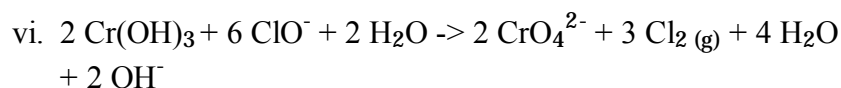
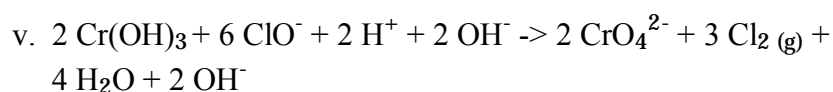
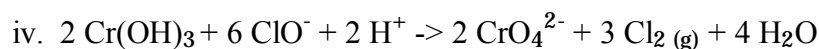
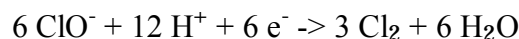
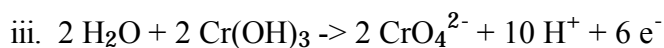
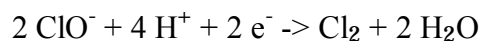
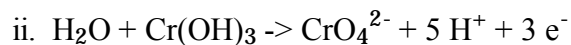
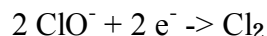
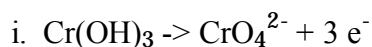
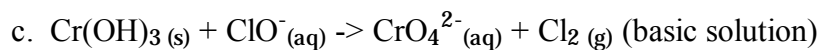
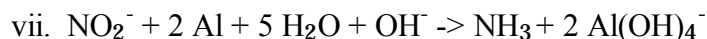


C. Basic solution

1. Steps: balance as if in acidic solution, then add equal numbers of OH^- to each so as to convert any H^+ to H_2O

2. Examples





III. Voltaic cells

A. Voltaic cells: (also known as galvanic cells) take advantage of the energy released in spontaneous redox reactions to do useful work

1. Batteries, fuel cells

2. Electrolytic cells are devices that use electrical energy from the surroundings to drive nonspontaneous reactions in a system

B. Cell structure: a voltaic cell consists of two half-cells that are electrically connected in such a manner that electrons flow from one metal electrode to another through an external pathway

1. A microscopic view of a voltaic cell

a. Two solid metals are connected by an external path (or circuit) and are called electrodes

i. Anode: oxidation; cathode: reduction

ii. Cations move toward the positively charged cathode while anions move toward the negatively charged anode

iii. This movement of ions, coupled with the flow of electrons through the external path, completes the circuit

b. A salt bridge connects the two half-cells, permitting the flow of

charge and preserving charge balance, but preventing the mixing of the solutions in the half-cells

- i. The electrolyte solution in the salt bridge contains ions that will not react with other ions or the electrodes in the half-cells, often KCl or sodium nitrate solutions
2. "Waterfall analogy:" in any voltaic cell electrons flow from the anode through the external circuit to the cathode
 - a. Just as things located "high" have more gravitational potential energy than things in a "low" position, certain materials have an intrinsically "higher" electrical potential energy than other materials with "lower" electrical potential energies

C. Cell notation: shorthand designations of the half-reactions in a voltaic cell

1. $\text{Zn}_{(s)} \mid \text{Zn}^{2+}_{(aq)} (1 \text{ M}) \parallel \text{Cu}^{2+}_{(aq)} (0.1 \text{ M}) \mid \text{Cu}_{(s)}$
 - a. "|" indicates a phase boundary, and "||" indicates a salt bridge
 - b. States of materials in the half-cells must be described, and the concentrations of ions in solutions must also be included
 - c. By cell notation convention the anode is on the left, the cathode is on the right, and the electrodes are the extreme ends of the notation
2. Some half-reactions in voltaic cells involve a gas or two different ions in the same solution
 - a. $\text{H}^{+}_{(aq)} (1 \text{ M}) \mid \text{H}_2 (g) (1 \text{ atm}) \mid \text{Pt}_{(s)}$
 - b. $\text{Fe}^{3+}_{(aq)} (1 \text{ M}), \text{Fe}^{2+}_{(aq)} (1 \text{ M}), \mid \text{Pt}_{(s)}$

IV. Electromotive force (emf): the driving force that "pushes" electrons from the anode to the cathode through the external circuit, attributable to differences between the two half-cells

A. Standard cell potential (also called the standard emf) depends on the reactions occurring in the half-cells, the concentrations of reactants, and temperature

