ACID-BASE EQUILIBRIA

1. Explain why $Fe(H_2O)_6^{3+}$ is a stronger acid than $Fe(H_2O)_6^{2+}$.

2. What is the conjugate base of $Al(H_2O)_6^{3+}$?

3. Write the chemical equation that explains the acidity of an aqueous $CuSO_4$ solution and calculate the pH of a 0.20 M $CuSO_4$ solution.

4. Write the chemical equation that explains the acidity of an aqueous $NiSO_4$ solution and calculate the pH of a 0.10 M $NiSO_4$ solution.

DISSOLUTION AND THE SOLUBILITY-PRODUCT CONSTANT

Refer to Appendix D for K_{sp}'s and assume that all solutions are at 25 °C.

5. Write the chemical equation and the K_{sp} expression for the dissolution process of each of the following substances:
a) CoS **b)** HgI_2 **c)** $Al(OH)_3$

6. Write the chemical equation and the K_{sp} expression for the dissolution process of each of the following substances:
a) $Ba_3(PO_4)_2$ **b)** $MgNH_4PO_4$ **c)** Ag_2S

7. Express the K_{sp} expression of each of the compounds in Exercise 5 in terms of its molar solubility (x).

8. Express the K_{sp} expression of each of the compounds in Exercise 6 in terms of its molar solubility (x).

9. Write the chemical equations for the dissolution of each of the following substances and determine their molar solubilities:
a) AgI **b)** CaF_2

10. Write the chemical equations for the dissolution of each of the following substances and determine their molar solubilities:
a) $PbBr_2$ **b)** $BaSO_4$

11. The solubility of mercury(I) chloride is 0.0020 $g \cdot L^{-1}$. What is the K_{sp} of Hg_2Cl_2? Note: mercury(I) exists as Hg_2^{2+} ions.

12. The solubility of lithium phosphate is 0.39 $g \cdot L^{-1}$. What is the K_{sp} of lithium phosphate? Neglect the reaction of PO_4^{3-} with water.

13. The Au^{3+} concentration in a saturated solution of gold(III) chloride is 33 μM. What is the solubility-product constant of $AuCl_3$?

14. What is the molar solubility of silver chromate? What is the concentration of silver ions in a saturated solution of silver chromate?

15. What is the pH of saturated barium hydroxide?

16. Calculate the pH of a saturated solution of zinc hydroxide.

17. A 386-mg sample of $PbCl_2$ is washed with 10.0 mL of 0.10 M HCl. What is the maximum fraction of $PbCl_2$ that can dissolve in the wash?

18. What is the molar solubility of calcium fluoride in each of the following?
a) water **b)** 0.15 M KF **c)** 0.20 M $Ca(NO_3)_2$

19. What is the molar solubility of lead(II) sulfate in:
a) water **b)** 0.20 M $MgSO_4$ **c)** 0.11 M $Pb(NO_3)_2$

20. What is the molar solubility of $Fe(OH)_3$ in a solution buffered at pH = 5.00? What is the solubility at pH = 8.00?

PRECIPITATION AND SEPARATION OF IONS

21. Rank the following sulfides in order of decreasing solubility:
CdS CoS CuS FeS MnS

22. Rank the following sulfides in order of decreasing solubility:
CuS Cu_2S Ag_2S SnS ZnS

23. Would a precipitate form in a solution that contained the following concentrations?
- **a)** 0.01 M NaCl and 0.02 M $Pb(NO_3)_2$
- **b)** 1.0 mM $AgNO_3$ and 1 μM NaCl
- **c)** 5.0 mM KI and 2.0 mM $Pb(NO_3)_2$

24. The Co^{2+} and Cu^{2+} ions in a solution that is 0.01 M each are to be separated by precipitation of CuS.
- **a)** What sulfide ion concentration (to one significant figure) should be used to obtain optimum separation?
- **b)** What is the $[Cu^{2+}]$ after precipitation at this sulfide ion concentration?

25. Construct the reaction table for mixing 20.0 mL of 0.124 M $Ca(NO_3)_2$ and 30.0 mL of 0.0852 M KF.
- **a)** What mass of precipitate forms?
- **b)** What is the concentration of the excess reactant at equilibrium?
- **c)** What is the concentration of the limiting reactant at equilibrium?

26. Construct the reaction table for mixing 55 mL of 0.10 M $AgNO_3$ and 75 mL of 0.20 M K_2CrO_4.
- **a)** What mass of precipitate forms?
- **b)** What is the concentration of the excess reactant at equilibrium?
- **c)** What is the concentration of the limiting reactant at equilibrium?

