# Chapter 17

Buffers!!

Special guest stars:

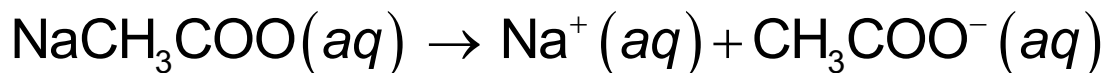**Titrations, and Solubility**

17.1 The Common-Ion Effect

- What is "the common ion effect?
    - It's what happens when you add more of the product ion to an acid/base reaction.

- This, like most things makes most sense with an example:

Example: What happens when you add Acetate to Acetic Acid? (1 of 2)

- Acetic acid is a weak acid:

  - $CH_3O_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$
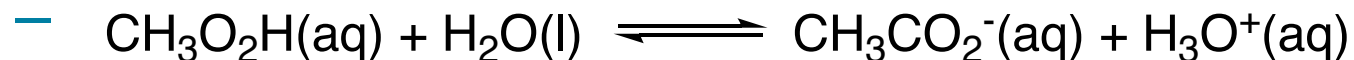
- Sodium acetate is a strong electrolyte:

  $$NaCH_3COO(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$$
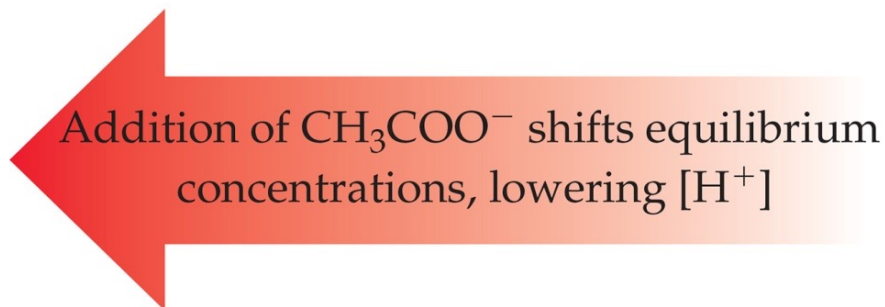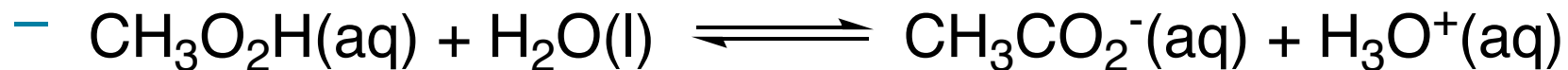
  - all of it dissociates:
    - Moles $NaCH_3COO$ = moles CH_3COO^-
  - What does that do to the equilibrium?

Effect of Acetate on the Acetic Acid Equilibrium
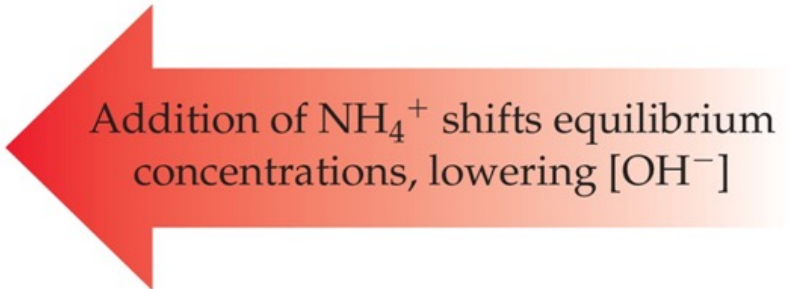
- Le Châtelier's principle says:
  - Add **product** ($CH_3CO_2^-$), **shift** to **reactants**.

  - $$CH_3O_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$$

Addition of CH_3COO^- shifts equilibrium concentrations, lowering $[H^+]$

Weak Bases Work the Same Way

- Adding the salt of a weak base will do the same thing.

$$NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
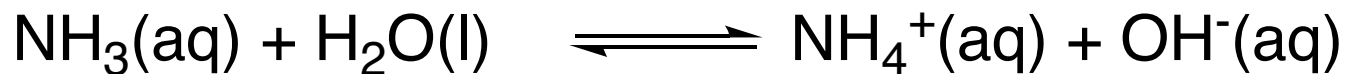
Addition of NH_4^+ shifts equilibrium concentrations, lowering $[OH^-]$

Example: Calculating pH for a Common Ion
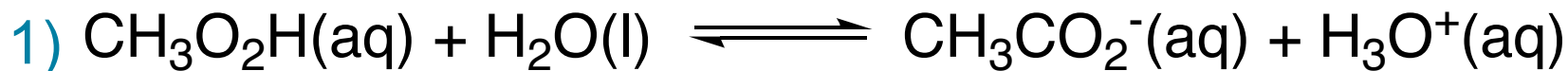
- What is the pH of a solution made by adding 0.30 mol of acetic acid and 0.30 mol of sodium acetate to enough water to make 1.0 L of solution?

- Assume the salt dissociates 100%.

- 0.3 moles sodium acetate = 0.3 moles acetate in 1L, 0.3 M

- Focus on the acetic acid equilibrium.

1) $CH_3O_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$

2)
$$1.8 x 10^{-5} = \frac{[H_3O]^+[CH_3OO^-]}{[CH_3OOH]}$$

3) $CH_3O_2H(aq) + H_2O(l) \rightleftharpoons CH_3CO_2^-(aq) + H_3O^+(aq)$

	CH_3CO_2H	H_3O^+	$CH_3CO_2^-$
Initial (*M*)	0.30	0	0.30
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$(0.30 - x)$	x	$(0.30 + x)$

$$1.8x10^{-5} = \frac{[H_3O]^+[CH_3OO^-]}{[CH_3OOH]}$$

$$1.8x10^{-5} = \frac{x(0.3 + x)}{0.3 - x}$$

Can we assume that *x* is so small that:

adding or subtracting it from 0.30 will not matter?

