NAME:  

CHEMISTRY 231 — Tellinghuisen  
1st Hour Exam — 2/9/00

Honor Code Pledge and Signature:

Fundamental Constants: \[ R = 8.31451 \text{ J mol}^{-1}\text{ K}^{-1} = 0.0820578 \text{ L atm mol}^{-1}\text{ K}^{-1} = 1.9872 \text{ cal mol}^{-1}\text{ K}^{-1} \]

I. (cont.)

F. \[ \text{Fe}^{3+}(aq) + \text{Cl}^- (aq) \rightleftharpoons \text{FeCl}_2^{2+}(aq) \]

G. \[ K^\circ = \frac{a(\text{FeCl}_2^{2+})}{a(\text{Fe}^{3+})a(\text{Cl}^-)} = \frac{\gamma_{2+}^{(m_2^2/m_0)}}{\gamma_{3+}^{(m_3^2/m_0)}\gamma_{(-1)}^{(m_0/0)}} = K_y \cdot K_m \]

\[ \text{Need } \gamma_{2+}, \gamma_{3+}, + \gamma^\circ \text{. Replace } 1_2 + 2_1 \text{ by } 2_2^2 + 2_1^2 \text{ as appropriate. Thus} \]

\[ \log_{10} \gamma_{2+} = \frac{4}{3} (-0.3595) = -0.479 \Rightarrow \gamma_{2+} = 0.331 \]

\[ \log_{10} \gamma_{3+} = \frac{9}{3} C(3) = -1.078 \Rightarrow \gamma_{3+} = 0.0875 \]

\[ \log_{10} \gamma^\circ = \frac{1}{3} ( ) = -0.1198 \Rightarrow \gamma^\circ = 0.755_9 \]

\[ \therefore K_y = 5.24 \Rightarrow K^\circ = 26.5_6 \]

H. \[ \Delta G^\circ = -RT \ln K^\circ = -8.13_0 \frac{\text{kJ}}{\text{mol}} \]

I. 1) \[ \Delta G_f^\circ [\text{FeCl}_3(aq)] = \Delta G_f^\circ [\text{Fe}^{3+}] + 3 \Delta G_f^\circ [\text{Cl}^-] = -9.7 + 3 \cdot (-131.228) = -398.3_9 \frac{\text{kJ}}{\text{mol}} \]

(2) \[ \Delta G_{aq}^\circ = \Delta G_f^\circ [\text{FeCl}_3(aq)] - \Delta G_f^\circ [\text{FeCl}_3(c)] = -64.4_3 \frac{\text{kJ}}{\text{mol}} \]

(3) \[ \Delta G^\circ = \Delta G_f^\circ [\text{FeCl}_2^{2+}] - \Delta G_f^\circ [\text{Fe}^{3+}] - \Delta G_f^\circ [\text{Cl}^-] \]

\[ \therefore \Delta G^\circ [\text{FeCl}_2^{2+}(aq)] = -8.13_0 - 9.7 - 131.228 \]

\[ = -144.0_6 \frac{\text{kJ}}{\text{mol}} \]
11. (30) The Henry's Law constant (mole-fraction based) for N₂ dissolved in water at 25°C is 86.4 kbar.

A. Give a balanced chemical equation that describes the process of relevance here.
B. Calculate the mole fraction and molality of N₂(g) in equilibrium with N₂(g) at 25°C and P = 1.00 bar (P°). [Take M = 28 for N₂ and 18 for H₂O.]
C. Use these results to evaluate K° on the molality scale for this process. (Assume fugacity and activity coefficients are 1.00.) Then calculate ΔG° for the process, and ΔG°(298) for N₂(g).
D. Now consider Henry's Law for HCl(g), which is a strong electrolyte in solution. Use the equilibrium approach to obtain an expression for HCl(g) (treated as ideal gas) in terms of K°, m, and γ_i, where the latter quantities are the stoichiometric values for HCl(g).

A. \( N₂(aq) \rightleftharpoons N₂(g) \)

B. \( P = K_i \cdot x_i \Rightarrow x_i = \frac{P}{K_i} = \frac{P°}{86.4 \times 10^3 P°} = 1.1574 \times 10^{-5} \)

C. \( \frac{x_i}{x_A} = \frac{m_i}{m_A} = \frac{m_i}{55.5 \text{ mol}} \Rightarrow m_i = 6.42 \times 10^{-4} \)

D. \( \text{HCl(aq) \rightleftharpoons HCl(g)} \Rightarrow K° = \frac{\alpha \left[HCl(g)\right]}{\alpha \left[HCl(aq)\right]} \approx \frac{p}{p°} \cdot \left(\frac{m_i}{m_A}\right)^2 \)

111. (30) Consider the Gibbs-Duhem equation for activity coefficients (γ) in a binary solution, in the form,

\[ x_B \ln \frac{y_B}{y_B} = -x_B \ln \gamma_B - x_A \ln \gamma_A \]

where A represents the solvent and B the solute.