1. Standard conditions: 1 M concentration for aqueous species, 1 atm pressure for gases, 298 K
2. Under standard conditions emf is called *the standard emf* and is indicated with the symbol E°_{cell}
3. $E^{\circ}_{\text{cell}} = E^{\circ}_{\text{red}} - E^{\circ}_{\text{ox}}$

B. E°_{cell} depends on the two half-reactions taking place

1. Could empirically determine the values of E°_{cell} for all possible half-cell

combinations (note: if the number of half-cells is N , then the total possible number of values would be $(N^2 - N)$)

2. Alternatively, could measure all half-cells relative to a standard reference electrode

a. Standard hydrogen electrode: $2 \text{H}^+_{(\text{aq})} (1 \text{ M}) + 2 \text{e}^- \rightarrow \text{H}_2 (\text{g}) (1 \text{ atm})$
: $E^\circ_{\text{red}} = 0.00 \text{ V}$

b. Standard calomel electrode

c. The set up

i. $\text{Zn}_{(\text{s})} + 2 \text{H}^+_{(\text{aq})} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + \text{H}_2 (\text{g})$

ii. The measured cell voltage is 0.76 V

iii. $E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = E^\circ_{\text{red}} - E^\circ_{\text{ox}} = 0.00 \text{ V} - 0.76 \text{ V} = -0.76 \text{ V}$

iv. Note that whenever a potential is assigned to a half-reaction it is for the reduction reaction, i.e., the reaction in the half-cell is written as a reduction

d. The resulting measured values are found in tables of standard reduction potentials (BLB Table 20.1)

C. Standard reduction potentials make it possible to predict both the direction and magnitude of electron flow for a large variety of voltaic cells

1. The more positive (or, the less negative) the value of the standard reduction potentials the greater the driving force for reduction

a. In comparing standard reduction potentials (BLB Table 20.1, see also Appendix E, p. 1128), there is a rough correlation with electronegativity trends, but it is only obviously apparent at the extreme values of the table (Li and F)

b. The more positive the standard reduction potential of a specie, the more powerful it is as an oxidizing agent

c. The more negative the standard reduction potential of a specie, the more powerful it is as a reducing agent

d. Oxidizing agents oxidize something else and reduce themselves

e. Reducing agents reduce something else and oxidize themselves

2. E°_{red} is an intensive property, i.e. it is independent of quantity

a. $\text{Fe}^{2+}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Fe}_{(\text{s})}$; $E^\circ_{\text{red}} = -0.76 \text{ V}$

b. $2 \text{Fe}^{2+}_{(\text{aq})} + 4 \text{e}^- \rightarrow 2 \text{Fe}_{(\text{s})}$; $E^\circ_{\text{red}} = -0.76 \text{ V}$