Calculating pH for a Common Ion

Yes!

$1.8 \times 10^{-5} <<< 0.3$ M

$$1.8 \times 10^{-5} = (x)(0.30 + x)/(0.30 - x)$$

Becomes:

$$1.8 \times 10^{-5} = \frac{(x)(0.30)}{(0.30)}$$

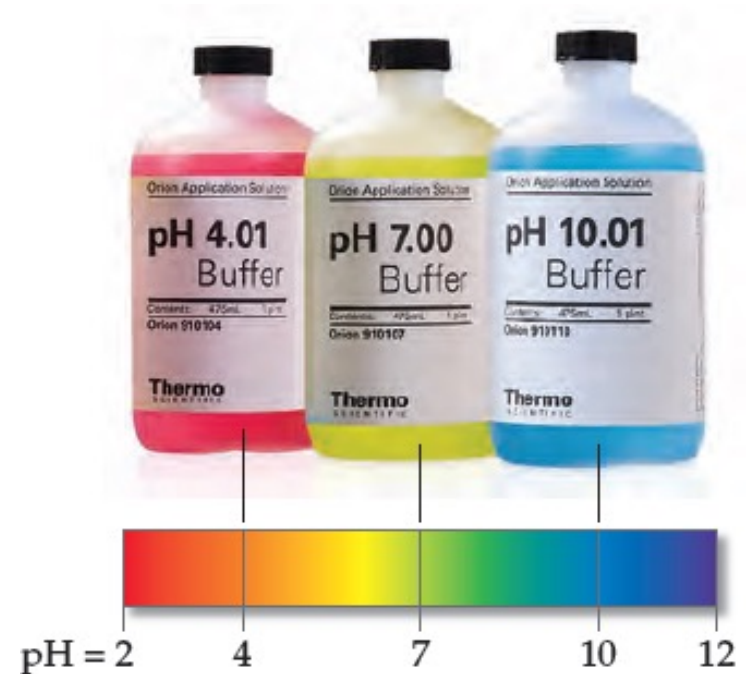which results in: $x = 1.8 \times 10^{-5} \text{M} = \left[H^+ \right]$

So: $\text{pH} = -\log\left[H^+ \right] = 4.74$

Note: $1.8 \times 10^{-5} << 0.3$ M
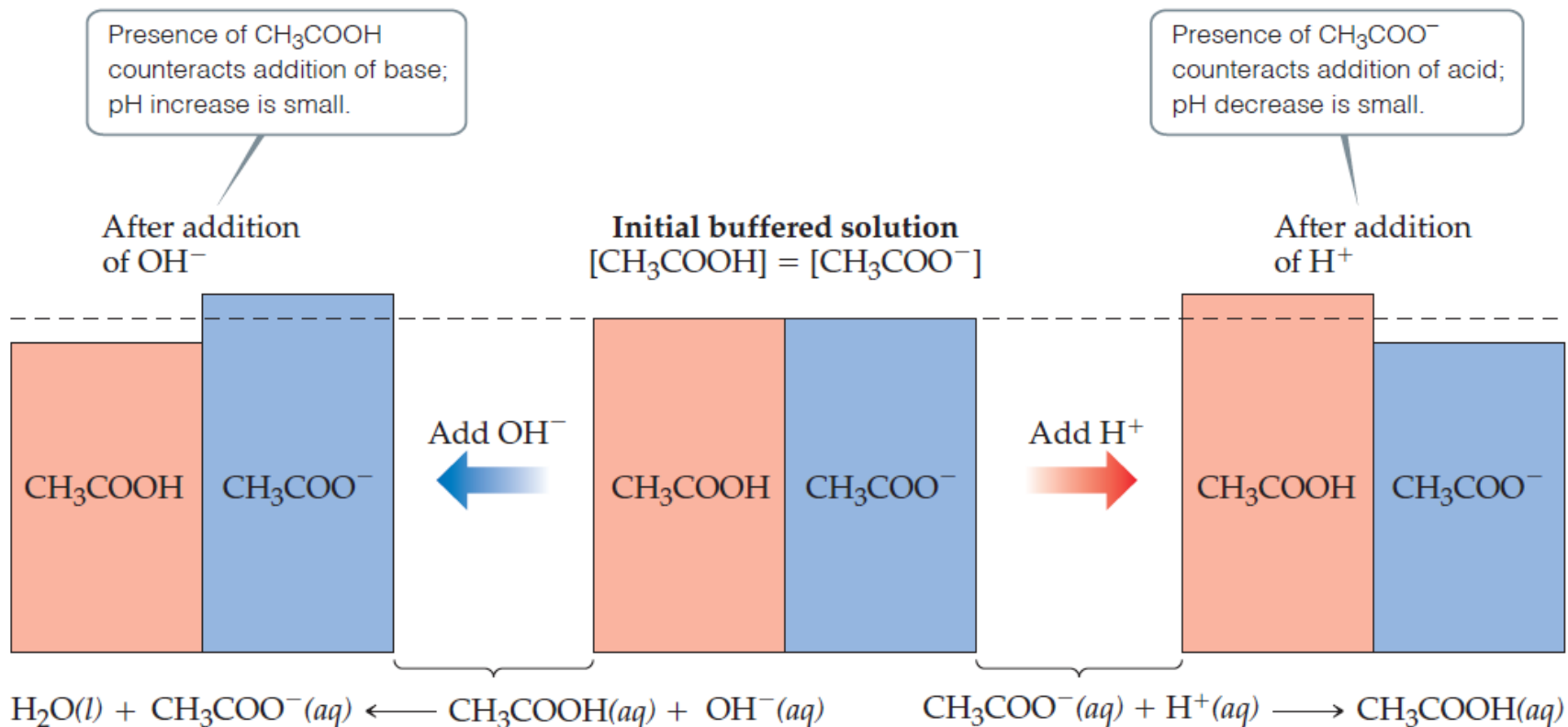
17.2 But why do we care??? Buffers!!

