CLASS

Lecture 13: 10.21.05 Electrochemical Equilibria

Today:

Reading: Engel and Reid 11.1-11.5, 11.8-11.9, 11.11-11.13

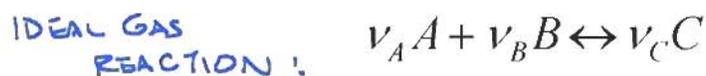**Supplementary Reading:**   Engel and Reid 11.14-11.15

ANNOUNCEMENTS:

FYI: AGI HAS NORMAL OFFICE HRS DURING LAB WEEKS

Last time

o   We analyzed the free energy change in chemical reactions:

IDEAL GAS
REACTION : $\quad \nu_A A + \nu_B B \leftrightarrow \nu_C C$

$$\Delta \bar{G}_{RXN} \equiv \left(\frac{\partial G_{RXN}}{\partial \xi} \right) = \overset{PRODUCTS}{\underset{i}{\sum} \nu_i \mu_i} - \overset{REACTANTS}{\underset{j}{\sum} \nu_j \mu_j}$$

EXTENT OF REACTION

$$\Delta \bar{G}_{RXN} = \Delta \bar{G}^o_{RXN} + RT \ln Q_p \overset{EQUIL!}{=} 0 \quad \leftarrow$$

$$\underbrace{\nu_C \mu^o_C - \nu_A \mu^o_A - \nu_B \mu^o_B}$$

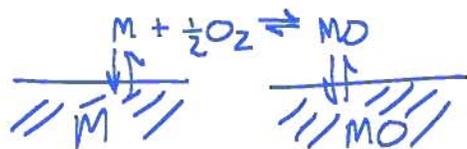$$\underbrace{\frac{\left(\frac{P_C}{P^o}\right)^{\nu_C}}{\left(\frac{P_A}{P^o}\right)^{\nu_A} \left(\frac{P_B}{P^o}\right)^{\nu_B}}}$$

AT EQUILIBRIUM, $\Delta \bar{G}_{RXN} \rightarrow 0$

$$- \frac{\Delta \bar{G}^o_{RXN}}{RT} = \ln K_p$$

EQUILIBRIUM CONSTANT

GAS—SOLID REACTIONS : [① O_2 INSOLUBLE IN SOLIDS
                        [② a_i FOR SOLIDS $\approx$ 1

$O_2 (g)$

$M + \frac{1}{2} O_2 \rightleftharpoons MO$

$\overline{M}$ $\overline{MO}$

$$\Delta \bar{G}_{RXN} = \Delta \bar{G}^o_{RXN} + RT \ln \frac{1}{\left(\frac{P_{O_2}}{P^o}\right)^{1/2}}$$

$$\underbrace{\mu^o_{MO} - \mu^o_M - \frac{1}{2} \mu^o_{O_2}}$$

An example calculation

- Calcium carbonate is a major component of many biological hard materials such as seashells, and is often studied to learn how organisms build materials via 'bottom up' molecular assembly (a process called biomineralization). It undergoes thermal decomposition on heating according to the reaction:

$$CaCO_{3(s)} \leftrightarrow CaO_{(s)} + CO_{2(g)}$$
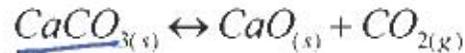
- Given the standard state free energies (free energies of formation) for each component, calculate the pressure of CO_2 in equilibrium with one mole of calcium carbonate at 2000 K:

$$\Delta \overline{G}^{''}_{f\,CaCO_{3(s)}} = \mu^{''}_{CaCO_{3(s)}} = -1,084 kJ/mole \qquad \Delta \overline{G}^{''}_{f\,CaO_{(s)}} = \mu^{''}_{CaO_{(s)}} = -603.3 kJ/mole$$

$$\Delta \overline{G}^{''}_{f\,CO_{2(g)}} = \mu^{''}_{CO_{2(g)}} = -394.4 kJ/mole$$

EQUILIBRIUM $\overline{\Delta G}_{RXN} = 0$

$$\overline{\Delta G}^{\circ}_{RXN} + RT \ln K_p = 0$$

$$-394.4 \times 10^3 \, J - 603.3 \times 10^3 \, kJ + 1,084 \times 10^3 \, J$$

$$= -RT \ln \left[\frac{\left(\frac{P_{CO_2}}{p^\circ}\right)}{1} \right] \qquad \frac{\left(\frac{P_{CO_2}}{p^\circ}\right) a^1_{CaO}}{a_{CaCO_3}}$$

$p^\circ = 1 \text{ atm}$

$$P_{CO_2} = 5.57 \times 10^{-3} \, atm$$

The electrochemical potential

- The function of batteries and other electrochemical processes such as electroplating and corrosion are governed by thermodynamics, and in particular by the action of chemical potentials. Design of improved batteries, including batteries fabricated from *solid* materials, is an intense area of current materials science & engineering research. Analysis of a battery provides an example of utilizing the general solution model for the chemical potential, and also introduces a (yet another) new form of internal energy- embodied in the electrochemical potential.

