- 6-A. Consider the following equilibria in aqueous solution:

- (1) $Ag^+ + Cl^- \rightleftharpoons AgCl(aq)$ $K = 2.0 \times 10^3$ (2) $AgCl(aq) + Cl^- \rightleftharpoons AgCl_2^ K = 9.3 \times 10^1$
- (3) $AgCl(s) \rightleftharpoons Ag^{+} + Cl^{-}$
- $K = 1.8 \times 10^{-10}$
- (a) Calculate the numerical value of the equilibrium constant for the reaction $AgCl(s) \implies AgCl(aq)$.
- (b) Calculate the concentration of AgCl(aq) in equilibrium with excess undissolved solid AgCl.
- $AgCl(s) + Cl^{-}$.
- 6-C. Find [La3+] in the solution when excess solid lanthanum iodate, La(IO3)3, is stirred with 0.050 M LiIO3 until the system reaches equilibrium. Assume that IO3 from La(IO3)3 is negligible compared with IO3 from LiIO3.
- 6-D. Which will be more soluble (moles of metal dissolved per liter of solution), Ba(IO₃)₂ ($K_{\rm sp} = 1.5 \times 10^{-9}$) or Ca(IO₃)₂ ($K_{\rm sp} = 7.1 \times 10^{-7}$)? Give an example of a chemical reaction that might occur that would reverse the predicted solubilities.
- 6-H. If each compound is dissolved in water, will the solution be acidic, basic, or neutral?

- (a) $Na^{+}Br^{-}$ (e) $(CH_{3})_{4}N^{+}CI^{-}$ (b) $Na^{+}CH_{3}CO_{2}^{-}$ (f) $(CH_{3})_{4}N^{+}$ \bigcirc $-CO_{2}^{-}$
- (c) NH₄Cl⁻
- (g) Fe(NO₃)₃
- (d) K₃PO₄
- 6-4. Write the expression for the equilibrium constant for each of the following reactions. Write the pressure of a gaseous molecule, X, as P_X .
- (a) $3Ag^{+}(aq) + PO_4^{3-}(aq) \rightleftharpoons Ag_3PO_4(s)$
- (b) $C_6H_6(l) + \frac{15}{2}O_2(g) \implies 3H_2O(l) + 6CO_2(g)$
- 6-6. From the equations

$$HOC1 \rightleftharpoons H^+ + OC1^ K = 3.0 \times 10^{-8}$$

$$HOCl + OBr^- \rightleftharpoons HOBr + OCl^ K = 15$$

find the value of K for the reaction $HOBr \rightleftharpoons H^+ + OBr^-$.

6-7. (a) A favorable entropy change occurs when ΔS is positive. Does the order of the system increase or decrease when ΔS is positive?

(b) A favorable enthalpy change occurs when ΔH is negative. Does the system absorb heat or give off heat when ΔH is negative?

(c) Write the relation between ΔG , ΔH , and ΔS . Use the results of parts (a) and (b) to state whether ΔG must be positive or negative for a spontaneous change.

6-9. The formation of tetrafluoroethylene from its elements is highly exothermic:

$$2F_2(g) + 2C(s) \rightleftharpoons F_2C \rightleftharpoons CF_2(g)$$

Fluorine Graphite Fetrafluoroethylene

(a) If a mixture of F₂, graphite, and C₂F₄ is at equilibrium in a closed container, will the reaction go to the right or to the left if F₂ is added?

(b) Rare bacteria from the planet Teflon eat C₂F₄ and make Teflon for their cell walls. Will the reaction go to the right or to the left if these bacteria are added?

(c) Will the reaction go right or left if solid graphite is added? (Neglect any effect of increased pressure due to the decreased volume in the vessel when solid is added.)

(d) Will the reaction go right or left if the container is crushed to one-eighth of its original volume?

(e) Does the equilibrium constant become larger or smaller if the container is heated?

6-14. Find the concentration of Cu⁺ in equilibrium with CuBr(s) and 0.10 M Br⁻.

6-19. A solution contains 0.050 0 M Ca²⁺ and 0.030 0 M Ag⁺. Can 99% of Ca²⁺ be precipitated by sulfate without precipitating Ag⁺? What will be the concentration of Ca²⁺ when Ag₂SO₄ begins to precipitate?

6-23. Identify the Lewis acids in the following reactions:

(a)
$$BF_3 + NH_3 \rightleftharpoons F_3\overline{B} - \stackrel{\dagger}{N}H_3$$

(b)
$$F^- + AsF_5 \rightleftharpoons AsF_6^-$$

6-36. Calculate [H⁺] and pH for the following solutions:

(a) 0.010 M HNO₃ (d) 3.0 M HCl

(b) $0.035~\rm M~\rm KOH$ (e) $0.010~\rm M~\rm [(CH_3)_4N^+]OH^-$ (c) $0.030~\rm M~\rm HCl$ Tetramethylammonium hydroxide

6-39. An acidic solution containing 0.010 M La³⁺ is treated with NaOH until La(OH)₃ precipitates. At what pH does this occur?