#91 Notes **Unit 11: Electrochemistry and Radiochemistry**

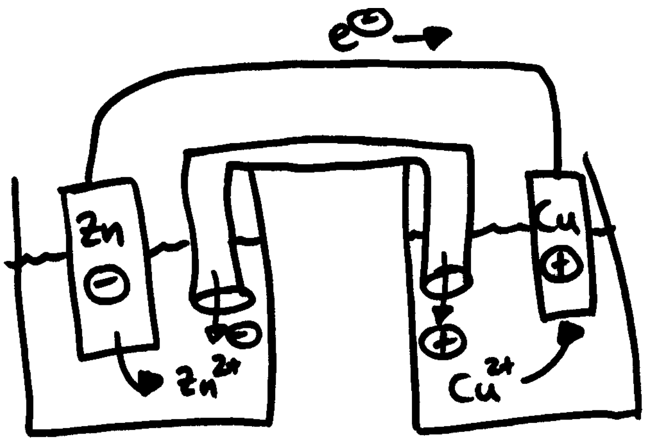
Ch. Electrochemistry and Radiochemistry

I. Galvanic Cells

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^-$ oxidizing

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



*O*xidized | *R*educed

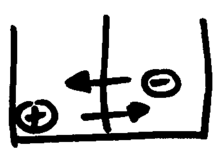
*A***n**ode (-) | *C*a**t**hode (+)

The salt bridge adds ions to keep the solutions balanced:

(-) ions are added to balance the **arriving** **Zn^{2+} (+) ions.**

(+) ions are added to replace the **departing** **Cu^{2+} (+) ions.**

** or cells separated by porous disk



Cell potential = electromotive force (emf) = ε_{cell}

From Reduction Potential Table:

$Zn^{2+}_{(aq)} + 2\ e^- \rightarrow Zn_{(s)}$ -0.76 v

$Cu^{2+}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)}$ 0.34 v

$Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2\ e^-$ +0.76 v

$Cu^{2+}_{(aq)} + 2\ e^- \rightarrow Cu_{(s)}$ 0.34 v

$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$ **1.10 v** **(+) is spontaneous**

**** If given 2 reduction potentials, make the reaction spontaneous. (flip one of them)**

The reduction potentials are arbitrary.
They are standardized on $2H^+ + 2e^- \rightarrow H_2$ equaling 0 volts.
(The energy can not be measured for a single reaction, only for the difference between 2 reactions.)

**To add the ½ reactions, the number of electrons must be equal, but…

Do not multiply ε by a number (ε is intensive; it does not matter how many times a reaction occurs)

Do change the sign when flipping a reaction.

Ex. 1a) Which is the strongest oxidizing agent and strongest reducing agent?

Ca^{2+}, Fe^{2+}, Cl_2

<u>Reduction Potentials</u>

$Ca^{2+} + 2\,e^- \rightarrow Ca$	-2.76 v
$Fe^{2+} + 2\,e^- \rightarrow Fe$	-0.44 v
$Fe^{3+} + e^- \rightarrow Fe^{2+}$	0.77 v
$Cl_2 + 2\,e^- \rightarrow 2\,Cl^-$	1.36 v

Best reducer = most positive reducer **(Cl_2 {+1.36 v} = best oxidizing agent**

<u>Oxidation Potentials</u>

$Ca \rightarrow Ca^{2+} + 2\,e^-$	2.76 v
$Fe \rightarrow Fe^{2+} + 2\,e^-$	0.44 v
$Fe^{2+} \rightarrow Fe^{3+} + e^-$	-0.77 v
$2\,Cl^- \rightarrow Cl_2 + 2\,e^-$	-1.36 v

Best oxidizer = most positive oxidizer, so $Ca \rightarrow Ca^{2+} + 2\,e^-$ +2.76 v

but since Ca not listed, the next best would be Fe {+0.44 v}

but since Fe not listed, the next best would be **Fe^{2+} {-0.77 v}(best reducing agent)**

Ex. 1b) Which can be reduced by Al?

