UNIT 5 – CHAPTER 16 STUDENT NOTES: ELECTROCHEMISTRY

Electrochemistry – interconversions of electrical and chemical energy

2 types of electrochemical cells

1. Voltaic – spontaneous reactions generate electrical energy
2. Electrolytic cells – electrical energy brings about nonspontaneous reaction

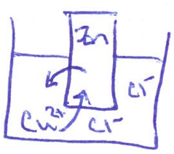
Voltaic Cells

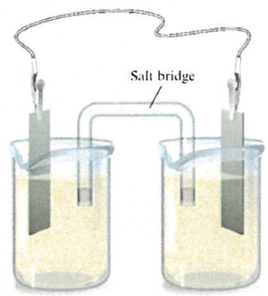
Oxidation – (more +) anode

Reduction – (more -) cathode

WHAT HAPPENS TO Zn METAL IN A $CuCl_{2(aq)}$ SOLUTION?

$Zn_{(s)} + CuCl_{2(aq)} \rightarrow ZnCl_{2(aq)} + Cu_{(s)}$





EX 1: When chlorine gas is bubbled through a water solution of NaBr, a spontaneous reaction occurs:

$$Cl_{2(g)} + 2\ Br^-_{(aq)} \rightarrow 2\ Cl^-_{(aq)} + Br_{2(l)}$$

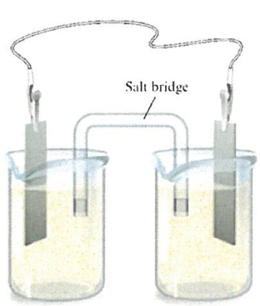
This reaction can serve as a source of electrical energy in a voltaic cell.

a) Draw the voltaic cell.

b) What is the cathode reaction? Anode reaction?

c) Which way do the e^- move in the external circuit?

d) Which way do the anions move? Which way do the cations move?



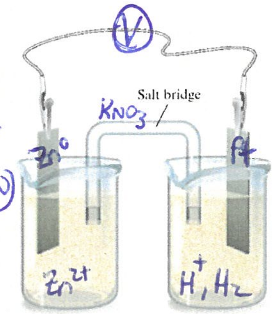
EX 2: Do the same as before for the following reaction:

$$Zn_{(s)} + 2\ H^{+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)}$$

½ CELL
$Zn_{(s)} \rightarrow Zn^{2+} + 2e^{-}$

½ CELL
$2H^{+} + 2e^{-} \rightarrow H_2$

ANODE (OXIDATION)



CATHODE (REDUCTION)

Summary of voltaic cells

1. Voltaic cells consist of two half-cells. They are joined by an external electrical circuit through which electrons move and a salt bridge through which ions move.

2. Each half-cell consists of an electrode dipping into a water solution. If a metal participates in the cell reaction, either as a product or a reactant, it is ordinarily used as the electrode; otherwise an inert electrode such as platinum is used.

3. In one half-cell, oxidation happens at the anode and reduction occurs at the cathode.

Standard voltages

Standard voltage – current flow is zero ions and molecules in solution at standard conditions (1 *M* for solutions, 1 atm for gases)

Zn-H^{+} cell as an example

You need two half-cells to measure a voltage

EX 3: What is the E^{0}_{red} for Cu^{2+} if E^{0} for Zn-Cu^{2+} is +1.101 V?

Strength of oxidizing-reducing agents

Oxidizing agent (reduction) – gains e^- *OXIDIZING AGENT IS REDUCED*

CATHODE

$Cu^{2+} + 2e^- \rightarrow Cu$

Reducing agent (oxidation) – releases e^- *REDUCING AGENT IS OXIDIZED*

ANODE

$Zn \rightarrow Zn^{2+} + 2e^-$

EX 4: Consider the following species in acidic solutions:

MnO_4^-, I^-, NO_3^-, H_2S, F^{2+}

Using the table of standard potentials:

a) Classify each of the these as an oxidizing and/or a reducing agent.

b) Arrange the oxidizing agents in order of increasing strength.