3. E°_{cell} values are calculated by combining the standard reduction potentials of the two half-cells; if the resulting value of E°_{cell} is positive then the reactions in the voltaic cell are spontaneous as written
- a. Given two half-cells, $\text{Zn} | \text{Zn}^{2+}$ and $\text{Cu} | \text{Cu}^{2+}$, which will be the anode? The cathode? What will E°_{cell} be?
- $\text{Zn}^{2+}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Zn}_{(\text{s})}$; $E^\circ_{\text{red}} = -0.76 \text{ V}$
 $\text{Cu}^{2+}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$; $E^\circ_{\text{red}} = +0.34 \text{ V}$
 - $\text{Zn}_{(\text{s})} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + 2 \text{e}^-$; $E^\circ_{\text{ox}} = +0.76 \text{ V}$
 $\text{Cu}^{2+}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Cu}_{(\text{s})}$; $E^\circ_{\text{red}} = +0.34 \text{ V}$
 - $\text{Zn}_{(\text{s})} + \text{Cu}^{2+}_{(\text{aq})} \rightarrow \text{Zn}^{2+}_{(\text{aq})} + \text{Cu}_{(\text{s})}$; $E^\circ_{\text{cell}} = +0.76 \text{ V} + 0.34 \text{ V} = +1.10 \text{ V}$
- b. Given two half-cells, $\text{Al} | \text{Al}^{3+}$ and $\text{Sn}^{2+} | \text{Sn}^{4+}$, which will be the anode? The cathode? What will E°_{cell} be?
- $\text{Al}^{3+}_{(\text{aq})} + 3 \text{e}^- \rightarrow \text{Al}_{(\text{s})}$; $E^\circ_{\text{red}} = -1.66 \text{ V}$
 $\text{Sn}^{4+}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Sn}^{2+}_{(\text{aq})}$; $E^\circ_{\text{red}} = +0.15 \text{ V}$
 - $\text{Al}_{(\text{s})} \rightarrow \text{Al}^{3+}_{(\text{aq})} + 3 \text{e}^-$; $E^\circ_{\text{red}} = +1.66 \text{ V}$
 $\text{Sn}^{4+}_{(\text{aq})} + 2 \text{e}^- \rightarrow \text{Sn}^{2+}_{(\text{aq})}$; $E^\circ_{\text{red}} = +0.15 \text{ V}$
 - $2 \text{Al}_{(\text{s})} \rightarrow 2 \text{Al}^{3+}_{(\text{aq})} + 6 \text{e}^-$; $E^\circ_{\text{red}} = +1.66 \text{ V}$
 $3 \text{Sn}^{4+}_{(\text{aq})} + 6 \text{e}^- \rightarrow 3 \text{Sn}^{2+}_{(\text{aq})}$; $E^\circ_{\text{red}} = +0.15 \text{ V}$
 - $2 \text{Al}_{(\text{s})} + 3 \text{Sn}^{4+}_{(\text{aq})} \rightarrow 2 \text{Al}^{3+}_{(\text{aq})} + 3 \text{Sn}^{2+}_{(\text{aq})}$; $E^\circ_{\text{cell}} = +1.66 \text{ V} + 0.15 \text{ V} = +1.81 \text{ V}$
- c. What is E°_{cell} for the reaction $2 \text{Br}^-(\text{aq}) + \text{I}_2(\text{s}) \rightarrow 2 \text{I}^-(\text{aq}) + \text{Br}_2(\text{l})$? Will it be product favored?
- $\text{Br}_2(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{Br}^-(\text{aq})$; $E^\circ_{\text{red}} = +1.07 \text{ V}$
 $\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$; $E^\circ_{\text{red}} = +0.54 \text{ V}$
 - $2 \text{Br}^-(\text{aq}) \rightarrow \text{Br}_2(\text{l}) + 2 \text{e}^-$; $E^\circ_{\text{red}} = -1.07 \text{ V}$
 $\text{I}_2(\text{s}) + 2 \text{e}^- \rightarrow 2 \text{I}^-(\text{aq})$; $E^\circ_{\text{red}} = +0.54 \text{ V}$
 - $2 \text{Br}^-(\text{aq}) + \text{I}_2(\text{s}) \rightarrow 2 \text{I}^-(\text{aq}) + \text{Br}_2(\text{l})$; $E^\circ_{\text{cell}} = -1.07 \text{ V} + 0.54 \text{ V} = -0.53 \text{ V}$; the forward reaction is not favored

V. Gibbs free energy, equilibrium, and electromotive force

- E°_{cell} is always positive for spontaneous reactions
- The relationship between free energy and E°_{cell} is described by the equation $\Delta G^\circ = -nFE^\circ_{\text{cell}}$

1. n = number of moles of electrons transferred in the reaction
2. F = Faraday's constant = $96,400 \text{ J/V}\cdot\text{mol}$
3. ΔG° is called the maximum work function, i.e., it describes the maximum amount of useful electrical work that can be obtained from a voltaic cell
4. For the voltaic cell $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$ E°_{cell} is 1.10 V. What is ΔG° for this cell?
 - a. $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(2 \text{ moles}) \times (96,400 \text{ J/V}\cdot\text{mol}) \times (1.10 \text{ V}) = -212 \text{ kJ}$

5. In the reaction of hydrogen gas and zinc ion $\text{H}_2(\text{g}) + \text{Zn}^{2+}(\text{aq}) + 2 \text{H}_2\text{O}(\text{l}) \rightarrow \text{Zn}(\text{s}) + 2 \text{H}_3\text{O}^+(\text{aq})$ ($E^\circ_{\text{cell}} = -0.76 \text{ V}$), is the reaction spontaneous? Is it product or reactant favored?
 - a. $\Delta G^\circ = -nFE^\circ_{\text{cell}} = -(2 \text{ moles}) \times (96,400 \text{ J/V}\cdot\text{mol}) \times (-0.76 \text{ V}) = -146.5 \text{ kJ}$
 - b. Reaction is nonspontaneous and is reactant favored

C. Given that at equilibrium $\Delta G^\circ = -RT \ln K$, and also given that $\Delta G^\circ = -nFE^\circ_{\text{cell}}$, then $+RT \ln K = +nFE^\circ_{\text{cell}}$, or $E^\circ_{\text{cell}} = (RT/nF) \ln K$

1. For the voltaic cell $\text{Zn} | \text{Zn}^{2+} || \text{Cu}^{2+} | \text{Cu}$ E°_{cell} is 1.10 V. What is the equilibrium constant (K_c) for this reaction?
 - a. $K_c = \exp(nFE^\circ_{\text{cell}} / RT)$; assume 298 K
 - b. $K_c = 1.49 \times 10^{37}$

