

# Chapter 17

## Additional Aspects of Equilibrium

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### Chapter 17 suggested problems

10th Ed. - 17.x: 11, 13, 15, 17, 19, 21, 27, 37, 39, 41, 45, 49, 53, 55, 59, 76, 87

11th Ed. - 17.x: 15, 17, 19, 21, 23, 29, 39, 41, 43, 47, 51, 55, 57, 61, 80, 91

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## Chapter Objectives

After completing this chapter, you should, *at a minimum*, be able to do the following. This information can be found in my lecture notes for this and other chapters and also in your text.

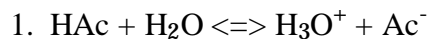
1. Correctly answer all of the questions suggested above and in the quiz for this chapter.
  2. Define basic terms such as common-ion effect, buffer, buffer capacity, Henderson-Hasselbach equation, titration, standard solution, titrant, buret, equivalence point, end point, indicator, homogeneous equilibria, heterogeneous equilibria, saturated solution, solubility product constant, solubility, molar solubility, slightly soluble, complex ion, ligand, coordination compounds, coordination number, formation constant, dissociation constant.
  3. Make basic equilibrium calculations involving the common-ion effect.
  4. Explain the basic theory of what a buffer is and how a buffer works.
  5. Calculate the pH and other properties of buffer solutions using both equilibrium theory and the Henderson-Hasselbach equation.
  6. Describe the basic features of an acid-base titration, including the shapes of the fundamental types of acid-base titrations.
  7. Calculate the pH at any point in an acid-base titration.
  8. Distinguish between the solubility of a substance and its solubility product constant.
  9. Calculate  $K_{sp}$  and use  $K_{sp}$  to calculate the solubility of slightly soluble substances.
  10. Make solubility calculations in which the common-ion effect plays a role and be able to theoretically explain the correctness of your results.
  11. Use the reaction quotient  $Q$  to predict whether or not precipitation will occur when two or more solutions are mixed.
  12. Explain when and how pH can play a role in the solubility of slightly soluble substances.
  13. Understand and explain the basic theory of complex ions, including nomenclature and equilibrium theory with respect to the formation and dissociation of complex ions.
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# Class Notes

## I. The common-ion effect

A. common-ion effect - a shift in the equilibrium occurs when a solute is added that participates in the equilibrium

B. What is the pH of a 0.25 M solution of acetic acid ( $K_a = 1.8 \times 10^{-5}$ )?



2.  $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Ac}^-] / [\text{HAc}]$

3.

	[HAc]	[H <sub>3</sub> O <sup>+</sup> ]	[Ac <sup>-</sup> ]
<b>initial</b>	0.25	0	0
<b>x</b>	-x	+x	+x
<b>eqb</b>	0.25 - x	x	x

4.  $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Ac}^-] / [\text{HAc}] = x^2 / 0.25 - x$

5. Using the quadratic equation  $x = 2.1 \times 10^{-3}$

6. If  $x = 2.1 \times 10^{-3}$  then  $[\text{H}_3\text{O}^+] = 2.1 \times 10^{-3}$  M and  $\text{pH} = 2.67$

C. What is the pH of a 0.25 M solution of acetic acid which is also has an acetate concentration of 0.10 M?

1.

	[HAc]	[H <sub>3</sub> O <sup>+</sup> ]	[Ac <sup>-</sup> ]
<b>initial</b>	0.25	0	.10
<b>x</b>	-x	+x	+x
<b>eqb</b>	0.25 - x	x	.10 + x

2.  $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Ac}^-] / [\text{HAc}] = (x)(.1 + x) / (.25 - x)$

3. Using the quadratic equation  $x = 4.5 \times 10^{-5}$

4. If  $x = 4.5 \times 10^{-5}$  then  $[\text{H}_3\text{O}^+] = 4.5 \times 10^{-5}$  M and  $\text{pH} = 4.35$

## II. Buffers

A. Solutions with the ability to resist pH change when acids or bases are added

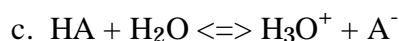
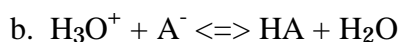
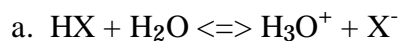
B. Most commonly consist of a conjugate acid/base pair which do not react with each other

1.  $\text{H}_2\text{CO}_3 / \text{HCO}_3^-$  - important physiological buffer

2.  $\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$  - important biochemical buffer

C. Mechanism of action: the buffer consist of either an  $\text{HA}/\text{A}^-$  or  $\text{B}/\text{HB}^+$  pair in solution

1. Addition of an acid  $\text{HX}$  to an  $\text{HA}/\text{A}^-$  buffer solution



d. Observations

i. Whether  $\text{HX}$  is a strong or weak acid, it will all be consumed because:

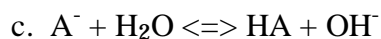
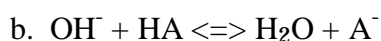
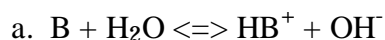
ii. All of the hydronium ion produced in step a. is consumed in step b.

iii. The only hydronium ion remaining in solution is that produced by the dissociation of weak acid  $\text{HA}$  in step c.

iv. The  $[\text{HA}]$  increases because it is produced by the reaction in step b.,

v. Therefore the solution pH decreases but only slightly, if to a measurable extent

2. Addition of a base  $\text{B}$  to an  $\text{HA}/\text{A}^-$  buffer solution



d. Observations

i. Whether  $\text{B}$  is a strong or weak base, it will all be consumed because:

ii. All of the hydroxide ion produced in step a. is consumed in step b.

iii. The only hydroxide ion remaining in solution is that produced by the dissociation of weak base  $\text{A}^-$  in step c.