If others reduce, then Al must oxidize: $Al \rightarrow Al^{3+} + 3e^-$ 1.676 v

$Ca^{2+} + 2\,e^- \rightarrow Ca$ -2.76 v when add get (-) voltage = nonspontaneous
$Fe^{2+} + 2\,e^- \rightarrow Fe$ -0.44 v

Fe^{2+}, Fe^{3+}, and Cl_2 will give overall (+) spontaneous voltage

but only **Fe^{2+} and Cl_2** are listed

#92 Notes II. Electrical Work/Free Energy

$W_{max} = -q\ \varepsilon_{max}$ (doing work, the system loses energy {current leaves})

W = work

q = charge

$q = n\ F$ n = mols of electrons

F = 1 Faraday = 96485 C / mol e^-

C = coulombs

$\Delta G = W_{max} = -\ q\ \varepsilon_{max} = -\ n\ F\ \varepsilon_{max}$

$\Delta G^o = -\ n\ F\ \varepsilon^o_{max}$

III. Nernst Equation

From last unit: $\Delta G = \Delta G^o + RT \ln Q$

$-\ n\ F\ \varepsilon_{max} = -\ n\ F\ \varepsilon^o_{max} + RT \ln Q$

$\varepsilon = \varepsilon^o - \frac{RT}{nF} \ln Q$

$\boldsymbol{\varepsilon = \varepsilon^o - \frac{0.0592}{n} \log Q}$

Ex. 1) $Al^{3+} + 3e^- \rightarrow Al$ -1.68 v

$Fe^{2+} + 2e^- \rightarrow Fe$ -0.44 v

Make the over all reaction spontaneous and calculate ε_{cell} for $[Al^{3+}]$ = 1.0 M and $[Fe^{2+}]$ = 3.0 M.

$2\ (\ Al \rightarrow Al^{3+} + 3e^-)$ +1.68 v

$3\ (\ Fe^{2+} + 2e^- \rightarrow Fe\ )$ -0.44 v

$2\ Al_{(s)} + 3\ Fe^{2+}_{(aq)} \rightarrow 2\ Al^{3+}_{(aq)} + 3\ Fe_{(s)}$ $\varepsilon^o_{cell} = 1.24$ v

$\varepsilon = \varepsilon^o - \frac{0.0592}{n} \log Q$ $Q = \frac{[Al^{3+}]^2}{[Fe^{2+}]^3} = \frac{(1.0\ M)^2}{(3.0\ M)^3} = \mathbf{0.037}$

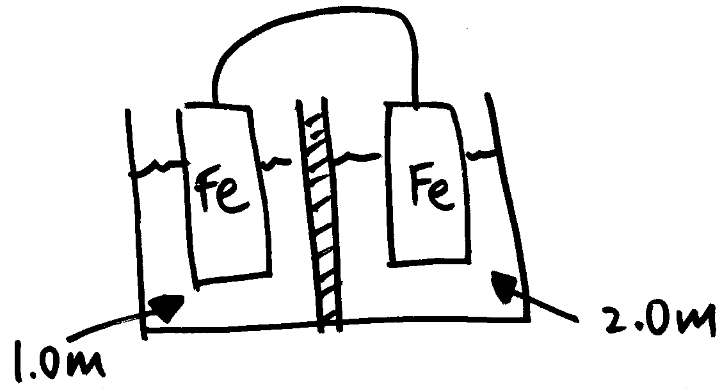
$\varepsilon_{cell} = 1.24\ v - \frac{0.0592}{6e^-} \log 0.037 = 1.24\ v + 0.014\ v =$ **1.25 v**

1b) Find ΔG.

$\Delta G = -\ n\ F\ \varepsilon = -\ (6\ e^-)\ (96485\ C/mol)\ (1.25\ v) =$ **-7.24×10^5 J/mol**

(1 joule = 1 C • 1 V)

Ex. 2)



Fe^{2+} Porous Wall Fe^{2+}

Which side is the cathode and where do the electrons flow?