D. How can predictions for nonstandard conditions be made?

1. Derivation

- a. $\Delta G = \Delta G^\circ + RT \ln Q$
- b. $\Delta G = -nFE_{\text{cell}}$
- c. $-nFE_{\text{cell}} = \Delta G^\circ + RT \ln Q = -nFE^\circ_{\text{cell}} + RT \ln Q$
- d. $E_{\text{cell}} = E^\circ_{\text{cell}} - (RT / nF) \ln Q$ (*Nernst Equation*)
- e. If using base 10 logarithms then $E_{\text{cell}} = E^\circ_{\text{cell}} - 0.0592 \text{ V} / n \log Q$

2. Examples

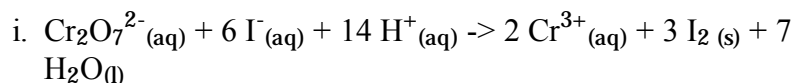
- a. Find E_{cell} for a cell in which $[\text{Cu}^{2+}] = 5.0 \text{ M}$ and $[\text{Zn}^{2+}] = 0.05 \text{ M}$ at 298 K.
 - i. Remember that $\text{Zn}(\text{s}) + \text{Cu}^{2+}(\text{aq}) \rightarrow \text{Zn}^{2+}(\text{aq}) + \text{Cu}(\text{s})$ and that

$$E^{\circ}_{\text{cell}} = 1.10 \text{ V}$$

$$\text{ii. } Q = [\text{Zn}^{2+}] / [\text{Cu}^{2+}]$$

$$\text{iii. } E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT / nF) \ln Q = +1.10 \text{ V} - (8.314 \text{ J/mol}\cdot\text{K} \times 298 \text{ K} / 2 \times 96,400 \text{ J/V}\cdot\text{mol}) \ln (.05/5) = 1.16 \text{ V}$$

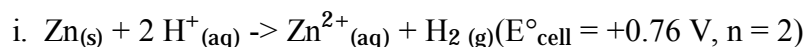
- b. The standard cell potential for the reaction of dichromate ion and iodide in acidic solution at 298 K is 0.79 V. What is E_{cell} if $[\text{Cr}_2\text{O}_7^{2-}] = 2.0 \text{ M}$, $[\text{H}^+] = 1.0 \text{ M}$, $[\text{I}^-] = 1.0 \text{ M}$, and $[\text{Cr}^{3+}] = 1.0 \times 10^{-5}$?



$$\text{ii. } Q = [\text{Cr}^{3+}]^2 / [\text{Cr}_2\text{O}_7^{2-}] \cdot [\text{H}^+]^{14} \cdot [\text{I}^-]^6 = 5.0 \times 10^{-11}$$

$$\text{iii. } E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT / nF) \ln Q = +0.79 \text{ V} - (8.314 \text{ J/mol}\cdot\text{K} \times 298 \text{ K} / 6 \times 96,400 \text{ J/V}\cdot\text{mol}) \ln (5.0 \times 10^{-11}) = +0.892 \text{ V}$$

- c. If the voltage in a $\text{Zn} | \text{H}^+$ cell is 0.45 V at 25°C when $[\text{Zn}^{2+}] = 1.0 \text{ M}$ and $P_{\text{H}_2} = 1.0 \text{ atm}$, what is the hydrogen ion concentration?



$$\text{ii. } E_{\text{cell}} = E^{\circ}_{\text{cell}} - (RT / nF) \ln Q$$

$$\text{iii. } E_{\text{cell}} - E^{\circ}_{\text{cell}} = (RT / nF) \ln Q$$

$$\text{iv. } (nF/RT)(E_{\text{cell}} - E^{\circ}_{\text{cell}}) = \ln Q$$

$$\text{v. } \exp [(nF/RT)(E_{\text{cell}} - E^{\circ}_{\text{cell}})] = Q = [\text{Zn}^{2+}] \cdot P_{\text{H}_2} / [\text{H}^+]^2$$

$$\text{vi. } [\exp [(nF/RT)(E_{\text{cell}} - E^{\circ}_{\text{cell}})]]^{-1} = [\text{H}^+]^2 / [\text{Zn}^{2+}] \cdot P_{\text{H}_2}$$

$$\text{vii. } [\text{Zn}^{2+}] \cdot P_{\text{H}_2} [\exp [(nF/RT)(E_{\text{cell}} - E^{\circ}_{\text{cell}})]]^{-1} = [\text{H}^+]^2$$

$$\text{viii. } \{[\text{Zn}^{2+}] \cdot P_{\text{H}_2} [\exp [(nF/RT)(E_{\text{cell}} - E^{\circ}_{\text{cell}})]]^{-1}\}^{1/2} = [\text{H}^+] = 5.78 \times 10^{-6}$$