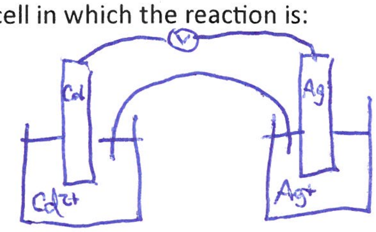
c) Arrange the reducing agents in order of increasing strength.

To calculate the E^0 from the E^0_{red} and E^0_{ox}

$$\mathbf{E^0 = E^0_{red} + E^0_{ox}}$$

EX 5: Using the table of standard potentials, calculate the E^0 for a voltaic cell in which the reaction is:

$$2\,Ag^+_{(aq)} + Cd_{(s)} \rightarrow 2\,Ag_{(s)} + Cd^{2+}_{(aq)}$$



RED: $2Ag^+_{(aq)} + 1e^- \longrightarrow Ag_{(s)}$ $E^0_{RED} = +.799V$

OXID: $Cd_{(s)} \longrightarrow Cd^{2+}_{(aq)} + 2e^-$ $E^0_{OXID} = +.402V$

$2Ag^+_{(aq)} + Cd_{(s)} \rightarrow 2Ag_{(s)} + Cd^{2+}_{(aq)}$ **1.201V**

2 general points

1. The calculated voltage, E^0, is always a (+) quantity for a reaction taking place in a voltaic cell.

2. The quantities E^0, E^0_{red}, and E^0_{ox} are independent of how the equation for the cell reaction is written. You never multiply the voltage by the coefficients of the balanced equation.

Spontaneity of redox reactions

To determine whether a given redox reaction is spontaneous, apply a simple principle:

> If the calculated voltage for a redox reaction is (+), the reaction will be spontaneous. If (-), the reaction will not be spontaneous.

EX 6: Determine if the following reactions are spontaneous.

a) $Ni_{(s)} + Zn^{2+}_{(aq\ 1\ M)} \rightarrow Ni^{2+}_{(aq\ 1\ M)} + Zn_{(s)}$

b) $Ni_{(s)} + Cu^{2+}_{(aq\ 1\ M)} \rightarrow Ni^{2+}_{(aq\ 1\ M)} + Cu_{(s)}$

c) $2\ Fe^{3+}_{(aq)} + 2\ I^-_{(aq)} \rightarrow 2\ Fe^{2+}_{(aq)} + I_{2(s)}$

*BOTH PULL e⁻; Fe^{3+} PULLS HARDER

RED: $2\ Fe^{3+} + 2e^- \rightarrow 2\ Fe^{2+}$ $\quad E^\circ_{RED} = +.769V$

OXID: $2I^- \rightarrow I_{2(s)} + 2e^-$ $\quad E^\circ_{OXID} = -.534V$

$.235\ V \rightarrow$ SPONTANEOUS

d) $Fe_{(s)}$ will oxidize to Fe^{2+} by treatment of hydrochloric acid. (The H^+ is only used because Cl^- cannot be reduced). Will this reaction occur?

$* Fe_{(s)} + 2HCl_{(aq)} \rightarrow FeCl_{2(aq)} + H_{2(g)} *$

NET IONIC: $Fe^{\emptyset}_{(s)} + 2H^+_{(aq)} \rightarrow Fe^{2+}_{(aq)} + H_2{}^{\emptyset}_{(g)}$

RED: $2H^+ + 2e^- \rightarrow H_2$ $\quad E^\circ_{RED} = .000V$

OXID: $Fe^{\emptyset}_{(s)} \rightarrow Fe^{2+}_{(aq)} + 2e^-$ $\quad E^\circ_{OXID} = +.409V$

$.409V \rightarrow$ SPONTANEOUS, WILL REACT

e) Will a reaction occur when the following species are mixed in an acidic solution:

$Cl^-, Fe^{2+}, Cr^{2+}, I_2$

E°_{RED}:

$Fe^{2+} + 2e^- \rightarrow Fe \quad = -.409V$

$I_2 + 2e^- \rightarrow 2I^- \quad = +.534V$

E°_{OXID}:

$2Cl^- \rightarrow Cl_2 + 2e^- \quad = -1.360V$

$Cr^{2+} \rightarrow Cr^{3+} + 1e^- \quad = +.408V$

$Fe^{2+} \rightarrow Fe^{3+} + 1e^- \quad = -.769V$

ONLY COMBINATIONS TO PRODUCE (+)E°:

RED: $I_2 + 2e^- \rightarrow 2I^-$ $\quad E^\circ_{RED} = +.534V$

OXID: $2Cr^{2+} \rightarrow 2Cr^{3+} + 2e^-$ $\quad E^\circ_{OXID} = +.408V$

$I_2 + 2Cr^{2+} \rightarrow 2I^- + 2Cr^{3+} \quad .942V$

Relations between E^o, ΔG^0, and K

E° AND $\Delta G^\circ = -nFE^\circ$

E° AND $K = E^\circ = \frac{(.0257)}{n} \ln K$

ΔG^0 = Free energy (-ΔG^0 is spontaneous)

K = equilibrium constant (K>1 is spontaneous)

E^0 is a measure of the spontaneity of a cell reaction

EX 7: For the reaction:

$$3\ Ag_{(s)} + NO_3^-{}_{(aq)} + 4\ H^+{}_{(aq)} \rightarrow 3\ Ag^+{}_{(aq)} + NO_{(g)} + 2\ H_2O_{(l)}$$

Calculate:

a) ΔG^0

b) K

EX 8: Calculate E^0, ΔG^0 and K for the reaction:

$$3\ Mn^{2+}{}_{(aq)} + 2\ MnO_4^-{}_{(aq)} + 2\ H_2O \rightarrow 5\ MnO_{2(s)} + 4\ H^+{}_{(aq)}$$

Effect of concentration on voltage

We have only worked with standard voltages (E^0) – (1 *M* solutions and 1 atm pressure). **When concentrations change, so does the voltage.**

Direction in which voltage shifts is predicted when you realize cell voltage is directly related to reaction spontaneity.

Voltage increases when [ ] reactant increases or [ ] product decreases

Voltage decreases when [ ] reactant decreases or [ ] product increases

After time, voltage drops and becomes zero as redox reaction reaches equilibrium

Comparing cell voltage (E) to concentration

Nernst equation – $E = E^0 - \frac{(0.0257\ V)}{n} \ln Q$ Q = reaction quotient

$$\mathbf{E = E^0 - \frac{(0.0592\ V)}{n} \log Q}$$

EX 9: Consider a voltaic cell in which the following reaction occurs:

$$O_{2(g)} + 4\ H^+_{(aq)} + 4\ Br^-_{(aq)} \rightarrow 2\ H_2O_{(l)} + 2\ Br_{2(l)}$$

Calculate the cell voltage (E) when O_2 = 1 atm and $[H^+] = [Br^-] = 0.10\ M$

EX 10: Consider a voltaic cell at 25°C in which the following reaction takes place.

$$2\ H_2O_{2(aq)} + 6\ H^+_{(aq)} + 2\ Au_{(s)} \rightarrow 2\ Au^{3+}_{(aq)} + 6\ H_2O$$

Calculate E^0

Write the Nernst equation for the cell.

Calculate E when $[Au^{3+}] = 0.250\ M$, $[H^+] = 1.25\ M$, $[H_2O_2] = 1.50\ M$.

Use of Nernst equation with pH

EX 11: Consider a voltaic cell at 25°C in which the following reaction takes place.

$$3\ O_{2(aq)} + 4\ NO_{(g)} + 2\ H_2O \rightarrow 4\ NO_3^-{}_{(aq)} + 4\ H^+_{(aq)}$$

Calculate E^0.

RED: $3(O_2 + 4H^+ + 4e^- \rightarrow 2H_2O)$ $E_{RED} = 1.229V$

OXID: $4(NO + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e^-)$ $E_{OXID} = -.964V$

$E^\circ = .265V$

Write the Nernst equation for the cell.

Calculate E when $[NO_3^-] = 0.250\ M$, $P_{NO} = 0.493$ atm, $P_{O2} = 0.315$ atm, pH = 4.85.