**Fe will reduce on one side and oxidize on the other side!
At first have both either reduce or oxidize:

$Fe^{2+}_{(aq)} + 2\,e^- \rightarrow Fe_{(s)}$ $\varepsilon^o = -\,0.44$ v
reduction

$\varepsilon = \varepsilon^o - \frac{0.0592}{n} \log Q$ $Q = 1 / [Fe^{2+}]^1$ (for both reducing)

Left

$\varepsilon_L = -0.44\text{ v} - \frac{0.0592}{2\,e^-} \log(1/1.0\text{ M})$

$\varepsilon_L = -0.44\text{ v} - 0 = \mathbf{-0.44\text{ v}}$ (reducing)

Right

$\varepsilon_R = -0.44\text{ v} - \frac{0.0592}{2\,e^-} \log(1/2.0\text{ M})$

$\varepsilon_R = -0.44\text{ v} + 0.009\text{ v} = \mathbf{-0.43v}$ (reducing)

To be spontaneous ε_{cell} must be positive: both are reducing so,
flip ε_L so that it oxidizes, +0.44 v
to get a overall positive

$\varepsilon_{cell} = \varepsilon_L + \varepsilon_R = +0.44\text{ v} + (-0.43)\text{ v} = \mathbf{0.01\text{ v}}$

↑ oxidize, Anode (-) ↑ reduce, Cathode (+)

Electrons flow to (+) cathode on the right side.

#93 Notes **IV. Electrolysis**

-forcing a current through a cell to make a nonspontaneous reaction react.

($\varepsilon_{cell} = (-)$)

Stoichiometry Steps:

1) Time
2) Current: 1 amp = 1 C/sec
3) Charge: 96485 C/mol e^-
4) # mols e^- / mols solid
5) g solid or reverse

Ex. 1) What mass of Co from aqueous Co^{2+} can be plated out in 3.0 hr with a current of 12 A?

$$\frac{3.0\text{ hr}}{} \left| \frac{3600\text{ sec}}{1\text{ hr}} \right| \frac{12\text{ C}}{\text{sec}} \left| \frac{1\text{ mol } e^-}{96485\text{ C}} \right| \frac{1\text{ mol Co}}{2\text{ mol e-}} \left| \frac{58.933\text{ g Co}}{1\text{ mol Co}} \right. = 39.58\text{ g} = 40\text{ g Co}$$

↑ 12 amp = 12 C/ 1 sec

↑ $Co^{2+} + 2e^- \rightarrow Co$ ($2\text{ mol } e^- / 1\text{ mol Co}$)

↑ periodic table (atomic mass)

Ch. Radiochemistry

The “attractive” nuclear force between protons and neutrons is usually stronger than the repulsion energy of the protons. But some isotopes have too many protons and not enough neutrons, so there is too much repulsion. These atoms are unstable (radioactive).
Atoms with more than 83 protons are always unstable (atomic #’s > 83).

I. Nuclear Decay Reactions (to become stable)

alpha (α) particle ${}_{2}^{4}He$ (nucleus only) -barely passes through paper

beta (β) particle ${}_{-1}^{0}e$ - stopped by 3 mm Al or 10 mm wood
(really a neutron is transformed into a proton, which remains in the nucleus, emitting an e^- and an anti-neutrino)

gamma (γ) is electromagnetic energy - stopped by 60 cm Al or 7cm Pb

positron particle ${}_{+1}^{0}e$ neutron ${}_{0}^{1}n$ proton ${}_{1}^{1}p$

emission (given off), so put particle on product side
capture (taken in), so put particle on the reactant side

Ex. 1) ${}^{265}Bh$ decays by α-emission.

$$\mathbf{{}_{107}^{265}Bh \rightarrow {}_{2}^{4}He + {}_{105}^{261}Db}$$

Ex. 2) ^{99}Mo decays by β-emission (β-).

$$\mathbf{{}_{42}^{99}Mo \rightarrow {}_{-1}^{0}e + {}_{43}^{99}Tc}$$

Ex. 3) ^{207}Bi decays by positron emission (β+).

$$\mathbf{{}_{83}^{207}Bi \rightarrow {}_{+1}^{0}e + {}_{82}^{207}Pb}$$

Ex. 4) ^{102}Rh decays by electron capture (e.c. or ε).

$$\mathbf{{}_{45}^{102}Rh + {}_{-1}^{0}e \rightarrow {}_{44}^{102}Ru}$$

#94 Notes II. Bombardments

-linear or cyclotron particle accelerators can be used to combine smaller atoms into larger atoms or to break up large atoms into smaller atoms.