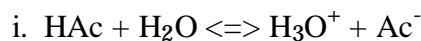
- iv. The  $[A^-]$  increases because it is produced by the reaction in step b.,
- v. Therefore the solution pH increases but only slightly, if to a measurable extent

3. Note that since  $[HA]$  and  $[A^-]$  are finite, the buffering ability of a buffer solution can eventually be overwhelmed

#### D. Important characteristics of buffers: solution pH and buffer capacity

1. Determining the pH of a buffer solution depends on the  $K_a$  of acid, on  $[HA]$  and  $[A^-]$ , and is treated as a common-ion problem

a. What is the pH of a buffer solution that has an acetic acid ( $K_a = 1.8 \times 10^{-5}$ ) concentration of .700 M and an acetate ion concentration of 0.600 M? Assume 1.00 L of solution.



ii.  $K_a = [H_3O^+] \cdot [Ac^-] / [HAc]$

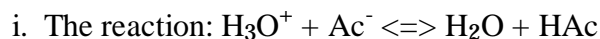
iii.

	[HAc]	[H <sub>3</sub> O <sup>+</sup> ]	[Ac <sup>-</sup> ]
<b>initial</b>	0.700	0	0.600
<b>x</b>	-x	+x	+x
<b>eqb</b>	0.700 - x	x	0.600 + x

iv.  $K_a = [H_3O^+] \cdot [Ac^-] / [HAc] = (x)(0.600 + x) / 0.700 - x$

v. Using the quadratic equation  $x = 2.1 \times 10^{-5}$  and pH = 4.68

b. How is pH affected if 1.00 mL of 1.00 M HCl is added to the above solution?



ii. 1.00 mL of 1.00 M HCl =  $2.1 \times 10^{-5}$  mole of  $H_3O^+$

iii. Must account for changes in concentrations before calculating solution pH; note that solution volume changes from 1000 mL to 1001 mL

	[H <sub>3</sub> O <sup>+</sup> ]	[Ac <sup>-</sup> ]	[HAc]
<b>initial moles</b>	0.001	0.600	0.700
<b>x</b>	-.001	-.001	+.001

<b>moles at completion</b>	0	0.599	0.701
<b>concentration (M)</b>	0	0.598	0.700

iv. What happens to solution pH?

	<b>[HAc]</b>	<b>[H<sub>3</sub>O<sup>+</sup>]</b>	<b>[Ac<sup>-</sup>]</b>
<b>initial</b>	0.700	0	0.598
<b>x</b>	-x	+x	+x
<b>eqb</b>	0.700 - x	x	0.598 + x

v.  $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Ac}^-] / [\text{HAc}] = (x)(0.598 + x) / 0.700 - x$

vi. Using the quadratic equation  $x = 2.1 \times 10^{-5}$  and  $\text{pH} = 4.68$

c. What change in pH occurs if 1.00 mL of 1.00 M HCl is added to 1.00 L of pure water?

i.  $1.0 \times 10^{-3}$  mole  $\text{H}_3\text{O}^+$  / 1001 mL solution =  $1 \times 10^{-3}$  M  $\text{H}_3\text{O}^+$   
;  $\text{pH} = 3$

ii. so the solution pH changes from 7 to 3

2. Buffer capacity: the amount of acid or base a buffer can absorb (i.e., react with) before changes in pH occur

a. Buffer capacity depends on the concentrations of acid and conjugate base in the solution

#### E. Preparation of buffer solutions

1. The pH of a prepared buffer solution depends on the  $\text{p}K_a$  of the acid and on the concentrations of acid and conjugate base in the solution

a. For any weak acid  $K_a = [\text{H}_3\text{O}^+] \cdot [\text{A}^-] / [\text{HA}]$

b.  $[\text{H}_3\text{O}^+] = K_a ([\text{HA}] / [\text{A}^-])$

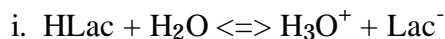
c.  $-\log [\text{H}_3\text{O}^+] = -\log K_a - \log ([\text{HA}] / [\text{A}^-])$

d.  $\text{pH} = \text{p}K_a - \log ([\text{HA}] / [\text{A}^-]) = \text{p}K_a + \log ([\text{A}^-] / [\text{HA}])$

e. This equation is called the Henderson-Hasselbach equation

2. Using the Henderson-Hasselbach equation

a. What is the pH of a buffer solution that is 0.12 M in lactic acid ( $K_a = 1.4 \times 10^{-4}$ ) and 0.10 M in lactate ion?



ii.  $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Lac}^-] / [\text{HLac}]$

iii.