Electrostatic energy contributions to the internal energy

- Batteries are based on electrochemical reactions that create and consume electrons (which provide the electrical current when the battery is connected to a circuit). Their operation involves the trafficking of charged components (electrons and ions).

Liquid electrolyte battery
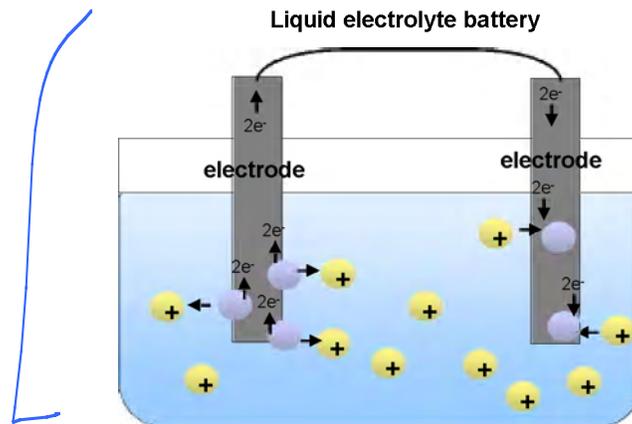
- Because the reactions generate charged components (ions in solution, and electrons in the electrodes), we have a new source of internal energy to consider in the system: **electrostatic potential energy**. Electrostatic potential energy arises due to the electrostatic 'pull' of opposite charges: an electrode with a buildup of negative charge attracts positively charged ions, and thus ions at a finite separation from such an electrode have a defined electrostatic potential energy.

The electrostatic potential is constant at distance r from a point charge. Lines of equipotential are circles in two dimensions. Broken lines indicate the direction of force and the field E.
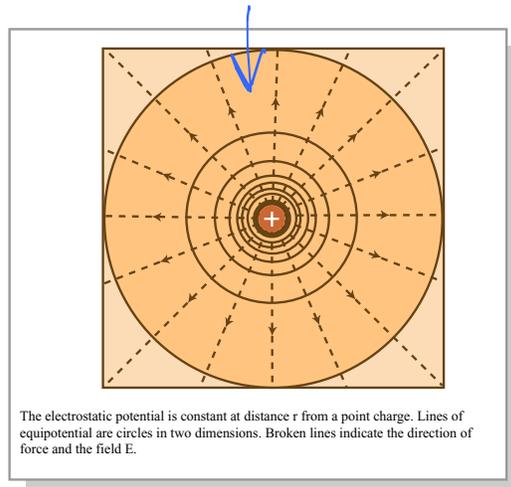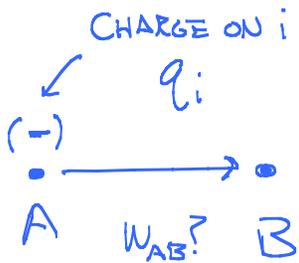
Figure by MIT OCW.

- Electrostatic potentials ϕ are related to the energy of attraction:

$$\frac{W_{AB}}{q_i} = \Delta\phi; \quad = \phi(x=B) - \phi(x=A) = -\int_A^B \vec{E} \cdot \vec{dl}$$

POTENTIAL DIFFERENCE

(Dill and Bromberg)

o   In this equation, w_{AB} is the work to move the species i with charge q_i (e.g., an ion in our solution) from position B, where the electrostatic potential is ϕ_B, to the position A, where the electrostatic potential is ϕ_A. E is the electric field (created by having different charges at A and B), and dl is the displacement vector the test charge moves through to go from A to B.

o   The potential at an arbitrary location in space is determined by bringing the charge to that location from an infinite distance away:

$$-\infty$$
$$\bullet\; -\;-\;-\;-\;-\;-\;-\;-\;-\;-\;-\;\rightarrow\; \overset{X'}{\bullet}$$

$$\Delta\phi = ? = \phi(X') - \phi(x = -\infty)$$

$$\Delta\phi = -\int_{-\infty}^{X'} \vec{E}\cdot d\vec{l} = \frac{w_X}{q_i} \qquad \overset{0}{\diagdown}$$