- A mixture of a weak acid and its conjugate base (salt product) **resists changes in pH.**

- But there has to be **enough** of each of them to do it.

- A reasonable buffer:
  - 10^{-3} M or more
  - of **Both AH and A⁻**

Ways to Make a Buffer

1) Mix a weak acid and its conjugate base salt

   1) Mix HA with A⁻ (acetic acid and acetate).

2) Mix a weak base and its conjugate acid salt.

   1) Mix B with HB (NH_3 and NH_4^+)

3) Add strong base to a weak acid

   1) That will make the conjugate base

   2) $CH_3COOH(aq) + NaOH(aq) \rightarrow CH_3COO^-(aq) + H_2O$

4) Add strong acid to a weak base

   1) That will make the conjugate acid.

   2) $NH_3 + HCl \rightarrow NH_4^+(aq) + Cl^-(aq)$

How a Buffer Works

Presence of CH_3COOH counteracts addition of base; pH increase is small.

Presence of CH_3COO^- counteracts addition of acid; pH decrease is small.

After addition of OH^-

Initial buffered solution $[CH_3COOH] = [CH_3COO^-]$

After addition of H^+

CH_3COOH CH_3COO^-

Add OH^-

CH_3COOH CH_3COO^-

Add H^+

CH_3COOH CH_3COO^-

$$H_2O(l) + CH_3COO^-(aq) \longleftarrow CH_3COOH(aq) + OH^-(aq)$$

$$CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH(aq)$$

- Adding a small amount of acid or base only slightly neutralizes one component of the buffer, so the pH doesn't change very much.

The Henderson-Hasselback Equation
The equation of buffers

- For a weak acid: $K_a = \dfrac{\left[H^+\right]\left[A^-\right]}{\left[HA\right]}$

- Take $-\log$ of both sides:

$$-\log K_a = -\log\left[H^+\right] + -\log\left(\dfrac{\left[A^-\right]}{\left[HA\right]}\right)$$

- Rearrange:

$$-\log\left[H^+\right] = -\log K_a + \log\left(\dfrac{\left[A^-\right]}{\left[HA\right]}\right)$$

  - Which is:

$$pH = pK_a + \log\left(\dfrac{\left[A^-\right]}{\left[HA\right]}\right)$$

Deriving the Henderson-Hasselback Equation

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

- **Henderson–Hasselbalch equation**.
  - Works with any weak acid or base and their respective salts.
  - There are four variables.
    - $[H_3O^+]$
    - K_a
    - $[HA]$
    - $[A-]$

Example:
Using the Henderson–Hasselback Equation to Find pH

- What is the pH of a buffer that is 0.12 *M* in lactic acid, $CH_3CH(OH)COOH$, and 0.10 *M* in sodium lactate?

  K_a for lactic acid is 1.4×10^{-4}.

$$-pH = pK_a + \log\left(\frac{\left[A^-\right]}{\left[HA\right]}\right)$$

$$= -\log\left(1.4 \times 10^{-4}\right) + \log\left[\frac{\left(0.10\ M\right)}{\left(0.12\ M\right)}\right]$$

$$= 3.85 + \left(-0.08\right) = 3.77$$

Exam 2 review

- Chapter 15 Equilibrium
  - What is Equilibrium?
    - Rate of forward = rate of reverse
    - No change in amount of stuff.

  - Equilibrium constants
    - A + B $\longleftrightarrow$ C + D $K_{eq} = \dfrac{[C]\,[D]}{[A][B]}$
  - Combining Equilibrium expressions/reactions
    - Add two reactions together, multiply K_{eq}'s
   - Switch the direction of a reaction $K_{rev} = 1/K_{for}$

Heterogeneous Equilibrium

- The equation for the reaction is
  $$CaCO_3 \text{ (s)} \rightleftharpoons CaO \text{ (s)} + CO_2 \text{ (g)}$$

- This results in $K_c = [CO_2]$ and $K_p = P_{CO_2}$

- Equilibria only happen in one phase
    - If there's gas then gas
    - Otherwise, liquid
    - Usually solid is pure.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$CO_2(g)$

$CO_2(g)$

CaCO$_3$ CaO

CaCO$_3$ CaO

Large amount of CaCO$_3$, small amount of CaO, gas pressure P

Small amount of CaCO$_3$, large amount of CaO, gas pressure still P
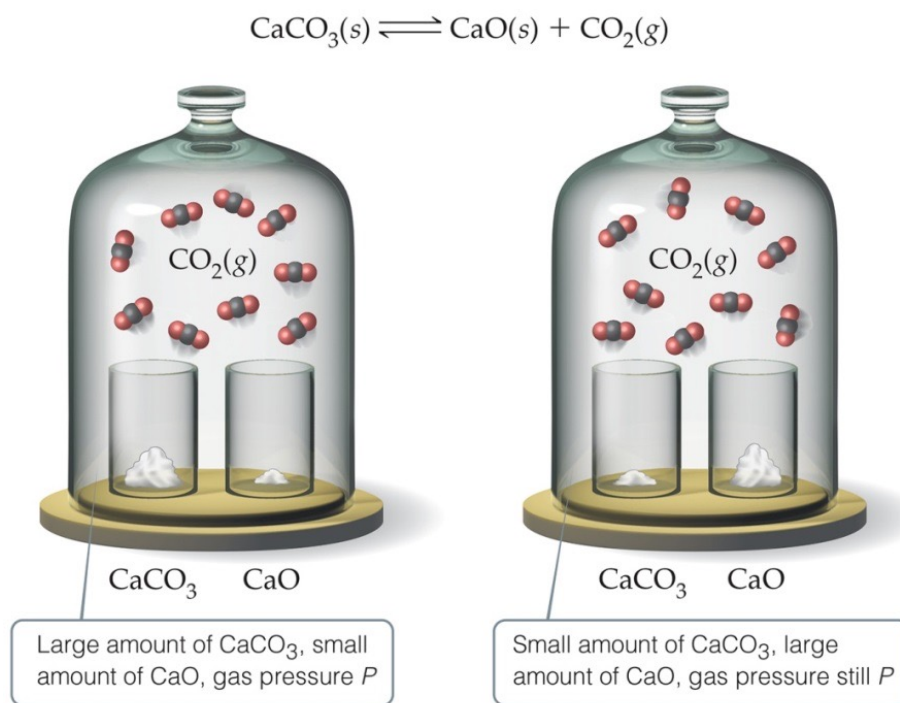
Ice Tables!