	[HAc]	[H <sub>3</sub> O <sup>+</sup> ]	[Ac <sup>-</sup> ]
<b>initial</b>	0.12	0	0.10
<b>x</b>	-x	+x	+x
<b>eqb</b>	0.12 - x	x	0.10 + x

iv.  $K_a = [\text{H}_3\text{O}^+] \cdot [\text{Lac}^-] / [\text{HLac}] = (x)(0.10 + x) / 0.12 - x$

v. Using the quadratic equation  $x = 1.68 \times 10^{-4}$  and  $\text{pH} = 3.78$

b. How many moles of ammonium chloride must be added to 2.0 L of a 0.10 M ammonia ( $K_b = 1.8 \times 10^{-5}$ ) solution to form a buffer solution with a pH of 9? Assume that addition of the salt does not change the volume of the solution.

i. Since  $K_b = 1.8 \times 10^{-5}$  for ammonia, for ammonium ion  $K_a = 5.56 \times 10^{-10}$ ;  $\text{p}K_a = 9.255$

ii.  $\text{pH} = \text{p}K_a + \log ([\text{A}^-] / [\text{HA}])$

iii.  $\text{pH} - \text{p}K_a = \log ([\text{A}^-] / [\text{HA}]) = \log [\text{A}^-] - \log [\text{HA}]$

iv.  $-\text{pH} + \text{p}K_a + \log [\text{A}^-] = \log [\text{HA}]$

v.  $\text{antilog} (-\text{pH} + \text{p}K_a + \log [\text{A}^-]) = [\text{HA}]$

vi.  $\text{antilog} (9.255 + 9.00 + (-1.00)) = 0.180 \text{ M}$

vii. Since there are two liters of solution, a total of 0.360 moles of salt must be added to the solution to make the ammonium concentration 0.180 M.

c. A buffer is made by adding 0.300 moles of acetic acid ( $K_a = 1.8 \times 10^{-5}$ ) and 0.300 moles of acetate ion to enough water to make a liter of solution. What is the pH of the buffer? What is the pH of the buffer after the addition of 0.020 moles of sodium hydroxide? What is the pH of the buffer after the addition of 0.020 moles of hydrochloric acid? Assume that addition of the HCl and NaOH do not result in a volume change.

i. What is the pH of the buffer?

a. Given  $K_a = 1.8 \times 10^{-5}$ ,  $\text{p}K_a = 4.75$

b. Since  $[\text{HAc}] = [\text{Ac}^-]$  then  $\text{pH} = \text{pK}_a = 4.75$

ii. What is the pH of the buffer after the addition of 0.020 moles of sodium hydroxide?

a.  $\text{HAc} + \text{OH}^- \rightleftharpoons \text{H}_2\text{O} + \text{Ac}^-$

b.

	[HAc]	[OH <sup>-</sup> ]	[Ac <sup>-</sup> ]
<b>initial moles</b>	0.300	0	0.300
<b>x</b>	-.02	-.02	+.02
<b>eqb moles</b>	0.280	0	0.320
<b>eqb conc</b>	0.280	0	0.320

c.  $\text{pH} = \text{pK}_a + \log \left( \frac{[\text{Ac}^-]}{[\text{HAc}]} \right) = 4.75 + \log \left( \frac{0.320}{0.280} \right) = 4.80$

d. Is it safe to ignore the contribution to the pH due to the dissociation of HAc?

e.  $\text{HAc} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Ac}^-$

f.

	[HAc]	[H <sub>3</sub> O <sup>+</sup> ]	[Ac <sup>-</sup> ]
<b>initial</b>	0.280	0	0.320
<b>x</b>	-x	+x	+x
<b>eqb</b>	0.280 - x	x	0.320 + x

g.  $\text{pK}_a = \log \left( \frac{x(0.320 + x)}{0.280 - x} \right)$

h. Using the quadratic equation  $x = 1.58 \times 10^{-5}$  and  $\text{pH} = 4.80$

iii. What is the pH of the buffer after the addition of 0.020 moles of hydrochloric acid?

a.  $\text{Ac}^- + \text{H}_2\text{O} \rightleftharpoons \text{HAc} + \text{OH}^-$

b.