$$\rightarrow w_X = \Delta\phi\, q_i = \phi(x)\, q_i$$

The electrostatic potential is constant at distance r from a point charge. Lines of equipotential are circles in two dimensions. Broken lines indicate the direction of force and the field E.
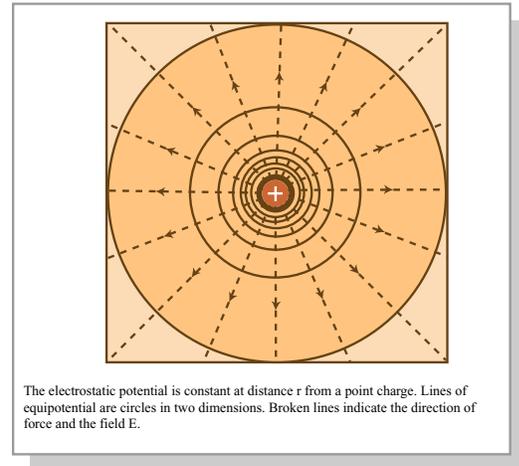
Figure by MIT OCW.

•   We need to introduce a new term in the fundamental equation for the internal energy to account for this new form of energy that arises due to the separation of charges in a system:

$$dU = TdS - PdV + \sum_{i=1}^{C} \mathcal{N}_i dn_i + dw_{+/-}$$

$$\underbrace{\phi_i q_i} = \phi_i dq_i$$

o   The new term accounts for the internal energy of charges added to a system at a potential ϕ.

•   We need to introduce some notation: The charge on each ion q_i is:

$$q_i = z_i\, e\, N_{AV}\, n_i = z_i\, \widetilde{F}\, n_i$$

$$= (\text{VALENCY})(\text{UNIT CHARGE})(\text{AVOGADRO'S \#})(\text{MOLES } i)$$

$$(\text{e.g.,} \; Cu^{++} \; z_i = +2)$$

$$\widetilde{F} \; \text{FARADAY CONSTANT} = \frac{\text{CHARGE}}{\text{MOLE } e^-} = e\, N_{AV}$$

$$\phi_i \, dq_i$$

$$dU = TdS - PdV + \sum_i^c N_i dn_i + \sum_{j=1}^c \phi_i z_i \tilde{\mathcal{F}} dn_i$$

- ...where z_i is the valency of the ion (charge per ion), e is the unit charge, and n_i is the number of moles of ions of type i. We simplify by introducing the Faraday constant F, which is the total charge of a mole of electrons. Recall the Gibbs free energy is:

$$G = H - TS = U + \underline{PV} - \underline{TS}$$

- So the differential of G, accounting for electrostatic effects, is:

$$\Longrightarrow \quad dG = -SdT + VdP + \sum_{i=1}^C \mu_i dN_i + \sum_{j=1}^C \phi_j z_j F \, dn_j$$

  o When each component in the system is ionizable, we can group together the last two sums:

$$dG = -SdT + VdP + \sum_{i=1}^C \mu'_i \, dN_i$$

  o Where μ'_i is called the *electrochemical potential*:

$$\mu'_i = \tilde{\mu}_i = \mu_i + \phi_i z_i \tilde{\mathcal{F}} \qquad \text{ELECTROCHEMICAL POTENTIAL}$$

  ▪ The electrochemical potential contains the intrinsic chemical potential of each component, plus the electrostatic potential acting on charged species. *Just as the chemical potential of a species must be the same in all phases at equilibrium, the electrochemical potential of charged components must be the same in all phases to reach electrochemical equilibrium.*

Application example: Analysis of a battery

Reminder: what's free in Gibbs free energy?

RECALL FROM LECTURE 9:

$$G = U - (-PV) - TS$$

$$dG = VdP - SdT + dw_{OTHER}$$

AT CONST. (T,P):

$$dG = dw_{OTHER}$$

$$\Delta G = w_{OTHER}$$

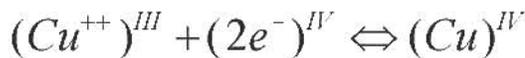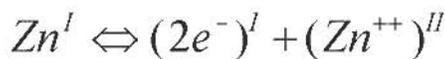FREE ENERGY MEASURES AMOUNT OF WORK I COULD GET OUT OF A PROCESS