A closed system initially containing 1.000×10^{-3} M H_2 and 2.000×10^{-3} M I_2 at 448 °C is allowed to reach equilibrium. At equilibrium the mixture shows concentration of HI is 1.87×10^{-3} M. Calculate K_c at 448 °C.

$$H_2\,(g) \quad + \quad I_2\,(g) \quad \rightleftharpoons \quad 2HI\,(g)$$
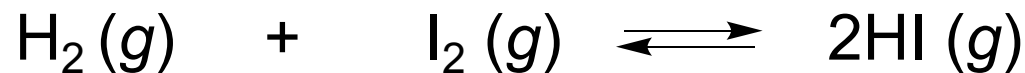
	$[H_2], M$	$[I_2], M$	$[HI], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			
At equilibrium			1.87×10^{-3}

Ice Tables!

2. Calculate changes.

change in [HI] is easy.

$$H_2\,(g) \quad + \quad I_2\,(g) \quad \rightleftharpoons \quad 2HI\,(g)$$

	$[H_2], M$	$[I_2], M$	$[HI], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change			$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

Ice Tables!

2. **Calculate changes.**

Use equation **stoichiometry** to complete **changes**

$$H_2 \, (g) \quad + \quad I_2 \, (g) \quad \rightleftharpoons \quad 2HI \, (g)$$

	$[H_2], M$	$[I_2], M$	$[HI], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium			1.87×10^{-3}

Ice Tables!

3. Calculate the **equilibrium** concentrations

$$H_2\,(g) \quad + \quad I_2\,(g) \quad \rightleftharpoons \quad 2HI\,(g)$$
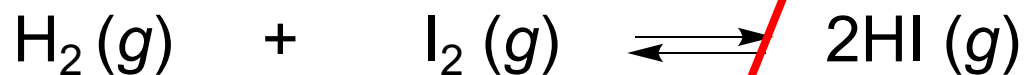
	$\left[H_2\right], M$	$\left[I_2\right], M$	$[HI], M$
Initially	1.000×10^{-3}	2.000×10^{-3}	0
Change	-9.35×10^{-4}	-9.35×10^{-4}	$+1.87 \times 10^{-3}$
At equilibrium	6.5×10^{-5}	1.065×10^{-3}	1.87×10^{-3}

4. Substitute values into the K_c expression.

Note: Equilibrium constants are unitless.

$$k_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$= \frac{(1.87 \times 10^{-3})^2}{(6.5 \times 10^{-5})(1.065 \times 10^{-3})}$$

$$= 51$$

Le Châtelier's Principle

System at Equilibrium:

Change anything, system moves to counteract that change.

Change Pressure,

Increase P, Equilibrium shifts to less gas

Change T, Equilibrium shifts to absorb/release heat.

Increase T, Equilibrium shifts in Endothermic direction.

Change reactants or products

Add products, equilibrium moves to reactants.

Chapter 19 Thermodynamics

Entropy.

Measure of randomness.

Increase in microstates.

What's got higher Entropy?

solids, lowest, liquids, gases.

Pure versus solutions.

Effect of Temperature on Entropy

Higher T, higher Entropy

S = q/T

Chapter 19 Thermodynamics

Entropy.

Measure of randomness.

Increase in microstates.

What's got higher Entropy?

solids, lowest, liquids, gases.

Pure versus solutions.

Effect of Temperature on Entropy

Higher T, higher Entropy

Δ**S = q/T**

Entropy has an absolute 0 (crystalline solid at 0 K)

Chapter 19 Thermodynamics

Driving force of all processes.

Entropy of the universe must increase….

$$\Delta G = \Delta H - T\Delta S$$

Gibbs Free Energy (system) is directly related to Entropy of universe.

ΔG negative, spontaneous (it happens)

ΔG positive, nonspontaneous (it doesn't happen)

Chapter 19 Thermodynamics

$$\Delta G = \Delta H - T \Delta S$$

Calculating stuff:

Calculate ΔG using values of formation

Calculate ΔG using ΔH and ΔS values

Relationship between ΔG and Equilibrium and Q:

$\Delta G = \Delta G° + Rt\ln(Q)$

$\Delta G° = -Rt\ln(K)$

Effect of T on Gibbs Free energy?

Concept of Entropy driven versus Enthalpy driven.

$$\Delta G = \Delta H - T\Delta S$$

Table 19.3 How Signs of ΔH and ΔS Affect Reaction Spontaneity

ΔH	ΔS	$-T\Delta S$	$\Delta G = \Delta H - T\Delta S$	Reaction Characteristics	Example
$-$	$+$	$-$	$-$	Spontaneous at all temperatures	$2\,O_3(g) \rightarrow 3\,O_2(g)$
$+$	$-$	$+$	$+$	Nonspontaneous at all temperatures	$3\,O_2(g) \rightarrow 2\,O_3(g)$
$-$	$-$	$+$	$+$ or $-$	Spontaneous at low T; nonspontaneous at high T	$H_2O(l) \rightarrow H_2O(s)$
$+$	$+$	$-$	$+$ or $-$	Spontaneous at high T; nonspontaneous at low T	$H_2O(s) \rightarrow H_2O(l)$

Chapter 13 Solutions/intermolecular forces

Intermolecular forces

      dipole-dipole

      H-bonding

      induced dipole-induced dipole

      Ionic forces.

