II. (30) Low-V Sparks.
A. The force exerted by a He\textsuperscript{2+} ion on an electron 100.0 Å away in a vacuum is calculated to have a magnitude of 4.61×10\textsuperscript{-12} N.
1. What is the direction of this force on the electron, toward the He\textsuperscript{2+} or away from it?
   Inward
2. What is the force if the electron is moved to a distance of 10.0 Å?
\[ F = \frac{eF'}{r^2} \]
\[ F' = 10^2 F = 4.61 \times 10^{-10} N \]
3. Back at a distance of 100.0 Å, the system is put in the dielectric medium H\textsubscript{2}O, having ε\textsubscript{r} = 80.
What is the force now?
\[ F' = \frac{F}{\varepsilon_r} = 5.76 \times 10^{-14} N \]
4. The He\textsuperscript{2+} ion is replaced by a Be\textsuperscript{2+} ion. What is the force on an electron 100.0 Å away in vacuum?
\[ F = \frac{eF'}{r^2} \]
\[ F' = 4.61 \times 10^{-10} N \]
B. Copper and zinc are both good electrical conductors. If a piece of Cu is brought into contact with a piece of Zn, are the electric potentials \( \Phi_{\text{Cu}} \) and \( \Phi_{\text{Zn}} \) the same or different?
   Different
C. (1) Give the definition of the electrochemical potential of component \( i \) in phase \( \alpha \), \( \mu_{\alpha}^i \), defining all terms.
(2) Then state the condition for phase equilibrium for two phases (\( \alpha \) and \( \beta \)) in physical contact in an electrochemical system. (3) Finally, state the condition for reaction equilibrium in a closed electrochemical system.
\[ \mu_{\alpha}^i = \mu_{\beta}^i + \frac{\Delta G_{i}^{\text{chem}}}{\Delta n_{i}} \]
\[ \mu_{\alpha}^i = \text{chemical potential of } i \text{ in phase } \alpha \]
\[ \Delta G_{i}^{\text{chem}} \]
\[ \Delta n_{i} \]
\[ \frac{\Delta G_{i}^{\text{chem}}}{\Delta n_{i}} \]
\[ \Delta G_{i}^{\text{chem}} \] is the change in Gibbs free energy.
\[ \frac{\Delta G_{i}^{\text{chem}}}{\Delta n_{i}} \] is the molar free energy change.
\[ \mu_{\alpha}^i \] is the chemical potential of component \( i \) in phase \( \alpha \).
\[ \mu_{\beta}^i \] is the chemical potential of component \( i \) in phase \( \beta \).
\[ \Delta n_{i} \] is the change in the number of moles of component \( i \).
D. Apply the condition for phase equilibrium in an electrochemical system to the electrons in the electrochemical cell, Cu\textsuperscript{2+}/Zn\textsuperscript{2+} | Ag\textsuperscript{+}/Cu\textsuperscript{+}, to determine whether the emf \( E \) equals \( \mu_{e}^{\text{Cu}} - \mu_{e}^{\text{Zn}} \) or \( \phi_{\text{Cu}^+} - \phi_{\text{Zn}^+} \) of this cell is positive, negative, or zero.
\[ \mu_{e}^{\text{Cu}^+} = \mu_{e}^{\text{Zn}^+} \]
\[ \mu_{e}^{\text{Cu}^+} - \phi_{\text{Cu}^+} = \mu_{e}^{\text{Zn}^+} - \phi_{\text{Zn}^+} \]
\[ \phi_{\text{Cu}^+} - \phi_{\text{Zn}^+} \] is the voltage difference.
Since \( \text{Cu}^{2+} \) and \( \text{Cu}^+ \) are chemically the same.
E. Now consider a piece of Zn metal dipping into an aqueous ZnSO₄ solution. The process, Zn → Zn²⁺ + 2 e⁻, occurs to a very slight extent. Apply the reaction equilibrium condition from C to this process to obtain an expression for the electric potential difference, \( \phi(Zn) - \phi(aq, ZnSO₄) \).

\[
\sum n_i \mu_i = 0 \rightarrow \mu_{Zn^{2+}} + 2 \mu_{e^-} = \mu_{Zn}
\]

\[
\mu_{Zn^{2+}} + 2 F \mu_{e^-} = \mu_{Zn}
\]

\[
\Delta G = \frac{1}{2} \left[ \mu_{Zn^{2+}} + 2 \mu_{e^-} - \mu_{Zn} \right]
\]

III. (35) Multicomponent Phase Diagrams. The accompanying figure shows the phase diagram for the binary Mg-Ni system in the solid-liquid region. This system forms two solid compounds, Mg₂Ni and MgNi₂. Use this diagram to answer the following questions.

A. What is the melting point of pure Mg?

B. How many liquid phases are there? __________

C. How many solid phases are there? __________

D. Identify a component melting point by giving its \( T \) and \( \Delta H \):

E. Identify a component melting point by giving its \( T \) and \( \Delta H \):

F. Suppose you start with 1.00 mol of Mg at 700°C and add Ni. What is the maximum amount of Ni that can be dissolved in Mg at this temperature without producing a solid phase?

G. In the previous question, what is the composition of the solid that first precipitates as Ni is added?

H. Suppose you repeat the dissolution experiment of F starting at 1400°C. How much Ni can you now dissolve in 1.00 mol of Mg without observing the formation of a solid phase?

