Chemistry 231 — Tellinghuisen
1st Hour Exam — 2/7/01

Honor Code Pledge and Signature:

Fundamental Constants: \( R = 8.31451 \text{ J mol}^{-1} \text{ K}^{-1} \) \( K_\text{f} = 1.0820578 \text{ atm} \text{ mol}^{-1} \text{ K}^{-1} = 1.9872 \text{ cal mol}^{-1} \text{ K}^{-1} \)

I. (20) Gas-Solution Equilibrium. HCl(g) becomes a strong electrolyte when dissolved in water.
A. Give a balanced chemical equation that describes the process of relevance here.
B. Express \( K^\circ \) for this reaction in terms of activities of reactants and products, and then re-express this in the Henry's Law form, \( P_{\text{HCl}} = \ldots \) [Treat HCl(g) as an ideal gas.]
C. Use tabulated thermodynamic data given below (p. 3) to calculate \( K^\circ \) at 25°C.
D. Estimate \( P_{\text{HCl}} \) in equilibrium with a 5.00-m² solution of HCl. At this concentration, \( \gamma_i = 2.38 \).

A. \( \text{H}^+(\text{aq}) + \text{Cl}^- (\text{aq}) \rightleftharpoons \text{HCl} (\text{s}) \)
B. \( K^\circ = \frac{a_1 [\text{HCl}(\text{g})]}{a_{\text{H}^+} a_{\text{Cl}^-}} = \frac{P_{\text{HCl}} / P^0}{\gamma_{\text{H}^+} \gamma_{\text{Cl}^-}} = \frac{P_{\text{HCl}} / P^0}{\gamma_i^2 (\gamma_i / m)^2} \)
C. \( \Delta G^\circ = \Delta G_f^\circ [\text{HCl}(\text{s})] - \Delta G_f^\circ [\text{H}^+(\text{aq})] - \Delta G_f^\circ [\text{Cl}^- (\text{aq})] \)
\[ = -95.299 - 0 - (-13.123) = 35.929 \text{ kJ/mol} \]
\( K^\circ = \exp \left[ -\frac{\Delta G^\circ}{RT} \right] = 5.08 \times 10^{-7} \)
D. \( P_{\text{HCl}} = P^0 \gamma_i^2 (\gamma_i / m)^2 \rightarrow \rho = P^0 K^\circ (\gamma_i / m)^2 \)
\( \rho = 7.19 \times 10^{-5} P^0 = 0.0539 + \ldots \)

II. (20) Vapor Pressure and Activity. Vapor pressure data for aqueous solutions of sucrose (\( M = 342.3 \)) at 50.0°C yield the practical osmotic coefficient, \( \phi(m) = 1 + b m \), where \( m \) is the sucrose molality and \( b = 0.0986 \).
A. Calculate \( \phi(m) \) and the activity \( a_A \) of the solvent for a solution having \( m = 2.50 \) m.
B. Calculate the activity coefficient \( \gamma_A \) for this same solution.
C. Obtain an expression for the molality scale sucrose activity coefficient \( \gamma_m \), in terms of \( b, m, \) and \( m^* \); and use it to evaluate \( \gamma_m \) for this same 2.50 m solution.

A. \( \phi(2.50 \text{ m}) = 1.2465 = \frac{-\ln a_A}{M_A \nu m} \)
\[ \ln a_A = -1.2465 \times M_A x_A - 2.50 = -0.05614 \]
\[ a_A = 0.9454 \]
B. \( a_A = \left[ \frac{\nu A x_A}{\gamma_A} \right] = \left[ \frac{M_A x_A}{\gamma_A} \right] = \frac{55.509}{55.509 + 2.50} = 0.9569 \)
\[ \gamma_A = 0.988 \]
C. \( \ln \gamma_m = \phi(m) - 1 + \int_0^m \frac{x(m') - 1}{m'} dm' \]
\[ = bm + \int_0^m b dm' = 2 bm \]
\[ \gamma_m = \exp[2 bm] = 1.637 \]
III. (15) Electrolyte Terminology. Consider the dissolution of Mg₃(PO₄)₂ in water.