Which is stronger? Who will dissolve in who?

Henry's law: $S_i = kP_i$

Rault's law: $pP_i = x_i(P_i)$

Chapter 16 acids/bases.

What is an acid? (more H^+, electron pair acceptor)

What is a base? (more $OH-$, Electron pair donor)

Aqueous dissociation:

K_W = [H+][OH-]

pH = -log[H+]

pH + pOH = 14

pH =7 is neutral.

pH of a weak acid/base given K_a

ICE tables with weak acids/bases.

Exam 2 the Breakdown

K and concentrations	I
Combining K_{eq}	I
Heterogeneous Equilibrium	I
LeChat.	I
Signs of Entropy, Enthalpy, Gibbs	I
Entropy	I
Spontaneity	I
Calculate ΔG	I
Intermolecular forces	I
Henry's law	I
pH	II
Weak acid	I
Lewis Acids	I

K_B	I
ICE table	I

Buffer Concentration. Vs. Buffer pH

- How does the buffer **concentration** affect pH of solution?

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

- It's the *ratio* of acid and conjugate base that determines pH.

- **Not concentration**

- 1M/1M = .01M/.01M

- **Both** have pH=pKa

Buffer Concentration vs. Buffer pH

- How does the buffer **concentration** affect pH of solution?

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

- It's the *ratio* of acid and conjugate base that determines pH.

- **Not concentration**

- 1M/1M = .01M/.01M

- **Both** have pH=pKa

- **But:** If you add 0.01 M acid to 1M solution, ratio barely changes
  - **So pH barely changes**

- Add 0.01M acid to .01 M solution, *pH changes hugely.*

- **Buffer capacity**

Buffer pH range.

- Buffers only work at certain pH ranges.
  - Why?
  - What's the range?

ges

$$HA(aq) + B(aq) \rightleftharpoons A^-(aq) + BH(aq)$$
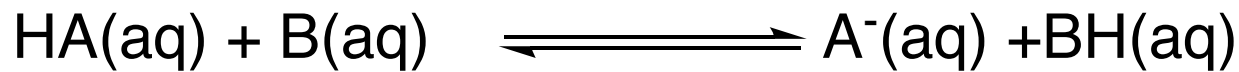
- Once HA is all gone,

- $B + H_2O \longrightarrow OH^- + BH$

- All the added base makes OH^-

- pH drops fast!

$$\left(\lceil A^- \rceil\right)$$

Addition of a Strong Acid or a Strong Base to a Buffer

Addition of the strong acid or base is a neutralization reaction.

1) Calculate like a stoichiometry problem to find $[HA]$ and $[A^-]$ when **all** of the added acid or base reacts. This is a limiting agent situation.

2) Use the Henderson–Hasselbalch equation to find pH. The equilibrium calculation is simplified by using this equation.

Addition of a Strong Acid or a Strong Base to a Buffer (2 of 2)
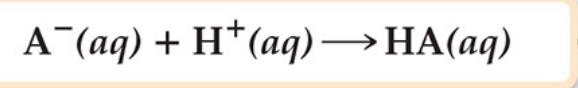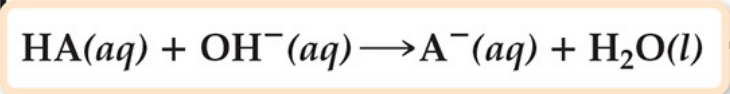
Example of pH Calculation for Buffer after Strong Base Addition

- A buffer is made by adding $0.300 \text{ mol } HC_2H_3O_2$ and $0.300 \text{ mol } NaC_2H_3O_2$ to enough water to make 1.00 L. 0.020 mol of NaOH is added. What's the pH?

1) Stoichiometry table – limiting reactant calculation

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

Before reaction (mol)	0.300	0.020	-	0.300
Change (limiting reactant) (mol)	-0.020	-0.020	-	+0.020
After reaction (mol)	0.280	0	-	0.320

2) Henderson–Hasselbalch equation:

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$

HA and A⁻ are in the same solution,
volume for each is the same
molarity ratio = moles ratio

$$pH = pK_a + \log\left(\frac{n_{HA}}{n_{A^-}}\right)$$
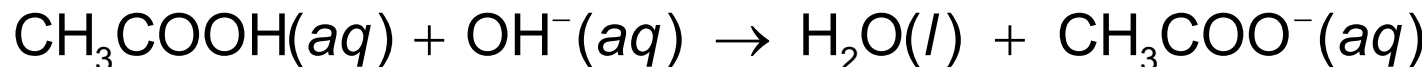$$pH = 4.74 + \log\left(\frac{0.320}{0.280}\right) = 4.80$$

Contrast Base Addition on pH for Buffer versus Water

Add 5.00 mL of 4.0 M NaOH to: a)

a) 1.000 L of a buffer that is 0.300 M acetate/0.3 M acetic acid.

b) 1.000 L of water

a)

$$CH_3COOH(aq) + OH^-(aq) \rightarrow H_2O(l) + CH_3COO^-(aq)$$

	CH_3COOH	OH^-	H_2O	CH_3COO^-
Before reaction (mol)	0.300	0.020	-	0.300
Change (limiting reactant) (mol)	−0.020	−0.020	-	+0.020
After reaction (mol)	0.280	0	-	0.320