	[Ac <sup>-</sup> ]	[H <sub>3</sub> O <sup>+</sup> ]	[HAc]
<b>initial moles</b>	0.300	0	0.300

<b>x</b>	-0.02	-0.02	+0.02
<b>eqb moles</b>	0.280	0	0.320
<b>eqb conc</b>	0.280	0	0.320

$$c. \text{pH} = \text{pK}_a + \log \left( \frac{[\text{Ac}^-]}{[\text{HAc}]} \right) = 4.75 + \log \left( \frac{0.280}{0.320} \right) = 4.69$$

### III. Acid-base titrations

A. A titration is a form of chemical analysis in which a solution with a known concentration is used to determine the concentration of a chemical in an unknown solution

1. Note: used to determine amounts or concentrations, not chemical identity of unknown substances.
2. The known solution is called a standard solution or a standard titrant.
3. A buret is used to deliver the titrant, and the unknown solution and the titrant are mixed together as the titrant is added.
4. Equivalence point: this is the point in a titration at which the amount of titrant added is equal to the amount of unknown chemical in the solution being titrated.
  - a. The equivalence point is reached when there is a very specific physical change in the mixture of titrant and unknown solution, such as a color change or the formation of a precipitate.
5. Indicators: chemicals used to indicate when the equivalence point is reached. Usually this indication is in the form of a color change.
  - a. End point: the point at which an indicator's color change takes place. Hopefully the equivalence point of the reaction and the end point of the indicator coincide.
  - b. Not all titration reactions require an indicator

B. Types of titrations

1. Acid-base
2. Precipitation
3. Redox

C. Titration calculations

1. A solution of HCl is standardized using solid sodium carbonate. If you begin with 0.263 g of sodium carbonate and must add exactly 28.35 mL of

HCl to reach the equivalence point, what is the acid concentration?

- Procedure: dissolve the sodium carbonate in water, then add HCl from a buret until the equivalence point is reached.
- Begin with a balanced equation for the reaction:  

$$\text{Na}_2\text{CO}_3(\text{aq}) + 2 \text{HCl}(\text{aq}) \Rightarrow 2 \text{NaCl}(\text{aq}) + \text{H}_2\text{O}(\text{l}) + \text{CO}_2(\text{g})$$
- $(0.263 \text{ g S.C.}) \times (1 \text{ mol S.C./}106.0 \text{ g S.C.}) \times (2 \text{ mol HCl/}1 \text{ mol S.C.})$   
 $= 0.00496 \text{ mol HCl}$
- $(0.00496 \text{ mol HCl/}28.35 \text{ mL}) \times (1000 \text{ mL/}1\text{L}) = 0.175 \text{ M HCl}$

#### D. Acid-base titrations and titration curves

### IV. Solubility equilibria

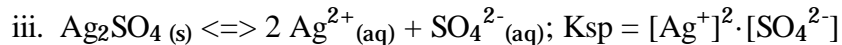
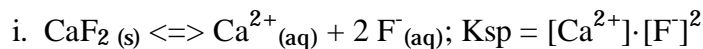
#### A. Homogeneous and heterogeneous equilibria

- Homogeneous equilibria: all reactants and products are in the same phase, e.g. the Haber process
- Heterogeneous equilibria: reactants and products are not in the same phase
  - $\text{CaCO}_3(\text{s}) \rightleftharpoons \text{CaO}(\text{s}) + \text{CO}_2(\text{g})$
  - The concentration of a pure liquid or solid does not change during the course of a reaction and is omitted from equilibrium constant expressions; only substances with concentrations that can vary during the course of the reaction are included in the equilibrium constant expression
  - While their concentration does not effect the position of the equilibrium, the substance(s) must be present for the reaction to occur

#### B. Solubility and equilibria

- Consider a saturated aqueous solution of an ionic compound
  - A saturated solution is one containing the maximum amount of dissolved solute and in which undissolved solute remains in the vessel
  - The reaction equation for dissolution of an ionic compound can be described and an equilibrium constant expression can be stated
    - $\text{BaSO}_4(\text{s}) \rightleftharpoons \text{Ba}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq})$
    - $K_c = [\text{Ba}^{2+}] \cdot [\text{SO}_4^{2-}] / [\text{BaSO}_4]$
    - $K_c \cdot [\text{BaSO}_4] = [\text{Ba}^{2+}] \cdot [\text{SO}_4^{2-}] = K_{sp}$

c.  $K_{sp}$  - the solubility product (solubility product constant) - describes the equilibrium between slightly soluble or "insoluble" ionic compounds and their ions in a saturated aqueous solution



## 2. Solubility and the solubility constant

a.  $K_{sp}$  describes the equilibrium between slightly soluble or insoluble ionic compounds and their ions in a saturated aqueous solution

b. Solubility - the amount of substance that will dissolve to form a saturated solution

i. Often expressed in grams of solute per liter of solution

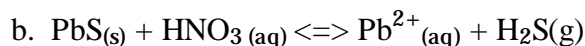
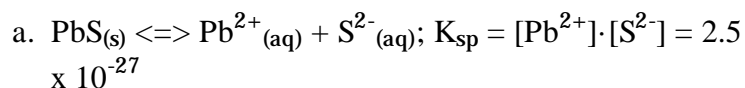
ii. Molar solubility - the number of moles of solute per liter of saturated solution

c. Solubility can be affected in various ways

i. Temperature

ii. common-ion effect

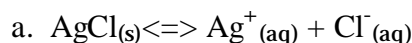
iii. Addition of substances that react with the insoluble solid



c. This always a consideration when the anion of the ionic compound is hydroxide, sulfide, carbonate, sulfite, etc.