Analysis of a Daniell Cell

- Batteries operate by extracting electrical work from a chemical reaction. Just as with chemical reactions, electrochemical reactions can be analyzed using the Gibbs free energy and chemical potential for determination of their equilibrium state at constant temperature and pressure. Let's examine how the second law is applied via Gibbs free energy considerations to a simple battery known as a Daniell cell, as shown below:
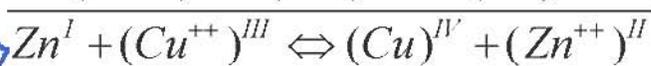
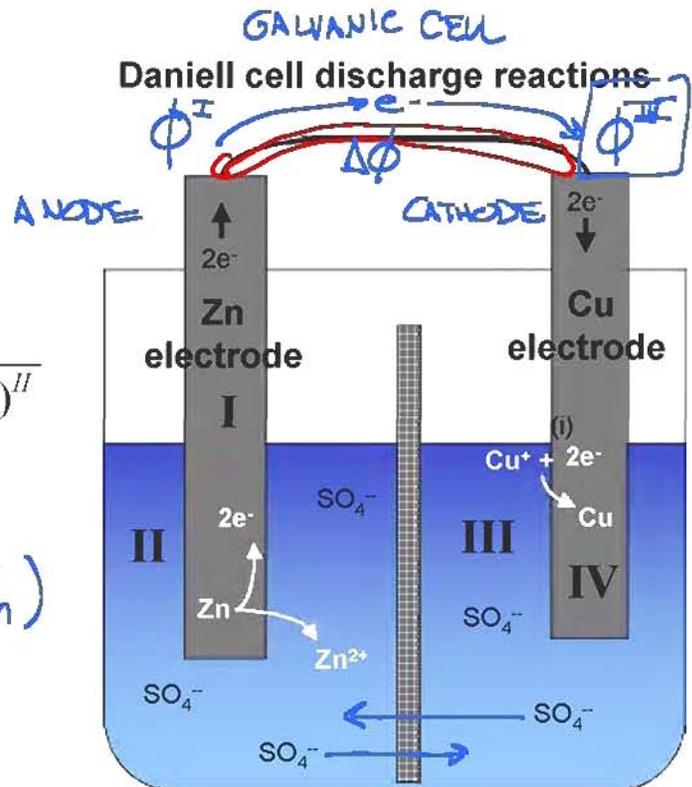$$\Delta \phi = \phi^{II} - \phi^{I}$$

WHAT IS $\Delta \phi$?

HALF-CELL REACTIONS:

$$Zn^{I} \Leftrightarrow (2e^{-})^{I} + (Zn^{++})^{II}$$

$$\frac{(Cu^{++})^{III} + (2e^{-})^{IV} \Leftrightarrow (Cu)^{IV}}{Zn^{I} + (Cu^{++})^{III} \Leftrightarrow (Cu)^{IV} + (Zn^{++})^{II}}$$

OVERALL

$$\Delta \bar{G}_{RXN} = \left(\bar{\mu}_{Zn^{++}} \right)^{II} + \left(\bar{\mu}_{Cu}^{IV} \right) - \left(\bar{\mu}_{Zn}^{I} \right)$$

$$- \left(\bar{\mu}_{Cu^{++}} \right)^{III}$$

GALVANIC CELL

Daniell cell discharge reactions

ϕ^{I} e^{-} ϕ^{II}

$\Delta \phi$

ANODE   CATHODE $2e^{-}$

$2e^{-}$

Zn electrode   **Cu electrode**

I

(i)

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

$2e^{-}$ SO_4^{-} Cu

III

II   **IV**

Zn SO_4^{-}

Zn^{2+}

SO_4^{-} SO_4^{-}

SO_4^{-}

- The battery is composed of a zinc electrode dipped into an aqueous solution of zinc sulfate, and a copper electrode dipped into a solution of copper sulfate. The two solutions are separated by a membrane, which ideally allows only sulfate ions to pass- the Zn^{++} ions and Cu^{++} ions on either side remain separated.

- The quantity of interest in our analysis is the potential difference between the two electrodes $\Delta\phi = (\phi^I - \phi^{IV})$- which determines the current that will flow when the battery is placed in service, and the amount of work that is obtained as the system equilibrates. The work to move two electrons through the external circuit from the zinc electrode to the copper electrode is:

$$\textcircled{1} \quad \tilde{d}w_{+/-} = \Delta\phi \, dq_{e-} = (\phi^{IV} - \phi^I) z_{e-} \tilde{\mathcal{F}} \, dn_{e-}$$

WORK TO MOVE A CHARGE THRU CIRCUIT

FREE ENERGY CHANGE TO DO THIS? (CONST. T,P)

$$dG = \sum_{i=1}^{C} \sum_{j=1}^{P} (\tilde{\mu}_i)^j \, dn_i^j$$

$$= (\tilde{\mu}_{e-})^{IV} dn_{e-}^{IV} + (\tilde{\mu}_{e-})^I dn_{e-}^I$$

CONSTRAINT: $dn_{e-}^{IV} = -dn_{e-}^I$

$$\textcircled{2} \quad dG = \left[(\tilde{\mu}_{e-})^{IV} - (\tilde{\mu}_{e-})^I \right] dn_{e-}^{IV}$$

$$dG = \tilde{d}w_{OTHER}$$

$$\left[(\tilde{\mu}_{e-})^{IV} - (\tilde{\mu}_{e-})^I \right] dn_{e-} = \Delta\phi \, z_{e-}^{-1} \tilde{\mathcal{F}} \, dn_{e-}$$

$$\boxed{\Delta\phi = \frac{-\left[(\tilde{\mu}_{e-})^{IV} - (\tilde{\mu}_{e-})^I \right]}{\tilde{\mathcal{F}}}}$$