27. Construct the reaction table for mixing 35.0 mL of 0.175 M $AgNO_3$ and 25.0 mL of 0.200 M KI.
- **a)** What mass of AgI forms?
- **b)** What is the concentration of the excess reactant at equilibrium?
- **c)** What is the concentration of the limiting reactant at equilibrium?

28. To what pH (to 0.1 pH unit) should a solution that is 0.020 M each in Ca^{2+} and Cd^{2+} ions be adjusted in order to best separate ions by precipitation of one of the hydroxides? What are the concentrations of the metal ions after the pH is adjusted to this value?

29. To what pH (to 0.1 pH unit) should a solution that is 0.030 M in Pb^{2+} and 0.030 M in Mg^{2+} be buffered in order to obtain maximum separation of the ions by precipitation of one of the hydroxides? What are the concentrations of the metal ions after the solution is buffered at this pH?

30. An acidic solution is 5 mM in each of the following metal ions: Co^{2+}, Ba^{2+}, Cu^{2+} and Zn^{2+}.
- **a)** Which of the metals precipitate as their hydroxides at pH = 6.00?
- **b)** Which of the metals precipitate as their hydroxides at pH = 8.00?
- **c)** At what pH does $Ba(OH)_2$ begin to precipitate?

31. Indicate whether or not a precipitate would form when the following solutions are mixed:
- **a)** 5.0 mL of 0.10 M HCl and 5.0 mL of 1.0 mM $Pb(NO_3)_2$
- **b)** 5.0 mL of 0.10 M KOH and 5.0 mL of 0.10 mM $Mn(NO_3)_2$
- **c)** 5.0 mL of 0.10 M Na_2SO_4 and 5.0 mL of 0.10 mM $Ba(NO_3)_2$

32. What $[I^{1-}]$ is needed to start precipitation of AgI from a saturated solution of AgCl?

33. Solid NaCl is added to a solution that is 0.10 M in Pb^{2+} and 0.10 M in Ag^{1+}.
- **a)** Which compound precipitates first?
- **b)** What is the concentration of the first ion precipitated when the second ion starts to precipitate?

COMPLEX IONS

Refer to Table 8.3 for formation constants

34. What is the concentration of free Cu^{2+} in a solution made by mixing 25.0 mL of 1.00 M $CuSO_4$ and 1.00 L of 0.500 M NH_3?

35. What is the concentration of free Ni^{2+} in a solution made by mixing 10.0 mL of 0.652 M $NiSO_4$ and 475 mL of 2.00 M NH_3?

36. What is the free silver ion concentration in a 0.24 M $Ag(NH_3)_2^{1+}$ solution?

37. What is the free cyanide ion concentration in a 0.10 M $Fe(CN)_6^{3-}$ solution?

COMPETING EQUILIBRIA

38. Use the data in Table 8.3 and Appendix D to determine the equilibrium constants for the following reactions.

a) $AgCN(s) + CN^{1-} \rightleftharpoons Ag(CN)_2^{1-}$

b) $CuS(s) + 4NH_3(aq) \rightleftharpoons Cu(NH_3)_4^{2+} + S^{2-}$

39. Use the data in Table 8.3 and Appendix D to determine the equilibrium constants for the following reactions.

a) $Fe(OH)_2(s) + 6CN^{1-} \rightleftharpoons Fe(CN)_6^{4-} + 2OH^{1-}$

b) $Ag_2S(s) + 4NH_3(aq) \rightleftharpoons 2Ag(NH_3)_2^{1+} + S^{2-}$

40. Consider the dissolution of CaF_2 in hydrochloric acid.

a) Write the reaction for the dissolution.

b) What is the equilibrium constant for the reaction?

41. Consider the dissolution of $Al(OH)_3$ in hydrochloric acid.

a) Write the reaction for the dissolution.

b) What is the equilibrium constant for the reaction?

42. The pH of a solution that is 0.05 M in Zn^{2+} is slowly raised.

a) At what pH does $Zn(OH)_2$ (K_{sp}= $4.5x10^{-17}$) begin to precipitate?

b) Refer to Table 8.3 and determine the equilibrium constant for the reaction: $Zn(OH)_2(s) + 2OH^{1-}(aq) \rightleftharpoons Zn(OH)_4^{2-}(aq)$

c) At what pH does the solid $Zn(OH)_2$ dissolve again?