## C. Calculating $K_{sp}$ and using $K_{sp}$ to calculate solubility

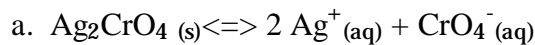
1. A saturated AgCl solution is found to have  $[\text{Ag}^{+}] = 1.35 \times 10^{-5} \text{ M}$ . What is the  $K_{sp}$  of AgCl?



b.  $K_{sp} = [\text{Ag}^{+}][\text{Cl}^{-}]$

c. Since  $[\text{Ag}^{+}] = [\text{Cl}^{-}]$  (based on stoichiometry),  $K_{sp} = [\text{Ag}^{+}][\text{Cl}^{-}] = (1.35 \times 10^{-5} \text{ M})(1.35 \times 10^{-5} \text{ M}) = 1.82 \times 10^{-10}$

2. A saturated solution of silver chromate is found to have  $[\text{Ag}^+] = 1.30 \times 10^{-4} \text{ M}$ . What is the  $K_{\text{sp}}$  of  $\text{Ag}_2\text{CrO}_4$ ?



b.  $K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}]$

c.

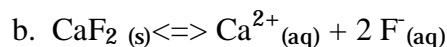
	$[\text{Ag}_2\text{CrO}_4]$	$[\text{Ag}^+]$	$[\text{CrO}_4^{2-}]$
<b>initial</b>		0	0
<b>x</b>		+2x	+x
<b>eqb</b>		2x	x

d. Since  $[\text{Ag}^+] = 2x = 1.30 \times 10^{-4} \text{ M}$ ,  $x = 1.30 \times 10^{-4} / 2 = 6.50 \times 10^{-5} = [\text{CrO}_4^{2-}]$

e.  $K_{\text{sp}} = [\text{Ag}^+]^2 [\text{CrO}_4^{2-}] = (2x)^2 (x) = 4x^3 = 4(6.50 \times 10^{-5})^3 = 1.1 \times 10^{-12}$

3. If the molar solubility of calcium fluoride is  $1.24 \times 10^{-3} \text{ M}$ , find the  $K_{\text{sp}}$  of calcium fluoride.

a. The molar solubility tells us that for every liter of solution,  $1.24 \times 10^{-3}$  moles of calcium fluoride dissolves and dissociates



c.  $K_{\text{sp}} = [\text{Ca}^{2+}] [\text{F}^-]^2$

d.

	$[\text{CaF}_2]$	$[\text{Ca}^{2+}]$	$[\text{F}^-]$
<b>initial</b>		0	0
<b>x</b>		+x	+2x
<b>eqb</b>		x	2x

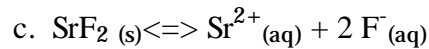
e.  $x = 1.24 \times 10^{-3}$

f.  $K_{\text{sp}} = [\text{Ca}^{2+}] [\text{F}^-]^2 = (x)(2x)^2 = 4x^3 = 4(1.24 \times 10^{-3})^3 = 7.63 \times 10^{-9}$

4. If  $1.1 \times 10^{-2}$  grams of strontium fluoride dissolves in 100 mL of water, find the  $K_{\text{sp}}$  of  $\text{SrF}_2$ .

a.  $(1.1 \times 10^{-2} / 100 \text{ mL}) \times (1000 \text{ mL} / \text{L}) = 0.11 \text{ SrF}_2 \text{ g/L}$

b.  $(0.11 \text{ SrF}_2 \text{ g/L}) \times (1 \text{ mol SrF}_2 / 125.62 \text{ g SrF}_2) = 8.76 \times 10^{-4} \text{ mol/L}$   
(molar solubility of  $\text{SrF}_2$ )



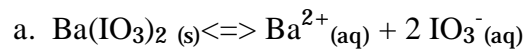
d.  $K_{\text{sp}} = [\text{Sr}^{2+}][\text{F}^-]^2$

e.

	$[\text{SrF}_2]$	$[\text{Sr}^{2+}]$	$[\text{F}^-]$
<b>initial</b>		0	0
<b>x</b>		+x	+2x
<b>eqb</b>		x	2x

f.  $x = 8.76 \times 10^{-4} \text{ mol/L}$

g.  $K_{\text{sp}} = [\text{Sr}^{2+}][\text{F}^-]^2 = (x)(2x)^2 = 4x^3 = 4(8.76 \times 10^{-4})^3 = 2.69 \times 10^{-9}$

5. The  $K_{\text{sp}}$  of barium iodate is  $6.0 \times 10^{-10}$ . What is its molar solubility?

b.  $K_{\text{sp}} = [\text{Ba}^{2+}][\text{IO}_3^-]^2$

c.

	$[\text{Ba}(\text{IO}_3)_2]$	$[\text{Ba}^{2+}]$	$[\text{IO}_3^-]$
<b>initial</b>		0	0
<b>x</b>		+x	+2x
<b>eqb</b>		x	2x

d.  $K_{\text{sp}} = (x)(2x)^2 = 4x^3$

e.  $x = (K_{\text{sp}} / 4)^{1/3} = 5.31 \times 10^{-4} \text{ M}$

6. The  $K_{\text{sp}}$  of antimony (III) sulfide is  $1.7 \times 10^{-93}$ . What is its molar solubility?

b.  $K_{\text{sp}} = [\text{Sb}^{3+}]^2[\text{S}^{2-}]^3$

c.