Complete analysis of the multi-phase equilibria in a battery

- So how do we determine the potential difference at equilibrium? We've shown that equilibrium at constant temperature and pressure in a closed system requires the Gibbs free energy is minimized. We have shown that the Gibbs free energy is minimized when the chemical potentials of each component are equal to that of the *same* component in the other phases. This holds for both mass transfer between different phases and for chemical reactions. In our electrochemical cell, we have both occurring.

- We carry out our analysis by separating the mass transfer equilibria and chemical reaction equilibria:
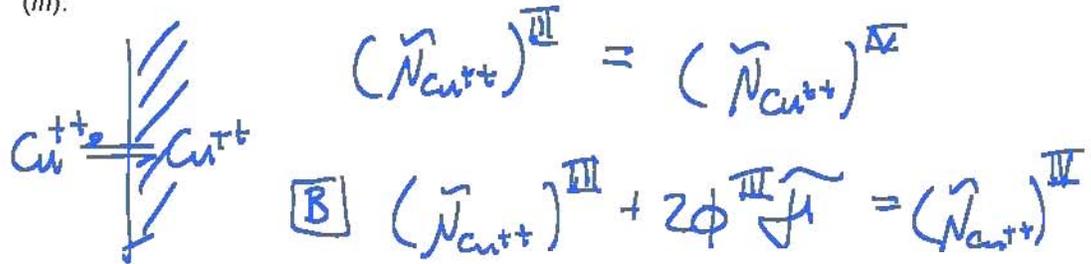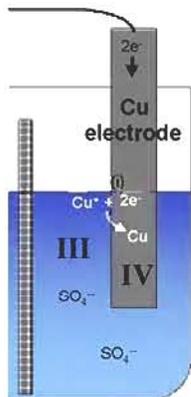
  - *MASS TRANSFER*:

    - **Equilibrium between solid electrode I and liquid solution II.** Zinc ions are being formed in the electrode and transferring to the $ZnSO_4$ solution, thus the chemical potential of Zn in each phase (the solid phase *I* and the liquid phase *II*) must be equal:

    $$Zn \rightleftharpoons Zn^{++} \qquad \left(\tilde{\mu}_{Zn^{++}}\right)^{II} = \left(\tilde{\mu}_{Zn^{++}}\right)^{I}$$

    $$\boxed{A} \quad \mu_{Zn^{++}}^{II} + z_i\phi^{II}\tilde{\mathcal{F}} = \left(\tilde{\mu}_{Zn^{++}}\right)^{I}$$
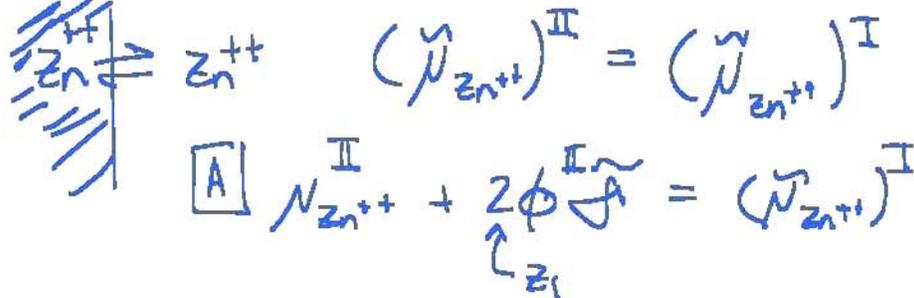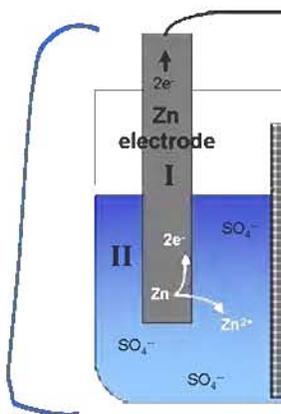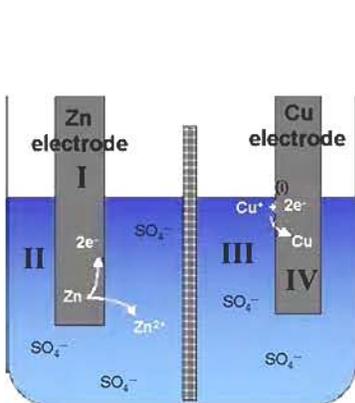
      - We the use the electrochemical potential here, because the ions are charged components.