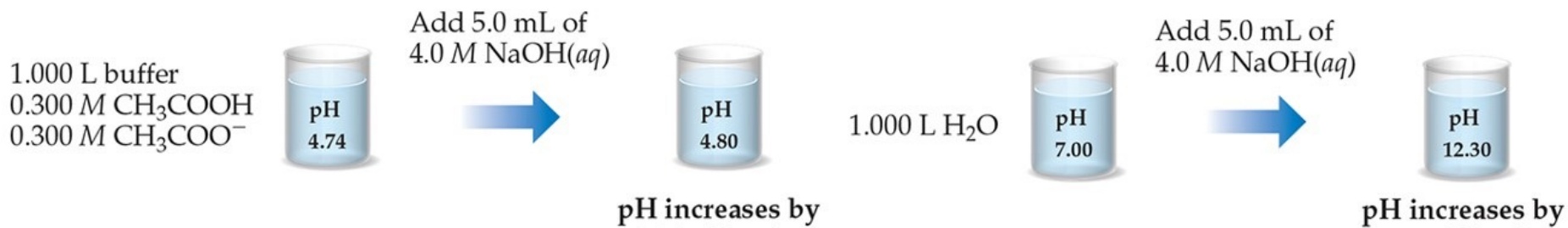$$pH = -\log\left(1.8 \times 10^{-5}\right) + \log\left(\frac{0.302}{0.298}\right) = 4.75$$

Contrast Base Addition on pH for Water versus Buffer

b) Pure water

$$(4.0\,\text{mol/L}) \times 5.00 \times 10-3\text{L} = 2.0 \times 10^{-2}\,\text{mol}$$

$$2.0 \times 10^{-2}\,\text{mol} / 1.005\text{L} = 0.0199\ \text{M}$$

$$pOH = -\log\left[OH^-\right] = -\log(0.0199) = 2.70$$

$$pH = 14.00 - 1.70 = \textbf{12.30}$$

pH change minimized using buffer:

Adding base to buffer: 4.80 to 4.75 **is 0.05 units**

Adding base to water: 7.00 to 12.30 is **5.30 units**

1.000 L buffer
0.300 M CH_3COOH
0.300 M CH_3COO^-

pH 4.74

Add 5.0 mL of 4.0 M NaOH(aq)

pH 4.80

pH increases by

1.000 L H_2O

pH 7.00

Add 5.0 mL of 4.0 M NaOH(aq)

pH 12.30

pH increases by

17.3 Acid–Base Titrations

- An acid (or base) solution of **known** concentration

- is slowly added to a base (or acid) solution of **unknown** concentration.

- Addition until the **equivalence point** is reached.
  - amount of acid =amount base.

- Equivalence point seen by monitoring pH change.

Burette containing NaOH(*aq*) of known concentration

pH meter

Beaker containing HCl(*aq*) of unknown concentration
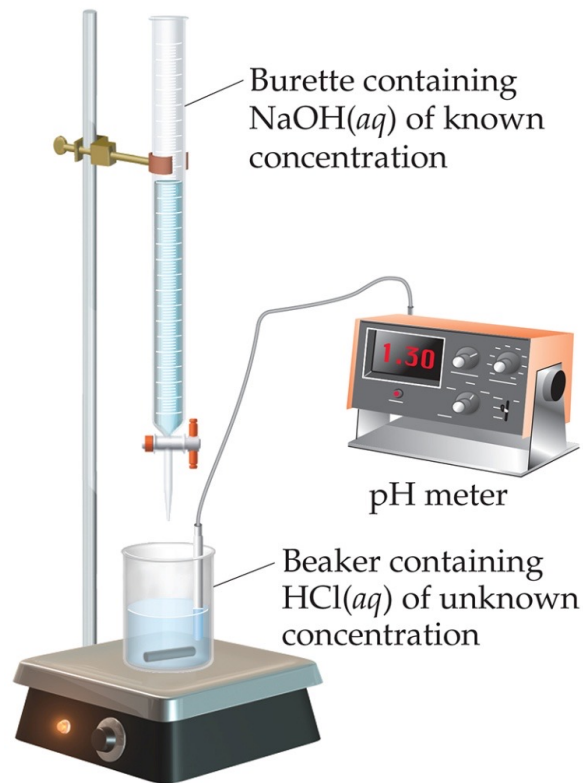
Titration of a Strong Acid with a Strong Base

- Plot pH versus mL of strong base.