A. Give the values of ν₊, ν₋, ν₀, and ν₋ for this solute, and calculate ν₂.

\[ \nu_+ = 3; \nu_- = 2; \nu_0 = 5; \nu_{-2} = +2; \nu_{-3} = -3 \]

\[ \nu_{2} = \nu_+ \nu_+ \nu_0 \rightarrow \nu_{2} = (2 \times 3 \times 5) = 30 \]

B. Suppose that for a 0.040 mol/l solution of Mg₃(PO₄)₂ in water, \( \alpha = 0.45 \). Identify the ion pairs in this solution, and calculate molalities of all species.

\[ \nu_{P} = \text{MgPO}_{4}^- \]

\[ \text{Mg}^{2+} - 0.45 \times 3 \times 0.04 \text{ mol l}^{-1} = 0.054 \text{ mol l}^{-1} \]

\[ \nu_{p} = 0.12 \text{ mol l}^{-1} - \text{m} \text{Mg} \text{PO}_{4}^- = 0.066 \text{ mol l}^{-1} \]

\[ \nu_{p} = 0.080 - 0.066 = 0.014 \text{ mol l}^{-1} \]

C. Calculate the ionic strength of this solution.

\[ I_{m} = \frac{1}{2} \sum z_i^2 m_i = \frac{1}{2} [2^2 (0.054) + (-1)^2 (0.066) + (-3)^2 (0.014)] \]

\[ = 0.204 \text{ mol l}^{-1} \]

IV. (35) Solubility, \( K_{sp} \), and Standard Thermochemical Data. BaF₂ (\( M = 175.34 \)) is only slightly soluble in water at 25°C and \( pF \), having \( K_{sp} = 1.84 \times 10^{-7} \).

A. Write a balanced chemical equation for the process for which \( K \) is the solubility product \( K_{sp} \).

B. Use the given value of \( K_{sp} \) to estimate the solubility of BaF₂ in water at 25°C. [Hint: First assume activity coefficients are 1.0; then use your results in the Davies equation to estimate \( \gamma \) and refine your estimate of the solubility. (One such refinement will suffice.)]

C. The CRC handbook lists the solubility as 0.12 g/100 cc at 25°C. Account for any difference between this result and your estimate in part C.

D. Using thermodynamic data tabulated above (p. 3), calculate the following quantities for BaF₂(aq):

\[ \Delta H_{f}, \Delta S_{f}, \text{and} \Delta G_{f} \]

E. Similarly, calculate \( S_{m}^{\circ} \) for BaF₂(aq).

A. \[ \text{BaF}_2 (s) \rightarrow 2 \text{Ba}^{2+} (aq) + 2 \text{F}^- (aq) \]

B. \[ K_{sp} = \alpha [\text{Ba}^{2+}][\alpha (\text{F}^-)^2] = \gamma_{+}^2 m_{+} m_{-} \]

\[ \gamma_{+} = 1 \rightarrow 1.84 \times \gamma_{-} = m \text{ (2m)}^2 = 4 m^3 \]

\[ \leq \left[ m = \frac{0.00358 \text{ mol l}^{-1}}{m} \right] \]

\[ I_{m} = \frac{1}{2} [2^2 m + (-1)^2 2m] = 3 m = 0.01075 \text{ mol l}^{-1} \]

\[ \gamma_{+} = 0.808 \rightarrow m_{+} = 8.72 \times 10^{-6} \Rightarrow m = 0.00436 \text{ mol l}^{-1} \]

C. 0.12 g/100 cc ≈ 1.209 g/mol. \( K_{sp} \approx 0.0068 \text{ mol l}^{-1} \). This is greater than found from \( K_{sp} \). Difference due to 2+ pairing.