    - **Equilibrium between solid electrode IV and liquid phase III.** Cu ions are leaving solution to enter the copper electrode and be converted into copper metal- these must also equilibrate between the solid electrode phase (*IV*) and the $CuSO_4$ solution phase (*III*):

    $$Cu^{++} \rightleftharpoons Cu^{++} \qquad \left(\tilde{\mu}_{Cu^{++}}\right)^{III} = \left(\tilde{\mu}_{Cu^{++}}\right)^{IV}$$

    $$\boxed{B} \quad \left(\tilde{\mu}_{Cu^{++}}\right)^{III} + z_i\phi^{III}\tilde{\mathcal{F}} = \left(\tilde{\mu}_{Cu^{++}}\right)^{IV}$$

- **Equilibrium between liquid phases II and III.** Lastly, sulfate ions can pass through the membrane, and so these ions must equilibrate in each liquid phase *II / III*:

$$SO_4^{--} \rightleftharpoons SO_4^{--} \qquad \left(\tilde{N}_{SO_4^{--}}\right)^{II} = \left(\tilde{N}_{SO_4^{--}}\right)^{III}$$

$$N_{SO_4^{--}}^{II} - 2\phi^{II}\tilde{f} = N_{SO_4^{--}}^{III} - 2\phi^{III}\tilde{f}$$

$$z_i$$

APPROXIMATION: $\quad N_{SO_4^{--}}^{II} \cong N_{SO_4^{--}}^{III}$

$$\hookrightarrow \phi^{II} \cong \phi^{III}$$

- o *Chemical reaction:*
  - The two electrode reactions provide a further set of equations for the chemical potentials. We assume in this analysis that the reactions take place with all the components present in the electrode solid phases (i.e., ions from solution enter the solid phase first, and there they react):
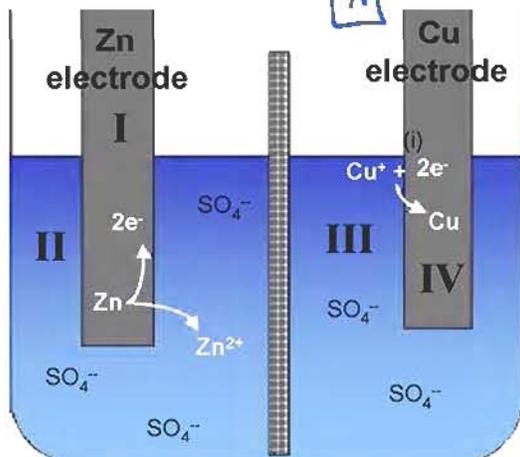
$$\Delta\phi = -\frac{\left[\left(\tilde{N}_{e^-}\right)^{IV} - \left(\hat{N}_{e^-}\right)^{I}\right]}{\tilde{f}}$$

AT EQUILIBRIUM:

$$Zn^{I} = \left(Zn^{2+}\right)^{I} + 2\left(e^{-}\right)^{I} \rightarrow \quad 2\left(\tilde{N}_{e^-}\right)^{I} + \left(\tilde{N}_{Zn^{++}}\right)^{I} - N_{Zn}^{I} = 0$$

$$\left(Cu^{2+}\right)^{IV} + 2\left(e^{-}\right)^{IV} = Cu^{IV} \rightarrow \quad \left(N_{Cu}^{IV}\right) - 2\left(\tilde{N}_{e^-}\right)^{IV} - \left(\tilde{N}_{Cu^{++}}\right)^{IV} = 0$$

OVERALL: $2\left(\tilde{N}_{e^-}\right)^{I} + \underbrace{\left(N_{Zn^{++}}\right)^{I} - N_{Zn}^{I} + N_{Cu}^{IV} - 2\left(\tilde{N}_{e^-}\right)^{IV} - \left(\tilde{N}_{Cu^{++}}\right)^{IV}}_{} = 0$

$\boxed{A}$

$\Delta \bar{G}_{RXN}$ $\boxed{B}$

$$\boxed{\left(\tilde{N}_{Zn^{++}}\right)^{II} - N_{Zn}^{I} + N_{Cu}^{IV} - \left(\tilde{N}_{Cu^{++}}\right)^{III}}$$

$$= + 2\left[\left(\tilde{N}_{e^-}\right)^{IV} - \left(\tilde{N}_{e^-}\right)^{I}\right]$$

$$= - 2\Delta\phi\tilde{f}$$

$$\boxed{\Delta\phi = -\frac{\Delta\bar{G}_{RXN}}{2\tilde{f}}} \quad \text{NERNST EQUATION}$$