I. By how much is the melting point of Ni depressed by the addition of 2.00 mol of Mg to 8.00 mol of Ni?

J. What phases are present at labeled point R, and in what amounts, if the system contains 2.00 mol total of Ni and Mg? Also, give \( n_{Mg} \) and \( n_{Ni} \) for each phase present. (Show work clearly.)

\[
X_{Ni} = 0.80 \rightarrow 1 \text{ mol Ni} + 1 \text{ mol Mg} \quad \text{Also, equal amounts of the two solid compounds Mg₂Ni [0.667 Mg, 0.333 Ni] and MgNi₂ [0.333 Mg, 0.667 Ni]}
\]

K. Continuing with the theme of the preceding question, analyze the composition of a system containing 2.00 mol total of Ni and Mg, at the point \( x_{Ni} = 0.60, T = 900°C \). (i.e., determine the compositions of the phases, their amounts, and the amounts of Ni and Mg in each.)

\[
1.20 \text{ mol Ni} + 0.80 \text{ mol Mg (solid)} \quad \text{Two phases in equilibrium}
\]

- Liquid: \( x_{Ni} = 0.36 \) + solid MgNi₂. Relative amounts,

\[
\frac{n_{Ni}}{n_{Mg}} = \frac{(0.667 - 0.36)}{(0.60 - 0.36)} = 0.28. \quad \text{Also,}
\]

\[
\frac{n_{Ni}}{n_{Mg}} = 2.00 \text{ mol, so } n_{Ni} = 1.562 \text{ mol, } n_{Mg} = 0.938 \text{ mol.}
\]

L. Solid: \( 0.158 \text{ mol Ni} + 0.28 \text{ mol Mg.}

IV. (35) Galvanic cells. The cell Pt₁₅H₂(g)/HCl(aq)/AgCl(s)/Ag(c)/Pt₉, was referred to frequently in class, in the text, and in homework problems.

A. Write the half reactions that occur at each electrode.

B. Write the overall electrochemical reaction, and the overall chemical reaction.

C. Which electrode is the anode and which the cathode, for the cell as written?

D. Is this a cell with or without transference.

A. Left: \( H_2(g) \rightarrow 2 H^+(aq) + 2e^- \quad \text{Right:} \quad 2e^- (Pt_R) + 2 AgCl(c) \rightarrow 2 Ag(c) + 2 Cl^-(aq) \)

B. Electrochemical: \( 2e^- (Pt_R) + H_2(g) + 2 AgCl(c) \rightarrow 2 H^+(aq) + 2 Cl^-(aq) + 2 Ag(c) \)

C. Anode: \( Pt_L \mid H_2(g) \mid \) C. Cathode: \( AgCl(c) \mid Ag(c) \mid Pt_R \)

D. Without transference.
E. Give an expression that relates \( E \) for this cell to \( E^o \) and the activities of all reactants and products. At \( P = P^\circ \), several of the activities are very well approximated as unity. Rewrite the expression accordingly.

F. \( E \) for this cell was studied at \( P_{H_2} = 1.00 \text{ atm} \) and 25°C in homework problem 64. The accompanying figure illustrates a least-squares fit of these data. From these results,
1. Determine \( E^o \).
2. Obtain an expression for the stoichiometric activity coefficient of HCl(aq).
3. Calculate \( y_1 \) at \( m = 0.200 \text{ m}^2 \).

\[
E = E^o - \frac{RT}{nF} \ln Q = E^o - \frac{RT}{2F} \ln \frac{[a(H^+)]^2 [a(Cl^-)]^2 [a(H_2)]}{[a(H_2)\text{aq}]}^2 a(H_2)
\]

At \( P = P^\circ \), \( a(H_2) = a(H_2)\text{aq} = 0 \) + \( a(H_2) \times 0 \).

\[
E = E^o - \frac{RT}{2F} \ln \frac{[a(H^+)]^2 [a(Cl^-)]^2}{2} E^o - \frac{RT}{2F} \ln [a(H_2)\text{aq}]
\]

\[
a[\text{HCl}(aq)] = K_a^2 (m/m_o)^2 \quad a[\text{H}_2^+](g) \approx P_{H_2}/P^\circ = 1.01325
\]

\[
\ln \frac{a(H_2)\text{aq}}{[a(H_2)]} = 2 \ln K_a^2 + 2 \ln (m/m_o) - \frac{1}{2} \ln (1.01325)
\]

\[
E + \frac{2RT}{F} \ln \left( \frac{m/m_o}{(1.01325)} \right) = E^o - \frac{2RT}{F} \ln K_a
\]

\[
E' = E^o - \frac{2RT}{F} \ln K_a
\]

1. \( E^o = \text{intercept} = 0.22219 \text{ mV} \)
2. \( bm^{1/2} + cm = -\frac{2RT}{F} \ln K_a \)
   \( \ln K_a = -\frac{2}{2RT} \left[ bm^{1/2} + cm \right] \)
   \( K_a = e^{-\frac{2}{2RT} (bm^{1/2} + cm)} \)
3. \( m = 0.200 \text{ m}^2 \Rightarrow K_a = e^{-0.2605} = 0.770_6 \)