A. Suppose that the activity coefficient \( \gamma_B \) has been determined as a function of composition for the solution. Following the procedure outlined in class, solve for \( \gamma_B \) in Eq. (1) and then obtain an integral expression that could be used to evaluate \( \ln \gamma_B \) as a function of \( x_B \). Include proper integration limits for determination of \( \gamma_B \).

B. In simple solutions, the activity coefficient of the solvent is given by \( \gamma_A = \exp(x_B \cdot \chi_B) \). Use the integral form of the Gibbs-Duhem equation you just derived to obtain an expression for \( \gamma_A \gamma_B \) in such solutions.

C. Next, obtain \( \gamma_B \) as a function of \( x_B \). Then re-express it as a function of \( x_A \).

D. More generally, \( \ln \gamma_A \) might be expressed as a polynomial in \( x_B \). Solve \( \ln \gamma_A = a + bx_B + cx_B^2 + dx_B^3 \), where \( a, b, c, d \) are dimensionless numerical coefficients. As discussed in class, the properties of \( \gamma_A \) and of the integral equation you derived in (A) suffice to determine that \( a = b = 0 \). Explain.

A. \( \text{dln} \gamma_B = \frac{x_A}{x_B} \text{dln} \gamma_A = \frac{x_B - 1}{x_B} \text{dln} \gamma_A = \left(1 - \frac{x_B}{x_B}ight) \text{dln} \gamma_B \)

B. \( \gamma_B = e^{x_B^2} - \ln \gamma_B = x_B^2 \Rightarrow \text{dln} \gamma_B = 2x_B^2 \text{dln} \gamma_B \)

C. \( \gamma_A = A \cdot \gamma_B \), where A is a constant. Also, \( x_B \to 1 \) as \( x_B \to 1 \), so \( A \cdot \chi_B = 1 + A = 1 \).

D. \( \gamma_B = \exp \left[(1 + x_B^2 - 2x_B)\right] = \exp \left[c(1-x_B)\right] = e^{cX_B^2} \)

[Note: As shown in class 1-26, B + c can also be done by variable integration giving \( \ln \gamma_B = cX_B^2 - 2cX_B + \text{const} \). Then the integration constant is set to give \( \gamma_B \rightarrow 1 \) at \( x_B = 0 + \gamma_B \rightarrow 1 \) at \( \chi_B = 1 \).]
D. \( \frac{a}{x} \to 1 \) as \( x \to 0 \), so \( \ln \frac{a}{x} \to 0 \) as \( x \to 0 \). Hence \( a = 0 \).

Suppose we have \( \ln \frac{a}{x} = bx + b \). Then \( d \ln \frac{a}{x} = b \, dx \), and the integral in (A) becomes:

\[
\ln \frac{a}{x} = \int_0^a x \, b' \, dx = \int_0^a \frac{x}{x'} \, b \, dx = b \, x - b \, \ln x + b \, \ln x_0 \to -\infty.
\]

Since \( x \) must remain finite, we cannot have the term \( b \cdot x \) in \( \ln \frac{a}{x} \).

IV. (20) For aqueous solutions of formic acid, \( \text{HCOOH}, K_a = 0.000180 \) at 25°C and \( P \).

A. Give a balanced chemical equation for the process of concern here, and express \( K_a \) in terms of activities of reactants and products. (The molality scale is assumed here.)

B. Neglecting activity coefficients, calculate the \( H^+ \) molality in a 0.150-\( m^+ \) solution.

C. Use this result to compute \( \gamma_\text{a} \) by the Davies equation, and then use this to revise your calculation of the \( H^+ \) molality.

D. Now suppose that KCl is added to this same solution, to a concentration of 0.250 \( m^- \). Redo your calculation of \( \gamma_\text{a} \) and of \( m(H^+) \) for this solution.

A. \( \text{HCOOH} (aq) \rightleftharpoons \text{H}^+ (aq) + \text{HCOO}^-(aq) \)

B. \( K_a \approx \frac{m_+ \cdot m^-}{m_0 - m_+} = \frac{x}{0.150 - x} \to x = 0.0051 \, m_0 \)

C. \( I_m = m_+ = m_0 = 0.0051 \to \gamma_\text{a} = 10 \)

\[
6 \cdot \gamma = 0.926 \to K_a = \frac{x}{\gamma^2} = \frac{x}{0.150 - x} = 2.98 \times 10^{-4}
\]

\( 6 \cdot x = 0.0055 \, m_0 \)

D. \( I_m \approx m_+ (\text{KCl}) + m_0 (\text{HA}) \approx 0.2555 \)

\[
6 \cdot \gamma = 10 - 0.1321 = 0.7377 \to \frac{x^2}{0.150 - x} = 3.30 \times 10^{-4}
\]

\( 6 \cdot x = 0.0068 \, m_0 \)