Materials Design of Other Current Battery and Fuel Cell Technologies

Lithium ion batteries

o   The basic thermodynamic analysis applied above to explain the voltage obtained in a Daniell cell holds for much more complex batteries of current interest, such as lithium ion batteries:
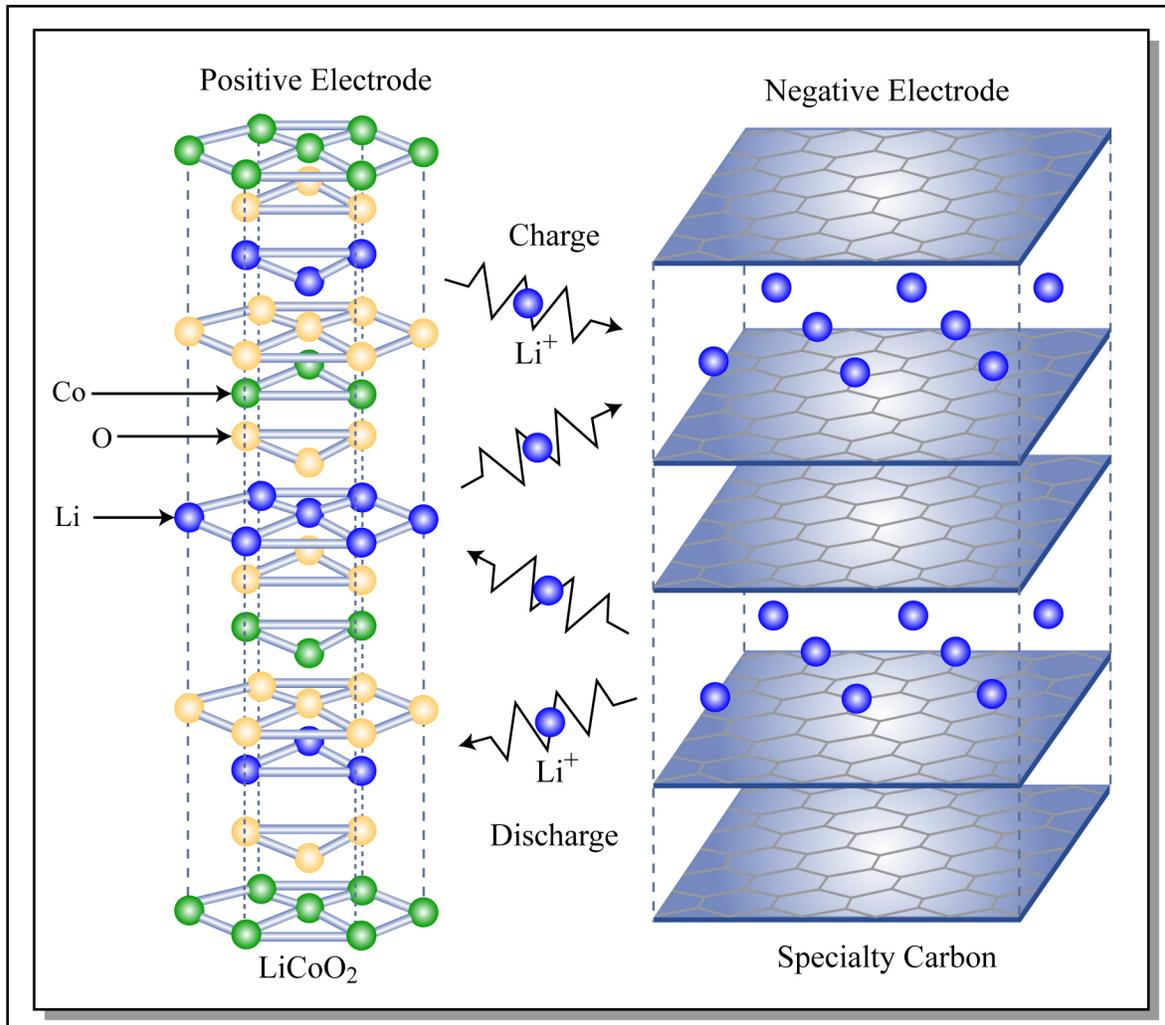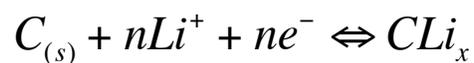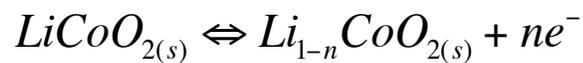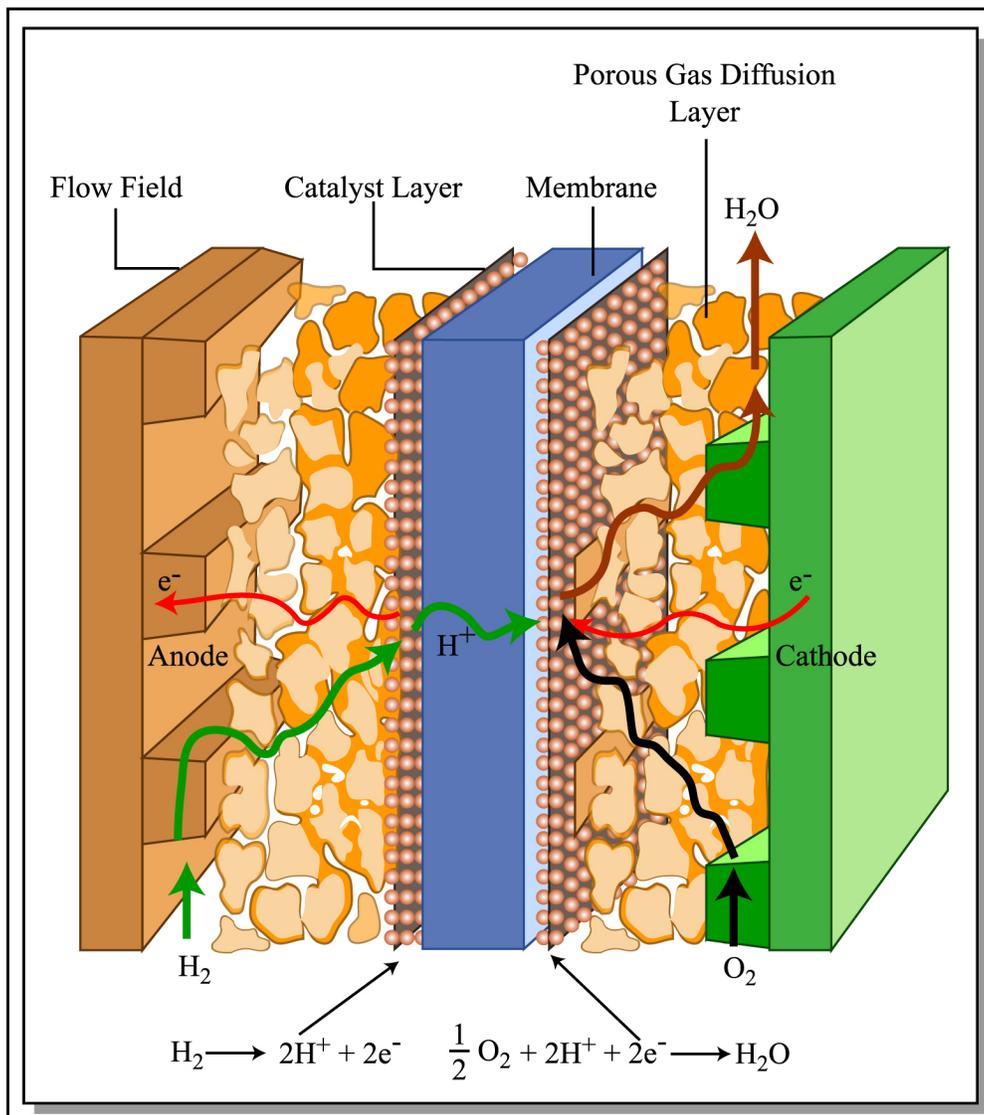