	$[\text{Sb}_2\text{S}_3]$	$[\text{Sb}^{3+}]$	$[\text{S}^{2-}]$
<b>initial</b>		0	0
<b>x</b>		+2x	+3x
<b>eqb</b>		2x	3x

d.  $K_{\text{sp}} = (2x^2)(3x)^3 = (4x^2)(27x^3) = 108x^5$

e.  $x = (K_{sp} / 108)^{1/5} = 1.1 \times 10^{-19} \text{ M}$

f. How many molecules of  $\text{Sb}_2\text{S}_3$  dissolve in an equilibrium solution?  
 $(1.1 \times 10^{-19} \text{ mol / L}) \times (6.02 \times 10^{23} \text{ molecules / 1 mole}) = 66,220$   
 molecules

g. How many liters of water will it take to dissolve 1 mole of  $\text{Sb}_2\text{S}_3$ ?  
 $(1.1 \times 10^{-19} \text{ mol / L})^{-1} = 9.09 \times 10^{18} \text{ L}$ , or about 13 cubic miles of  
 water to dissolve 339.7 grams of the substance

## V. Factors that affect solubility - the common-ion effect

A. The presence of ions similar to those in an ionic compound will affect ionization of the compound

1. This effect is as predicted by LeChatelier's principle

B. The molar solubility of silver (I) chloride is  $1.35 \times 10^{-5}$  (or 0.0019 g/L). What is the silver ion concentration of a saturated silver chloride solution? If solid  $\text{AgCl}$  is placed in 1.00 L of a 0.55 M  $\text{NaCl}$  solution, what will the silver ion concentration be?

1. Initially: since  $\text{AgCl}_{(s)} \rightleftharpoons \text{Ag}^+_{(aq)} + \text{Cl}^-_{(aq)}$  and since the molar solubility of  $\text{AgCl}$  is  $1.35 \times 10^{-5}$  then  $[\text{Ag}^+] = 1.35 \times 10^{-5} \text{ M}$

2. In the  $\text{NaCl}$  solution

	$[\text{AgCl}]$	$[\text{Ag}^+]$	$[\text{Cl}^-]$
<b>initial</b>		0	0.55
<b>x</b>		+x	+x
<b>eqb</b>		x	0.55 + x

3.  $K_{sp} = [\text{Ag}^+][\text{Cl}^-] = (x)(.55 + x)$

4.  $0 = x^2 + .55x - K_{sp}$

5.  $x = 3.3 \times 10^{-10} = [\text{Ag}^+]$

C. Calculate the solubility of barium sulfate in pure water and then in 0.010 M barium nitrate.  $K_{sp} = 1.1 \times 10^{-10}$

1.  $\text{BaSO}_4 (s) \rightleftharpoons \text{Ba}^{2+}_{(aq)} + \text{SO}_4^{2-}_{(aq)}$

2. In pure water

	$[\text{BaSO}_4]$	$[\text{Ba}^{2+}]$	$[\text{SO}_4^{2-}]$
<b>initial</b>		0	0
<b>x</b>		+x	+x
<b>eqb</b>		x	x

3.  $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (x)(x) = (x)^2$
4.  $x = (K_{sp})^{1/2} = 1.049 \times 10^{-5} = [\text{Ba}^{2+}]$  (note that this is also the molar solubility of barium sulfate)
5. In 0.010 M barium nitrate

	$[\text{BaSO}_4]$	$[\text{Ba}^{2+}]$	$[\text{SO}_4^{2-}]$
<b>initial</b>		0.010	0
<b>x</b>		+x	+x
<b>eqb</b>		0.010 + x	x

6.  $K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (0.010 + x)(x)$
7.  $0 = x^2 + .01x - K_{sp}$
8.  $x = 1.1 \times 10^{-8} = [\text{SO}_4^{2-}]$  so the molar solubility of barium sulfate has decreased to  $1.1 \times 10^{-8}$  M, or roughly by a factor of 1,000

## VI. Precipitation calculations

- A. Based on a comparison of the concentration of ions in solution and the value of  $K_{sp}$  for the compound, we can predict whether or not precipitation will occur
  1. Estimation is based on the reaction quotient  $Q$ , which is calculated using the equilibrium constant expression but with actual rather than equilibrium concentrations of products and reactants

2.