$E = .265V - \left(\frac{.0257}{12}\right) \cdot \ln \frac{[H^+]^4 \cdot [NO_3^-]^4}{(pO_2)^3 \cdot (pNO)^4}$

$E = .359V$

*pH = −LOG[H⁺]

$[H^+]$ = ANTILOG(−pH)

= ANTILOG(−4.85)

$[H^+] = 1.41\times10^{-5}$

EX 12: Consider a voltaic cell in which the following reaction takes place.

$$2\ NO_3^-{}_{(aq)} + 3\ H_{2(g)} \rightarrow 2\ NO_{(g)} + 2\ OH^-_{(aq)} + 2\ H_2O$$

RED: $2(NO_3^- + 2H_2O + 3e^- \rightarrow NO + 4OH^-)$ $E_{RED} = -.140V$

OXID: $3(H_2 + 2OH^- \rightarrow 2H_2O + 2e^-)$ $E_{OXID} = .828V$

$E^\circ = .688V$

Calculate E^0.

Write the Nernst equation for the cell.

Calculate E when $[NO_3^-] = 0.015\ M$, $P_{NO} = 0.722$ atm, $P_{H2} = 0.237$ atm, pH = 9.50.

$E = .688V - \left(\frac{.0257}{6}\right) \cdot \ln \frac{(pNO)^2 \cdot [OH^-]^2}{[NO_3^-]^2 \cdot (pH_2)^3}$

$E = .725V$

*pH + pOH = 14

pOH = 14 − 9.50

pOH = 4.5

$[OH^-]$ = ANTILOG(−4.5)

$[OH^-] = 3.16\times10^{-5}$

Use of the Nernst equation to determine ion concentration

In chemistry, the most important use of the Nernst equation lies in the experimental determination of the concentration of ions in solution. Suppose you measure the cell voltage, E, and know all but one species in the two half-cells. It should then be possible to calculate the concentration of that species using the Nernst equation.

EX 13: Consider a voltaic cell in which the reaction is:

$$Zn_{(s)} + 2\ H^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + H_{2(g)} \qquad E = 0.560\ V$$

It is found that the voltage is +0.560 V when $[Zn^{2+}] = 1.0\ M$, $pH_2 = 1.0$ atm, what must be the concentration of H^+ in the H_2-H^+ half-cell?

CALCULATE E° AND n:

RED: $2H^+ + 2e^- \rightarrow H_{2(g)}^{\emptyset} = 0.000V$

OXID: $Zn^{\emptyset}_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^- = +.762V$

+.762V

n = 2

"PLUG AND CHUG"

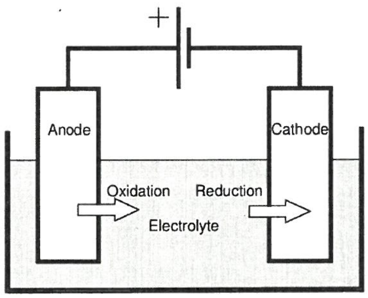
$E = E^\circ - \left(\frac{.0257}{n}\right) \cdot \ln Q$

$.560 = .762V - \left(\frac{.0257}{2}\right) \cdot \ln Q$

$5.60 = .762V - \left(\frac{.0257}{2}\right) \cdot \ln \frac{(1)^1 \cdot (1)^1}{[H^+]^2}$ (Zn^{2+}, pH_2)

$[H^+] = 4\times10^{-4} M$

Electrolytic cells: A **nonspontaneous** redox reaction is made to occur by pumping electrical energy into the system



- Battery acts as an electron pump, **pushing** e^- into the cathode and **removing** them from the anode
- Electrolysis – process of pumping e^- in the redox reaction

There is a simple relationship between the amount of electricity passed through an electrolytic cell and amounts of substance produced by oxidation and reduction at the electrodes.