43. At what pH should a solution be saturated with H_2S to separate 0.020 M Pb^{2+} and Zn^{2+}? What are the concentrations of the ions after separation?

44. At what pH should a solution be saturated with H_2S to separate 0.010 M Co^{2+} and Fe^{2+}? What are the concentrations of the ions after separation?

MISCELLANEOUS PROBLEMS

45. Indicate whether each of the following salts produces an acidic, a neutral, or a basic solution in water.

$Fe(NO_3)_3$	KF	$AlBr_3$
$ZnSO_4$	KCl	NH_4Cl

46. For which of the following compounds does solubility increase as the pH of the solution is lowered?

$CaCO_3$	PbI_2	$PbSO_3$
ZnS	AgBr	$Mg(OH)_2$

47. Consider the following equilibrium:

$PbI_2(s) + 3OH^{1-}(aq) \rightleftharpoons Pb(OH)_3^{1-}(aq) + 2I^{1-}(aq)$

Use LeChâtelier's Principle to predict the effect on the solubility of PbI_2 of each of the following:

a) H^{1+} (H_3O^{1+}) ions are added.

b) The concentration of I^{1-} is decreased.

c) The amount of PbI_2 is increased.

d) The pH of the solution is increased.

48. To image the upper gastrointestinal (GI) tract for medical evaluation of intestinal disorders, a suspension of $BaSO_4$ is ingested. The heavy element Ba absorbs X-rays so that the soft tissue of the intestine becomes visible to X-ray imaging. In order to minimize the physiological absorption of Ba, which is toxic, the suspension is frequently prepared using a Na_2SO_4 solution. Calculate the difference in the Ba^{2+} solubility in a solution of pure water and a solution of 0.10 M Na_2SO_4. (This concentration has approximately the same osmotic balance as cellular fluids.) The K_{sp} of $BaSO_4$ is $1.1x10^{-10}$.

49. In a foundry that produces plumbing fittings, the brass components are cleaned with nitric acid, which dissolves and oxidizes the copper and zinc of brass resulting in a solution of Cu^{2+} and Zn^{2+}. Given that K_{sp} of $Cu(OH)_2$ is 2.2×10^{-20} and K_{sp} of $Zn(OH)_2$ is 4.5×10^{-17}, determine the pH to which the effluent must be adjusted to precipitate the copper and zinc hydroxides such that the levels of Cu and Zn in the water are below the federal clean water standards of 50. ppm? Are the solubilities of these two species sufficiently different such that the copper and zinc could be separated during this neutralization process? Assume the density of the water sample is 1.00 $g \cdot cm^{-3}$.

50. Kidney stones are caused by the precipitation of either calcium oxalate, $Ca(C_2O_4)$, or calcium phosphate, $Ca_3(PO_4)_2$, in the kidneys. If the normal concentration of Ca^{2+} in the kidneys is 2.5 mM, at what concentration of oxalate ion will kidney stones begin to form? K_{sp} of $Ca(C_2O_4) = 2.3 \times 10^{-9}$.

51. Explain why the solubility of PbF_2 increases with the addition of HNO_3, but the solubility of $PbCl_2$ is unaffected.

52. The compound hydroxyapatite, $Ca_5(PO_4)_3OH$, forms the hard enamel layer that coats our teeth. Drinking fluorinated water, or brushing with fluorinated tooth paste, replaces some of the OH^{1-} ions with F^{1-}. The two dissolution reactions

$$Ca_5(PO_4)_3OH \rightleftharpoons 5Ca^{2+} + 3PO_4^{3-} + OH^{1-} \quad \text{and}$$

$$Ca_5(PO_4)_3F \rightleftharpoons 5Ca^{2+} + 3PO_4^{3-} + F^{1-}$$

have comparable equilibrium constants. Which of the two materials, $Ca_5(PO_4)_3OH$ or $Ca_5(PO_4)_3F$, is predicted to be more resistant to the weak acids formed during food digestion? (Hint: What effect do the relative base strengths of the hydroxide and fluoride ions have?)

53. A sample of drinking water was found to contain 500 ppm of Fe^{3+}, which is well above clean water levels. How much phosphate ion must be added to 1000 L of the water supply in order to precipitate excess iron from the solution so that the final Fe^{3+} concentration is less than 50. ppm? Assume the density of the water sample is 1.00 $g \cdot cm^{-3}$