<b><math>Q = K_{sp}</math></b>	system is at eqb
<b><math>Q &lt; K_{sp}</math></b>	system not at eqb, solution not saturated, forward reaction occurs
<b><math>Q &gt; K_{sp}</math></b>	system not at eqb, solution supersaturated, reverse reaction occurs

## B. Examples

1. After placing solid silver (I) chloride in a solution the  $[\text{Ag}^+]$  and  $[\text{Cl}^-]$  are  $1.2 \times 10^{-5}$ . Is the system at equilibrium? ( $K_{sp} = 1.8 \times 10^{-10}$ )
  - a.  $Q = [\text{Ag}^+][\text{Cl}^-] = (1.2 \times 10^{-5})^2 = 1.4 \times 10^{-10}$
  - b. Since  $Q < K_{sp}$  the reaction is not at equilibrium and the forward reaction will continue until equilibrium is reached
2. The  $K_{sp}$  for nickel (II) carbonate is  $6.6 \times 10^{-9}$ . A solution is  $1.5 \times 10^{-6}$  M in  $\text{Ni}^{2+}$  ion. Sodium carbonate is added to the solution so that the solution carbonate concentration is  $6.0 \times 10^{-4}$  M. Does precipitation occur?

- a.  $Q = [\text{Ni}^{2+}][\text{CO}_3^{2-}] = (1.5 \times 10^{-6})(6.0 \times 10^{-4}) = 9.0 \times 10^{-10}$
- b. Since  $Q < K_{\text{sp}}$  no precipitate will form
3. The strontium ion concentration of a solution is  $2.5 \times 10^{-4}$  M. If sodium sulfate is added such that the sulfate concentration of the solution is  $2.5 \times 10^{-4}$  M, will strontium sulfate precipitate? ( $K_{\text{sp}} = 2.8 \times 10^{-7}$ )
- a.  $Q = [\text{Sr}^{2+}][\text{SO}_4^{2-}] = (2.5 \times 10^{-4})^2 = 6.25 \times 10^{-8}$
- b. Since  $Q < K_{\text{sp}}$  no precipitate will form
- c. What is the minimum sulfate concentration required to cause precipitation of strontium sulfate to begin in this solution?
- d.  $Q = K_{\text{sp}} = 2.8 \times 10^{-7}$
- e.  $K_{\text{sp}} = [\text{Sr}^{2+}][\text{SO}_4^{2-}]$
- f.  $[\text{SO}_4^{2-}] = K_{\text{sp}}/[\text{Sr}^{2+}] = 2.8 \times 10^{-7} / 2.5 \times 10^{-4} = 1.12 \times 10^{-3}$  M
4. What is the minimum iodide concentration required to initiate precipitation of lead (II) iodide from a 0.050 M solution of lead (II) nitrate? The  $K_{\text{sp}}$  for lead (II) iodide is  $8.7 \times 10^{-9}$ .
- a.  $K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2$
- b.  $[\text{I}^-] = \{K_{\text{sp}}/[\text{Pb}^{2+}]\}^{1/2} = 4.17 \times 10^{-4}$

#### VII. Factors that affect solubility - pH

- A. The solubility of slightly soluble ionic compounds containing basic anions increases as the hydrogen ion concentration of the solution increases and as pH decreases
1. These anions include carbonate, phosphate, cyanide, sulfide, hydroxide, etc.
- B. Some anions react with hydrogen ion to form a gas
1. Principally - but not exclusively - carbonate, sulfite, sulfide, and cyanide
- C. For quantitative calculation of the effect of acids on solubility, remember the general rules about the acid/base behavior of the conjugates of acids and bases (for this class only need a qualitative understanding)

#### VIII. Factors that affect solubility - complex ion formation

- A. Since most transition metals have one or more empty orbitals, especially as ions, they can behave as Lewis acids
- B. There are a number of materials that behave as Lewis bases in the presence of

transition metal ions

1.  $F^-$ ,  $Cl^-$ ,  $Br^-$ ,  $I^-$ ,  $OH^-$ ,  $CN^-$ ,  $NO_2^-$ ,  $H_2O$ ,  $NH_3$ ,  $CO$ , etc.

C. Complex ions: the central atom, which is usually but not always a transition metal (e.g., an exception:  $Na_2SiF_6$ ), forms one or more coordinate covalent bonds with one or more Lewis bases (called *ligands*), one coordinate covalent bond per empty orbital

1. A central atom and its ligands are called complexes, or, metal complexes
2. If the complex has a net charge it is called a complex ion
3. Compounds containing complexes or complex ions are called *coordination compounds*
4. In forming a complex (i.e. in forming coordinate covalent bonds with the transition metal ion) the ligands are said to coordinate to the metal
5. Metal complexes and complex ions are distinct chemical species with physical and chemical properties that differ from those of either the metal (metal ion) or the ligands (i.e., these differences can be in color, redox properties, etc. and are often conspicuously different, especially with respect to color)
6. The number of ligands binding to the central atom (ion) is called the *coordination number* of the compound
  - a. The most common coordination numbers are 4 and 6
  - b. Some metal ions exhibit constant coordination numbers regardless of ligand
    - i. The coordination number of  $Cr^{3+}$  and  $Co^{3+}$  is always 6
    - ii.  $[Cr(H_2O)_4Cl_2]^+$
    - iii.  $[Co(NH_3)_5Cl]^{2+}$
  - c. Most metals have varying coordination numbers that depend on the ligand
    - i. The ratio of ligands to central atom is often determined by the relative sizes of the central atom and the ligands
    - ii.  $[FeF_6]^{3-}$  vs.  $[FeCl_4]^-$
7. Will not discuss the "whys" of coordination numbers in this class
8. The nomenclature of complex ions
  - a. When naming a coordination compound that is a salt, the cation is named first and the anion is named second