- From the start to near the equivalence point, the *pH goes up slowly.*

- Just before (and after) the equivalence point, *the pH rises rapidly.*

- At the equivalence point, pH = 7.
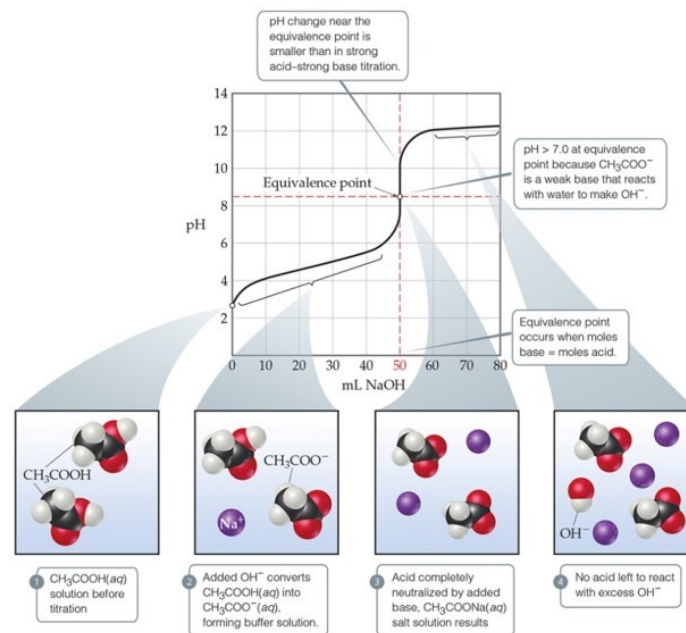
- As more base is added, the pH again levels off.
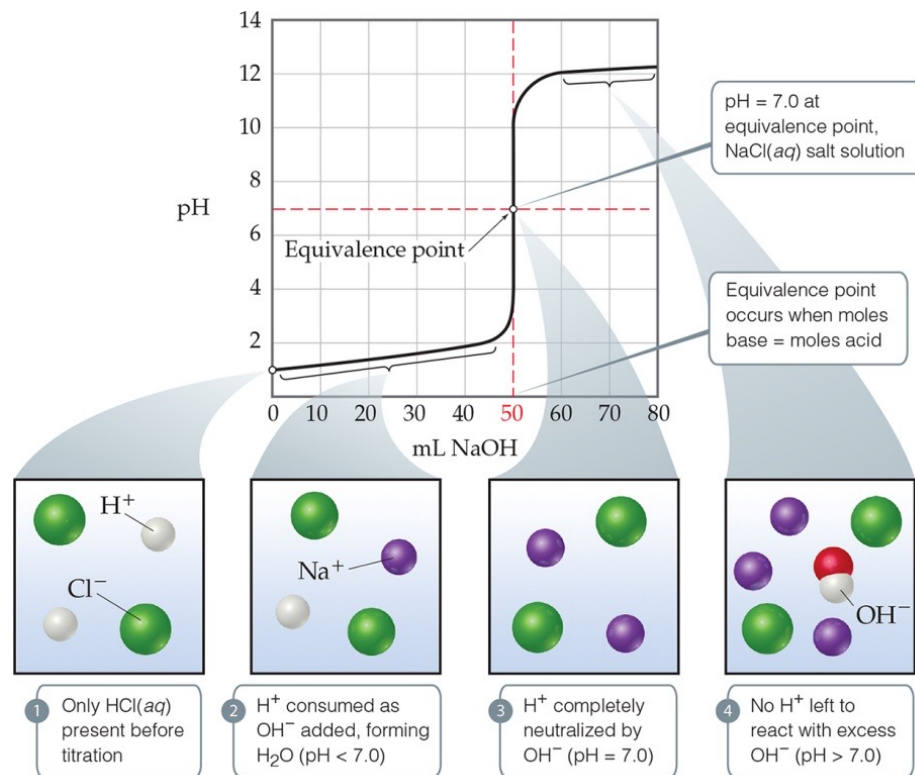
Titration of a Strong Base with a Strong Acid

- Start with a high pH (basic solution).

- pH = 7 at the equivalence point.
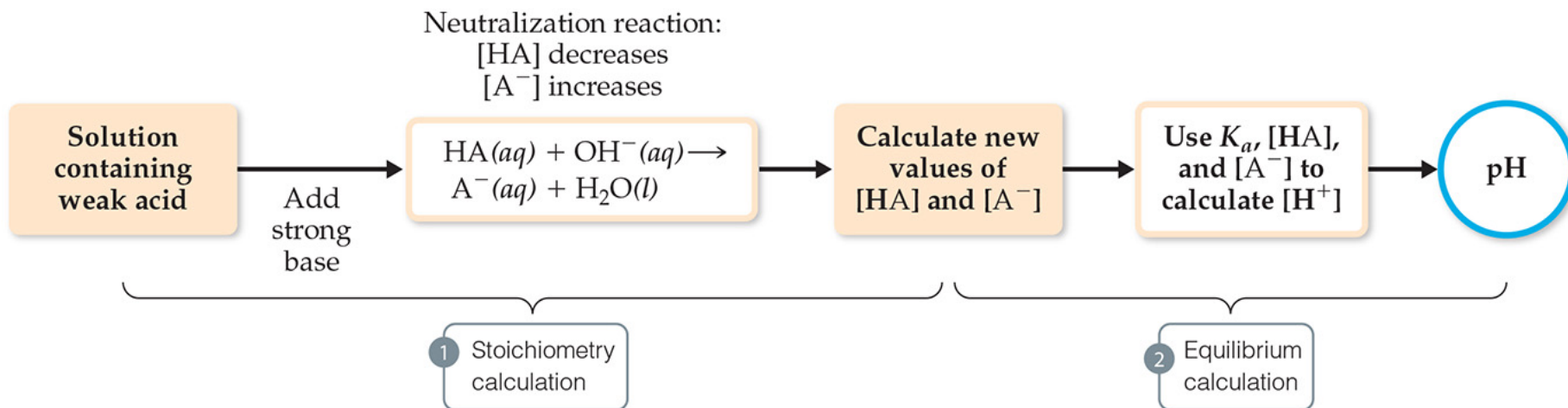
- Adding more acid, pH levels off.
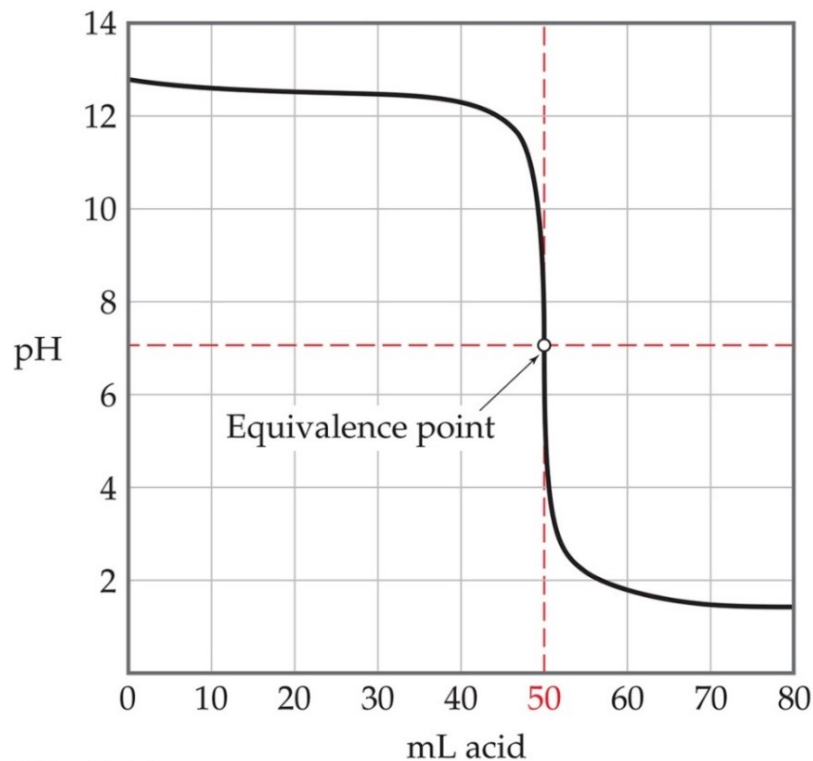
Titration of a Weak Acid with a Strong Base