Ex. 1) ^{249}Bk is bombarded by ^{22}Ne to make a new heavier element and 4 neutrons ($_0^1n$). Write the reaction.

$_{97}^{249}Bk + _{10}^{22}Ne \rightarrow 4\ _0^1n + _{107}^{267}Bh$

III. Half-lives

Radioactive decay reactions are 1st order, so **Rate = k [A]^1, $t_{1/2}$ = 0.693 / k**

ln A = -kt + ln A_o

Ex. 1) 28 g of ^{87}Sr has a ½ life of 2.8 hrs.

a) Find the decays/sec (decays = atoms).

$Rate = k [A]^1$ $\qquad t_{1/2} = 0.693 / k$ $\qquad \frac{2.8\text{ hr}}{} \left| \frac{3600\text{ sec}}{1\text{ hr}} \right. = 10080\text{ sec}$

$10080\text{ sec} = 0.693 / k$

$k = 6.875 \times 10^{-5}\text{ sec}^{-1}$

$Rate = k [A]^1 = (6.875 \times 10^{-5}\text{ sec}^{-1}) \left(\frac{28\text{ g } ^{87}Sr}{} \left| \frac{1\text{ mol}}{87\text{g}} \right| \frac{6.022 \times 10^{23}\text{ atoms}}{1\text{ mol}} \right)$

Rate = 1.3 X10^{19} decays/sec

b) How much is left after 4.0 hrs?

$t_{1/2} = 2.8\text{ hr}$ $\qquad t_{1/2} = 0.693 / k$

$2.8\text{ hr} = 0.693 / k$

$k = 0.2475\text{ hr}^{-1}$

$\ln A = -kt + \ln A_o$

$\ln A = -(0.2475\text{ hr}^{-1})(4.0\text{ hr}) + \ln(28\text{ g})$

$\ln A = -0.99 + 3.33$

$e^x (\ln A = 2.34)$

A = 10. g is left

c) How much decayed?

28 g *{initially}* – 10. g *{left}* = **18 g decayed**

IV. Nuclear Fission / Fusion
(splitting/ breaking apart) (combining)

-see Fusion reactions in textbook:

Sun: ${}_{1}^{1}H + {}_{1}^{1}H \rightarrow {}_{1}^{2}H + {}_{1}^{0}e$

$\downarrow$

${}_{1}^{1}H + {}_{1}^{2}H \rightarrow {}_{2}^{3}He$

$\downarrow$

${}_{2}^{3}He + {}_{2}^{3}He \rightarrow {}_{2}^{4}He + 2\ {}_{1}^{1}H$

or ${}_{2}^{3}He + {}_{1}^{1}H \rightarrow {}_{2}^{4}He + {}_{1}^{0}e$

Fission: ${}_{0}^{1}n + {}_{92}^{235}U \rightarrow {}_{52}^{137}Te + {}_{40}^{97}Zr + 2\ {}_{0}^{1}n$ (nuclear power plants)

${}_{0}^{1}n + {}_{94}^{239}Pu \rightarrow {}_{56}^{146}Ba + {}_{38}^{91}Sr + 3\ {}_{0}^{1}n$ (nuclear bombs)

Subcritical mass: the reaction dies out.
Critical mass: for each neutron that reacts, one neutron that is produced, causes a reaction.
Supercritical mass: exponential increase, explosion.

#95 Notes V. Binding Energy

-is the energy required to decompose a nucleus into its components.

ΔE is endothermic (+). (Energy is required to break the bonds.)

$E = mc^2$

Ex. 1) Calculate the binding energy in j/atom for the **nucleus** of ^{16}O.
(The mass of oxygen is 15.999 g.)

