Exercise A.1 K = 5360 at 298 K for the mixed-phase reaction:

 $\frac{1}{2}$ H₂ (g) + AgCl (s) \rightarrow Ag (solid) + Cl⁻ (aq) + H⁺ (aq) If a(Ag⁺) = a(Cl⁻) = 0.55, what is P(H₂) at equilibrium?

Exercise A.2 $K = 1.42 \times 10^{-5}$ at 298 K for the mixed-phase reaction

A (g, P=0.35 bar) + H₂O (liq)
$$\rightarrow$$
 B (aq, x=0.0020) + C (aq, x=0.0020)

Assume A behaves as an ideal gas, the activity coefficient of B is 2.5, and that B and C are not ions. What is the activity coefficient of C?

Problem 1 K = 1.00 at 298 K for the mixed-phase reaction

A(g) + H₂O (liq) \rightarrow C (aq, x=0.010) + D (g, P = 0.10 bar)

Assume the aqueous solution is ideal, C is not an ion, and that A and D behave like ideal gases. What is P(A) at equilibrium?

Exercise B. Consider the two equilibria below, which control the partitioning of formaldehyde between the gas and aqueous phases:

CH₂=O (g) \rightarrow CH₂=O (aq) Henry's Law constant k_{CH2=O} = 22.5 bar CH₂=O (aq) + H₂O (liq) \rightarrow CH₂(OH)₂ (aq) K_c = 45.6

If $P(CH_2O) = 1.00 \times 10^{-9}$ bar, what is $[CH_2(OH)_2 (aq)]$ at equilibrium? Note that K_c has standard state of 1 molar for all solution-phase species, including H₂O (liq). Assume the activity coefficient equals 1.00 for all aqueous phase species

Problem 2. Consider the two equilibria below, which control the partitioning of benzoic acid between the gas and aqueous phases:

 $\begin{array}{ll} C_7H_7O_2\ (g) \ \rightarrow \ C_7H_7O_2\ (aq) & \mbox{Henry's Law constant } k(C_7H_7O_2) = 2.05\ \mbox{Torr}\\ C_7H_7O_2\ (aq) \ + H_2O\ (liq) \ \rightarrow \ C_7H_6O_2^-\ (aq) \ + H_3O^+ & \mbox{K}_{\mbox{c}} = 1.13 \times 10^{-6}\\ \mbox{If } [C_7H_6O_2^-\ (aq)] \ = 6.3 \times 10^{-6}\ \mbox{moles/L and the pH= 5.0, what is the partial pressure of } C_7H_7O_2\ \mbox{at equilibrium? Note that } K_{\mbox{c}}\ \mbox{has standard state of 1 molar for all solution-phase species, including } H_2O\ \ (liq). Assume the activity coefficient equals 1.00\ \mbox{for all aqueous phase species} \end{array}$

Exercise C. Compute the ionic strengths of the following solutions:

- a) 0.0010 moles of solid Na₂SO₄ dissolved in $1.0 \text{ kg of H}_2\text{O}$
- b) 0.0010 moles of solid La₂(SO₄)₃ dissolved in 1.0 kg of H₂O

Exercise D. Compute the activities each of the ions in the solutions from Exercise C.

Problem 3. Compute the activities of each of the ions in the following solutions

a) 0.0010 moles of solid La(NO₃)₃ dissolved in 1.00 kg of H₂O

b) 0.0010 moles of solid NaCl plus 0.0010 moles KBr dissolved in 1.00 kg of H₂O

Problem 4

a) What information, <u>if any</u>, are you missing that you need to calculate γ_{\pm} for a solution of 0.010 moles of solid NaCl dissolved in 1.0 kg of acetonitrile?

b) What is the difficulty, <u>if any</u>, with using the Debye-Huckel Limiting Law to compute the activity coefficient of 0.0010 moles of solid $Ba(NO_3)_2$ plus 0.0010 moles Na_2SO_4 dissolved in 1.00kg of H_2O ?

Exercise E. Compute E°_{cell} for the following reactions:

- a) Na⁺ (aq) + Ag (s) \rightarrow Na (s) + Ag⁺ (aq)
- b) Hg₂Cl₂ (s) + H₂ (g) \rightarrow 2 H⁺ (aq) + 2 Cl⁻ (aq) + 2 Hg (l)
- c) Hg_2^{2+} (aq) + 2 Na (s) \rightarrow 2 Hg (liq) + 2 Na⁺ (aq)

Problem 5. The reaction: Ni (s) + 2 AgBr (s) \rightarrow Ni²⁺ (aq) + 2 Ag (s) + 2 Br⁻ (aq)

a) Calculate E°_{cell} for from the reduction potentials for the half reactions.

b) Calculate ΔG_r° and K for the reaction from E_{cell}°

c) Calculate E_{cell} and ΔG_r using the Debye-Huckel Limiting Law .

d) Is the reaction spontaneous in the forward direction?

<u>Given</u>: the Ni²⁺ (aq) is in one cell compartment as 0.0010 moles NiCl₂ dissolved in 1 L of water, and the Br⁻ is in a separate compartment as 0.0020 moles NaBr dissolved in 1 L of water.

Variations to Consider:

1) Given E_{cell} or ΔG_r for a reaction, and information about the concentrations or pressures of all but one species participating in the reaction, compute the activity of the last species.

2) In Exercise E.c, why do you get the wrong answer if you just subtract the two reduction potentials?

3) Plot E_{cell} vs ξ for a particular reaction.

- 4) Given concentrations at equilibrium, compute K, E°_{cell} , and ΔG°_{r} .
- 5) Le Chatelier's principle problems for ionic or non-ionic solutions.