- b. When naming a complex molecule or ion, name the ligands first, in alphabetical order, followed by the name of the metal
- i. If the ligand is a neutral molecule its common name is used, except for water (aqua), ammonia (ammine), and carbon monoxide (carbonyl)
  - ii. If the ligand is an anion ending in "ide," "ite," or "ate" the ending is changed to "o,"
    - a. Chloride: chloro
    - b. Cyanide: cyano
    - c. Sulfate: sulfato
    - d. Nitrite: nitrito
  - iii. When there is more than one of a simple ligand, the number of that ligand is indicated using prefixes di, tri, tetra, penta, hexa
  - iv. When there is more than one of a complex ligand (ethylenediamine, phenanthroline), the number of that ligand is indicated using prefixes bis, tris, tetrakis, pentakis, or hexakis, followed by the ligand name in parentheses
- c. If the complex ion is an anion the metal name is given the suffix "ate"
- d. The oxidation number of the metal is given in Roman numerals in parentheses following the name of the metal
- e. Examples
- i.  $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$  - tetraamminecopper (II) sulfate
  - ii.  $\text{K}_2[\text{CoCl}_4]$  - potassium tetrachlorocobaltate
  - iii.  $[\text{Cr}(\text{en})_2(\text{CN})_2]\text{Cl}$  - dicyanobis(ethylenediamine)chromium (III) chloride
  - iv.  $\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_3]$  - potassium amminetrichloroplatinate

#### D. Complex ion stability

1. The formation of complexes is often an energetically favorable process
2. The equilibrium constants that describe the formation of complexes (complex ions) are called formation constants ( $K_f$ )
3. Formation constants are often very large positive numbers
  - a. See Table 17.2, p. 742 (Ebbing)

- b. Values range from  $1 \times 10^7$  for  $\text{Ag}(\text{NH}_3)_2^+$  to  $9 \times 10^{41}$  for  $\text{Fe}(\text{CN})_6^{3-}$
4. Formation constants are the products of the equilibria constants involved in the formation of the complex
- For the formation of  $\text{Cd}(\text{CN})_4^{2-}$
  - $\text{Cd}^{2+}(\text{aq}) + \text{CN}^-(\text{aq}) \rightleftharpoons \text{CdCN}^+(\text{aq})$ ;  $K_1 = [\text{CdCN}^+] / [\text{Cd}^{2+}][\text{CN}^-] = 1.0 \times 10^6$
  - $\text{CdCN}^+(\text{aq}) + \text{CN}^-(\text{aq}) \rightleftharpoons \text{Cd}(\text{CN})_2(\text{aq})$ ;  $K_2 = [\text{Cd}(\text{CN})_2] / [\text{CdCN}^+][\text{CN}^-] = 1.3 \times 10^5$
  - $\text{Cd}(\text{CN})_2(\text{aq}) + \text{CN}^-(\text{aq}) \rightleftharpoons \text{Cd}(\text{CN})_3^-(\text{aq})$ ;  $K_3 = [\text{Cd}(\text{CN})_3^-] / [\text{Cd}(\text{CN})_2][\text{CN}^-] = 3.4 \times 10^4$
  - $\text{Cd}(\text{CN})_3^-(\text{aq}) + \text{CN}^-(\text{aq}) \rightleftharpoons \text{Cd}(\text{CN})_4^{2-}(\text{aq})$ ;  $K_4 = [\text{Cd}(\text{CN})_4^{2-}] / [\text{Cd}(\text{CN})_3^-][\text{CN}^-] = 1.9 \times 10^2$
  - Net:  $\text{Cd}^{2+}(\text{aq}) + 4 \text{CN}^-(\text{aq}) \rightleftharpoons \text{Cd}(\text{CN})_4^{2-}(\text{aq})$ ;  $K_f = [\text{Cd}(\text{CN})_4^{2-}] / [\text{Cd}^{2+}][\text{CN}^-]^4 = K_1 K_2 K_3 K_4 = 8.4 \times 10^{17}$
5. The reverse of the formation of a complex is its dissociation
6. The dissociation equilibrium is described by a dissociation constant ( $K_d$ )
7. For any complex, the relationship between formation and dissociation is described by  $K_f = K_d^{-1}$
- If 0.40 moles of sodium cyanide is added to 1.00 L of a 0.010M cadmium (II) nitrate solution, what will the cadmium (II) ion concentration be at equilibrium?

$$\text{i. } K_d = K_f^{-1} = (8.4 \times 10^{17})^{-1} = 1.2 \times 10^{-18} = [\text{Cd}^{2+}][\text{CN}^-]^4 / [\text{Cd}(\text{CN})_4^{2-}]$$

$$\text{ii. Skipping the math, } [\text{Cd}^{2+}] = 7 \times 10^{-19} \text{ (!)}$$

IX. Precipitation and separation of ions - see above

X. Qualitative analysis for metallic elements - skip

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