$_8^{16}O$ = 8 protons, 8 electrons, and 16-8 = 8 neutrons

↑

electrons not in nucleus, so ignore in reaction (but must subtract electrons from the atomic mass below in equation to get the mass of the nucleus)

$8\ _1^1p + 8\ _0^1n \rightarrow\ _8^{16}O$

m_p = 1.00728 amu (g/mol) = 1.67262×10^{-27} kg/atom
m_n = 1.00866 amu = 1.67493×10^{-27} kg/atom
m_e = 5.48580×10^{-4} amu = 9.10939×10^{-31} kg/atom

$\Delta m = m_{products} - m_{reactants}$

Δm = [15.999 g – 8 (5.48580×10^{-4} amu)] – [8 (1.00728 amu) + 8 (1.00866 amu)]
atom - electrons protons + neutrons

Δm = 15.999 amu – 0.0043886 amu – 8.05824 amu – 8.06928 amu

Δm = -0.1329086 amu

$E = mc^2$ (mass must be in kg)

$$E = \left(\frac{-0.1329086 \text{ g}}{\text{mol}} \left| \frac{1 \text{ kg}}{1 \times 10^3 \text{ g}} \right| \frac{1 \text{ mol}}{6.022 \times 10^{23} \text{ atoms}} \right) (3.00 \times 10^8 \text{ m/s})^2$$

$$E = \frac{\mathbf{-1.99 \times 10^{-11} \text{ J}}}{\textbf{atom}} \left| \frac{1 \text{ atom}}{16 \text{ nucleons}} \right. = \mathbf{-1.24 \times 10^{-12} \text{ J/nucleon}}$$

↑ ↑

(releases E as it forms) (8 protons & 8 neutrons in nucleus)

Binding Energy = +1.99 $\mathbf{\times 10^{-11}}$ **J/atom** (positive energy to break it apart)

Ex. 2) Calculate the amount of energy released per gram of hydrogen nuclei for the following reaction, if $_1^1H$ = 1.00782 amu, $_2^3He$ = 3.01603 amu, $_2^4He$ = 4.00260 amu.

$$_2^3He + _1^1H \rightarrow _2^4He + _{+1}^{0}e$$

$$\Delta m = [4.00260 \text{ amu} - 2(5.48580 \times 10^{-4} \text{ amu}) \quad + \quad 1(5.48580 \times 10^{-4} \text{ amu})]$$

$_2^4He$ nucleus $\qquad\qquad$ $_{+1}^{0}e$

$$- [3.01603 \text{ amu} - 2(5.48580 \times 10^{-4} \text{ amu}) \quad + \quad 1.00782 \text{ amu} - 1(5.48580 \times 10^{-4} \text{ amu})]$$

$_2^3He$ nucleus $\qquad\qquad$ $_1^1H$ nucleus

$$\Delta m = 4.00150284 + 5.48580 \times 10^{-4} - 3.01493284 - 1.00727142$$
$$\Delta m = -0.02015284 \text{ amu}$$

$$E = mc^2 = \left(\frac{-0.02015284 \text{ g}}{\text{mol}} \left| \frac{1 \text{ kg}}{1 \times 10^3 \text{ g}} \right.\right) (3.00 \times 10^8 \text{ m/s})^2 \left| \frac{1 \text{ mol } _1^1H}{} \right. = \mathbf{-1.80 \times 10^{12} \ J/g \ _1^1H}$$

↑

1.00782 g – 1(5.48580 X10^{-4} g)
grams of $_1^1H$ nucleus

**Always subtract electrons from atomic masses to get mass of nucleus, but if they are alone in the reaction, then include them.
If in kg/atom use those masses and change J/atom to J/mol at the end.

#96 Notes VI. Nuclear Power Plants

1) Fuel: $_{92}^{235}U$ & $_{94}^{239}Pu$ (produced in the reaction)

2) Moderator: H_2O, heavy H_2O, graphite, Be
 -slows down neutrons, but does not absorb them.

3) Control Rods: B, Cd, or Ga alloyed with Al or steel
 -absorbs excess neutrons not needed to keep the chain reaction going.

4) Coolant: He, H_2O, CO_2, liquid metals (Na)
 -removes heat from the reactor.

5) Heat Exchanger:
 -transfers heat from the hot coolant, to the cool water, that will make steam to turn the turbines.

6) Safety Shields: Pb or thick concrete
 -radiation shield around the reactors.

End of Notes (Assignments #97-99 are Review Assignments. There are no notes for these assignments.)