$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

$Cu^{2+}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)}$

$Au^{3+}_{(aq)} + 3\ e^- \rightarrow Au_{(s)}$

You can deduce that:

1 mole e^- → 1 mole Ag (107.9 grams of Ag)

2 mole e^- → 1 mole Cu (63.55 grams of Cu)

3 mole e^- → 1 mole Au (197.0 grams of Au)

Terms

Coulomb (C): quantity of electrical charge (1 mole e^- = 9.648×10^4 C)

Ampere (A): rate of current flow (1 A = 1 C/sec)

Joule (J): amount of electrical energy (1 J = 1 C · V)

Kilowatt hours (kWh): (1 kWh = 3.6×10^6 J)

EX 12: Chromium metal can be electroplated from a water solution of potassium dichromate. The reduction half-reaction is:

$$Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+_{(aq)} + 12\ e^- \rightarrow 2\ Cr_{(s)} + 7\ H_2O_{(l)}$$

a) How many grams of chromium will be plated by 1.00×10^4 C?

b) How long will it take to plate 1 gram of chromium using a current of 6.00 A?

c) If the applied voltage is 4.5 V, how many kilowatt hours of electrical energy are required to plate 1.00 grams of Cr?

Standard Potential in Water Solution at 25^{0}C

Acidic Solution, [H$^+$] = 1 *M*

Half-reaction	E^0_{red} (V)
$Li^+_{(aq)} + e^- \rightarrow Li_{(s)}$	-3.040
$K^+_{(aq)} + e^- \rightarrow K_{(s)}$	-2.936
$Ba^{2+}_{(aq)} + 2e^- \rightarrow Ba_{(s)}$	-2.906
$Ca^{2+}_{(aq)} + 2e^- \rightarrow Ca_{(s)}$	-2.869
$Na^+_{(aq)} + e^- \rightarrow Na_{(s)}$	-2.714
$Mg^{2+}_{(aq)} + 2e^- \rightarrow Mg_{(s)}$	-2.357
$Al^{3+}_{(aq)} + 3e^- \rightarrow Al_{(s)}$	-1.68
$Mn^{2+}_{(aq)} + 2e^- \rightarrow Mn_{(s)}$	-1.182
$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)}$	-0.762
$Cr^{3+}_{(aq)} + 3e^- \rightarrow Cr_{(s)}$	-0.744
$Fe^{2+}_{(aq)} + 2e^- \rightarrow Fe_{(s)}$	-0.409
$Cr^{3+}_{(aq)} + e^- \rightarrow Cr^{2+}_{(aq)}$	-0.408
$Cd^{2+}_{(aq)} + 2e^- \rightarrow Cd_{(s)}$	-0.402
$PbSO_{4(s)} + 2e^- \rightarrow Pb_{(s)} + SO_4^{2-}{}_{(aq)}$	-0.356
$Tl^+_{(aq)} + e^- \rightarrow Tl_{(s)}$	-0.336
$Co^{2+}_{(aq)} + 2e^- \rightarrow Co_{(s)}$	-0.282
$Ni^{2+}_{(aq)} + 2e^- \rightarrow Ni_{(s)}$	-0.236
$AgI_{(S)} + e^- \rightarrow Ag_{(s)} + I^-_{(aq)}$	-0.152
$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(S)}$	-0.141
$Pb^{2+}_{(aq)} + 2e^- \rightarrow Pb_{(s)}$	-0.127
$2\ H^+_{(aq)} + e^- \rightarrow H_{2(g)}$	0.000
$AgBr_{(s)} + e^- \rightarrow Ag_{(s)} + Br^-_{(aq)}$	0.073
$S_{(s)} + 2H^+ + 2e^- \rightarrow H_2S_{(aq)}$	0.144
$Sn^{4+}_{(aq)} + 2e^- \rightarrow Sn^{2+}_{(aq)}$	0.154
$SO_4^{2-}{}_{(aq)} + 4\ H^+ + 2e^- \rightarrow SO_{2(g)} + 2\ H_2O$	0.155
$Cu^{2+}_{(aq)} + e^- \rightarrow Cu^{1+}_{(aq)}$	0.161
$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$	0.339
$Cu^+_{(aq)} + e^- \rightarrow Cu_{(s)}$	0.518
$I_{2(s)} + 2e^- \rightarrow 2\ I^-_{(aq)}$	0.534
$Fe^{3+}_{(aq)} + e^- \rightarrow Fe^{2+}_{(aq)}$	0.769
$Hg_2^{2+}{}_{(aq)} + 2e^- \rightarrow 2\ Hg_{(l)}$	0.796
$Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$	0.799
$2\ Hg^{2+}_{(aq)} + 2e^- \rightarrow Hg_2^{2+}{}_{(aq)}$	0.908
$NO_3^-{}_{(aq)} + 4\ H^+ + 3e^- \rightarrow NO_{(g)} + 2\ H_2O$	0.964
$AuCl_{4(aq)} + 3e^- \rightarrow Au_{(s)} + 4\ Cl^-_{(aq)}$	1.001
$Br_{2(l)} + 2e^- \rightarrow 2\ Br^-_{(aq)}$	1.007
$O_{2(g)} + 4\ H^+_{(aq)} + 2e^- \rightarrow 2\ H_2O_{(l)}$	1.229
$MnO_{2(s)} + 4\ H^+_{(aq)} + 2e^- \rightarrow Mn^{2+}_{(aq)} + 4\ H_2O$	1.229
$Cr_2O_7^{2-}{}_{(aq)} + 14\ H^+_{(aq)} + 6e^- \rightarrow 2Cr^{3+}_{(aq)} + 7\ H_2O$	1.33
$Cl_{2(q)} + 2e^- \rightarrow 2\ Cl^-_{(aq)}$	1.360
$ClO_3^-{}_{(aq)} + 6\ H^+ + 5e^- \rightarrow ½\ Cl_{2(g)} + 3\ H_2O_{(l)}$	1.458
$Au^{3+}_{(aq)} + 3e^- \rightarrow Au_{(s)}$	1.498
$MnO_4^-{}_{(aq)} + 8\ H^+ + 5e^- \rightarrow Mn^{2+}_{(aq)} + 2\ H_2O_{(l)}$	1.512
$PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4\ H^+ + 2e^- \rightarrow PbSO_{4(s)} + 2\ H_2O$	1.687
$H_2O_{2(aq)} + 2\ H^+ + 2e^- \rightarrow 2\ H_2O_{(l)}$	1.763
$Co^{3+}_{(aq)} + e^- \rightarrow Co^{2+}_{(aq)}$	1.953
$F_{2(g)} + 2e^- \rightarrow 2\ F^-_{(aq)}$	2.889