- ix. Relevance: "this shows how a voltaic cell whose cell reaction involves H^+ can be used to measure $[\text{H}^+]$ of pH. a pH meter is a specially designed voltaic cell with a voltmeter calibrated to read pH directly." (BLB: 775)

VI. Electrolytic cells - use electrical energy to do work in a nonspontaneous chemical system, i.e., to drive an otherwise nonspontaneous reaction

A. Molten salt solutions

1. The extraction of magnesium and chlorine from brine

- a. $\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s}); E^\circ_{\text{red}} = -2.37 \text{ V}$
 $\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq}); E^\circ_{\text{red}} = +1.36 \text{ V}$
- b. $\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s}); E^\circ_{\text{red}} = -2.37 \text{ V}$
 $2 \text{Cl}^-(\text{aq}) \rightarrow \text{Cl}_2(\text{g}) + 2 \text{e}^-; E^\circ_{\text{ox}} = -1.36 \text{ V}$
- c. $\text{Mg}^{2+}(\text{aq}) + 2 \text{Cl}^-(\text{aq}) \rightarrow \text{Mg}(\text{s}) + \text{Cl}_2(\text{g}); E^\circ_{\text{cell}} = -2.37 \text{ V} + -1.36 \text{ V} = -3.73 \text{ V}$
- d. Note that $\Delta G^\circ = -nFE^\circ_{\text{cell}} = +719 \text{ kJ}$ and $K_{\text{c}} = 8.73 \times 10^{-127}$ (!)
2. To drive the reaction a pair of inert (often graphite) electrodes is inserted in the molten salt bath and a power source serves as an "electron pump"
- a. Oxidation still occurs at the anode and reduction still occurs at the cathode but the sign conventions are opposite from those for voltaic cells
- b. In voltaic cells the (-) electrode is where electrons are produced
- c. In electrolytic cells the (-) electrode is where electrons are "pumped"
- B. Aqueous solutions - the presence of water potentially complicates things since $2 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{H}_2(\text{g})$ ($E^\circ_{\text{cell}} = 0.00 \text{ V}$) and $2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{H}_2(\text{g}) + \text{OH}^-(\text{aq})$ ($E^\circ_{\text{cell}} = -0.83 \text{ V}$) are also possible reactions
1. For an aqueous solution of magnesium chloride
- a. Possible reduction reactions
- i. $\text{Mg}^{2+}(\text{aq}) + 2 \text{e}^- \rightarrow \text{Mg}(\text{s}); E^\circ_{\text{red}} = -2.37 \text{ V}$
- ii. $2 \text{H}_3\text{O}^+(\text{aq}) + 2 \text{e}^- \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{H}_2(\text{g}); E^\circ_{\text{cell}} = 0.00 \text{ V}$
- iii. $2 \text{H}_2\text{O}(\text{l}) + 2 \text{e}^- \rightarrow 2 \text{H}_2(\text{g}) + \text{OH}^-(\text{aq}); E^\circ_{\text{cell}} = -0.83 \text{ V}$
- b. Possible oxidation reactions
- i. $\text{Cl}_2(\text{g}) + 2 \text{e}^- \rightarrow 2 \text{Cl}^-(\text{aq}); E^\circ_{\text{red}} = +1.36 \text{ V}$
- ii. $\text{O}_2(\text{g}) + 4 \text{H}_3\text{O}^+(\text{aq}) + 4 \text{e}^- \rightarrow 6 \text{H}_2\text{O}(\text{l}); E^\circ_{\text{red}} = +1.23 \text{ V}$
- c. How can we know which reaction will occur? Remember that the more positive the standard reduction potential of the half-reaction, the easier it is to reduce, although concentration effects may also be significant
- i. At the cathode the ease of reduction is (iii) > (ii) > (i)
- ii. Which reduction occurs depends in part on $[\text{Mg}^{2+}]$; when

$[\text{Mg}^{2+}]$ is large (i) dominates but when $[\text{Mg}^{2+}]$ is small (ii) dominates

- iii. Complications can also occur when currents are large (as in commercial electrolytic cells) and when reactant concentrations are small
- iv. The dominance of one reduction reaction over another also depends on $[\text{Cl}^-]$

[Chemistry 1220 Index Page]

Last Modified 04/17/2009 14:49:46