D. \[ \Delta H_{f}^\circ = -537.64 + 2 (-332.63) = -1202.90 \text{ kJ mol}^{-1} \]

\[ S_{m}^{\circ} = 9.6 + 2 (-13.8) = -18.0 \frac{\text{cal} \text{K}^{-1} \text{mol}^{-1}} \]

E. \[ \Delta S_{f} = \frac{1}{2} [\Delta H_{f}^\circ - \Delta G_{f}^\circ] = S_{m}^{\circ} [\text{BaF}_2 (c)] - S_{m}^{\circ} [\text{elements}] \]

\[ \Delta S_{f} = -174.74 \frac{\text{cal} \text{K}^{-1} \text{mol}^{-1}} \]

\[ S_{m}^{\circ} [\text{BaF}_2 (c)] = 90.84 \frac{\text{cal} \text{K}^{-1} \text{mol}^{-1}} \]
V. (35) Excess Functions. The molar excess Gibbs energy of solution for mixtures of methylcyclohexane (MCH) and tetrahydrofuran (THF) at 30.0°C can be represented as a function of the mole fraction \( x \) of MCH,

\[
G_m = RT a x (1-x);
\]

\( a = 0.4857; \)

A. Calculate \( \Delta G_{\text{mix}} \) for mixing 2.00 mol MCH and 3.00 mol THF at 30.0°C.

B. Starting with the thermodynamic definition of \( G_m \), take \( \partial \alpha_m \) of \( G_m \) to obtain an expression for \( \ln \gamma_i \).

C. Apply this result to the expression given above for MCH/THF solutions to obtain an expression for \( \gamma_{\text{MCH}} \) in terms of \( x \) and \( a \).

D. Obtain numerical values for \( \gamma_{\text{MCH}} \) for the solution in part A and also in the limit \( x \to 1 \). Does your latter result confirm what convention is being used here for activities?

A. \[
\Delta G_{\text{mix}} = \Delta G_{\text{id}} + G^E = nRT \sum x_i \ln x_i + nG_m^E
\]

\[
= 5.00 RT \left[ 0.40 \ln(0.40) + 0.60 \ln(0.60) \right] + 5.00RT
\]

\[
= -3.365RT + 5.00 \times 0.11657RT
\]

\[
= -2.782RT = -7.012kT
\]

B. \[
G_m^E = \Delta G_{\text{mix}} - \Delta G_{\text{id}} = nRT \sum x_i \ln(\gamma_i) - nRT \sum x_i \ln x_i
\]

\[
= nRT \sum x_i \ln \gamma_i = RT \sum x_i \ln \gamma_i
\]

\[
\left( \frac{\partial G_m^E}{\partial \ln \gamma_i} \right)_{T,P,n_j} = RT \ln \gamma_i \rightarrow \ln \gamma_i = \frac{1}{RT} \left( \frac{\partial G_m^E}{\partial \ln \gamma_i} \right)_{T,P,n_j}
\]

C. \[
\frac{\partial G_m^E}{\partial n_A} = \frac{\partial}{\partial n_A} \left( n_A + n_B \right) G_m^E = G_m^E + n \frac{\partial G_m^E}{\partial n_A}
\]

\[
= G_m^E + n \frac{\partial G_m^E}{\partial n_A} \frac{\partial n_A}{\partial x_A} = G_m^E + n \frac{\partial G_m^E}{\partial \gamma_i} \frac{\partial \gamma_i}{\partial x_A}
\]

\[
\sum \ln \gamma_i = \frac{1}{RT} \left( \frac{\partial G_m^E}{\partial \ln n_A} \right) = a x (1-x) + (1-x) a (1-2x)
\]

\[
= a x (1-x)[x + 1 - 2x] = ax^2
\]

D. \( x_A = 0.4 \rightarrow x_B = 0.6 \rightarrow \gamma_A = 1.191 \)

\( x_A = 1.0 \rightarrow x_B = 0 \rightarrow \gamma_A = 1 \quad [\text{Caw. I}] \)