Basic Solution, [OH$^-$] = 1 *M*

Half-reaction	E^0_{red} (V)
$Fe(OH)_{2(s)} + 2e^- \rightarrow Fe_{(s)} + 2\ OH^-_{(aq)}$	-0.891
$2\ H_2O_{(l)} + 2e^- \rightarrow H_{2(g)} + 2\ OH^-_{(aq)}$	-0.828
$Fe(OH)_{3(s)} + 2e^- \rightarrow Fe(OH)_{2(s)} + 2\ OH^-_{(aq)}$	-0.547
$S_{(s)} + 2e^- \rightarrow S^{2-}_{(aq)} + 2\ OH^-_{(aq)}$	-0.445
$NO_3^-{}_{(aq)} + 2H_2O + 3e^- \rightarrow NO_{(g)} + 4\ OH^-_{(aq)}$	-0.140
$NO_3^-{}_{(aq)} + H_2O + 2e^- \rightarrow NO_2^-{}_{(aq)} + 2\ OH^-_{(aq)}$	0.004
$ClO_4^-{}_{(aq)} + H_2O + 2e^- \rightarrow ClO_3^-{}_{(aq)} + 2\ OH^-_{(aq)}$	0.394
$O_{2(g)} + 2\ H_2O + 4e^- \rightarrow 4\ OH^-_{(aq)}$	0.401
$ClO_3^-{}_{(aq)} + 3H_2O + 6e^- \rightarrow Cl^-_{(aq)} + 6\ OH^-_{(aq)}$	0.614
$ClO^-_{(aq)} + H_2O + 2e^- \rightarrow Cl^-_{(aq)} + 2\ OH^-_{(aq)}$	0.890