Figure by MIT OCW.

$$LiCoO_{2(s)} \Leftrightarrow Li_{1-n}CoO_{2(s)} + ne^-$$

$$C_{(s)} + nLi^+ + ne^- \Leftrightarrow CLi_x$$

Hydrogen fuel cells

Figure by MIT OCW.

5000 psi!

References

Reference Type: Book
Record Number: 3
Author: Dill, K.; Bromberg, S.
Year: 2003
Title: Molecular Driving Forces
City: New York
Number of Pages: 704
Call Number: QC311.5.D55 2003

Reference Type: Book
Record Number: 16
Author: Crow, D.R.
Year: 1994
Title: Principles and Applications of Electrochemistry
City: New York
Publisher: Blackie Academic & Professional
Number of Pages: 282
Call Number: QD553.C92.1994

Reference Type: Book
Record Number: 10
Author: Gaskell, D.R.
Year: 1981
Title: Introduction to Metallurgical Thermodynamics
City: New York
Publisher: Hemisphere
Number of Pages: 611

Reference Type: Electronic Source
Record Number: 1
Author: Carter, W.C.
Year: 2002
Title: 3.00 Thermodynamics of Materials Lecture Notes

Reference Type: Online Multimedia
Record Number: 33
Author: Company, Ford Motor
URL: http://www.ford.com/en/vehicles/specialtyVehicles/environmental/fuelCell/focusFCVHybrid.htm