- four distinct regions:

1. Initial pH uses K_a calculation.

2. Between initial pH and equivalence point (excess acid) uses limiting reactant then Henderson-Hasselback.

3. At the equivalence point.

4. After the equivalence point (excess strong base).

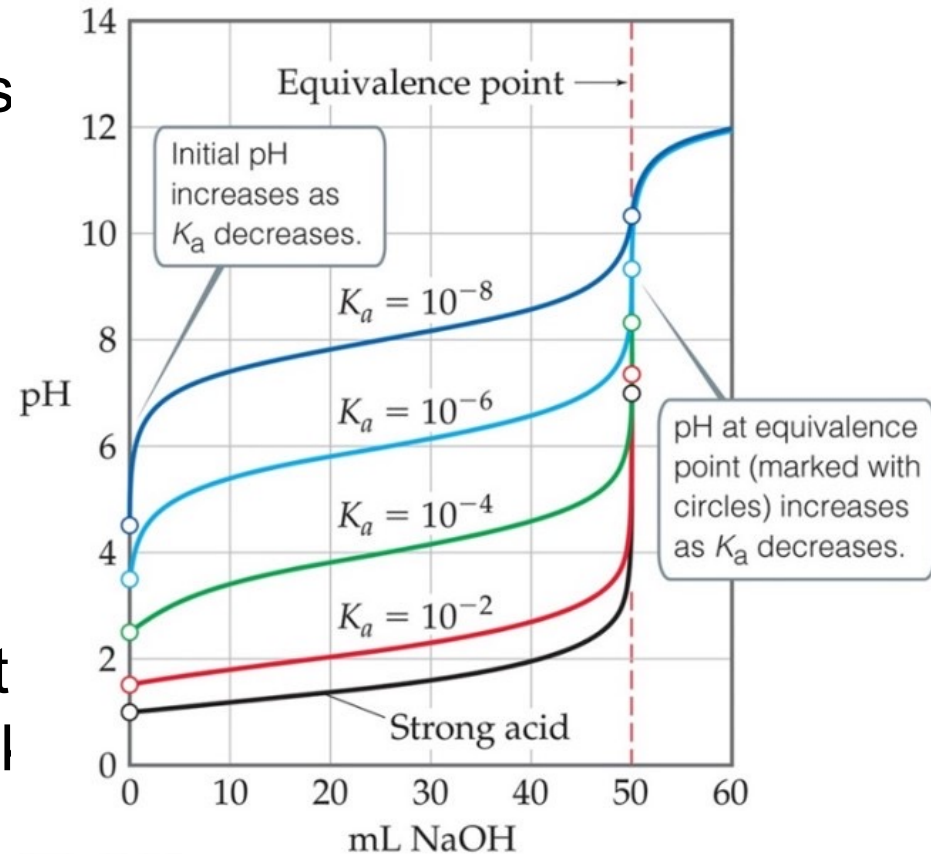# Calculating pH When a Weak Acid is Neutralized—Excess Acid

Neutralization reaction:
[HA] decreases
[A⁻] increases

| Solution containing weak acid | → Add strong base | $HA(aq) + OH^-(aq) \rightarrow A^-(aq) + H_2O(l)$ | → | Calculate new values of [HA] and [A⁻] | → | Use K_a, [HA], and [A⁻] to calculate [H⁺] | → | pH |

1 Stoichiometry calculation

2 Equilibrium calculation

- Calculate the moles of weak acid and strong base.

- Write the neutralization reaction.

- Track limiting reactant change using the table. Gives you moles of remaining acid and the moles of anion formed.

- Substitute into the Henderson-Hasselbalch equation to find pH.

Calculating pH for titrating a **Weak Acid** With a **Strong Base**

- The pH is **Not 7.00** at the equivalence point.

- Calculate the moles of weak acid and strong base.

- Write the neutralization equation.

- Substitute into table.

- **Titration point:** moles strong base = moles weak acid.
  - No more HA, only A$^-$

- Find molarity of weak acid using the new volume.

- Use the equations of either the K_b of the anion or the K_a of the weak acid to determine the pH (like in Chapter 16).
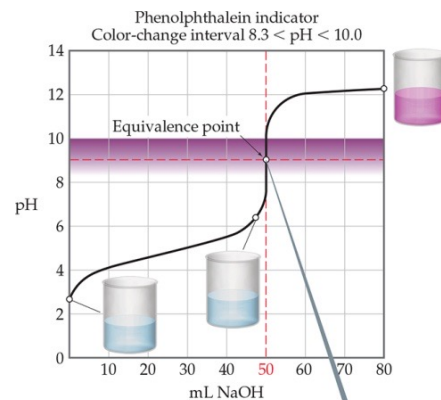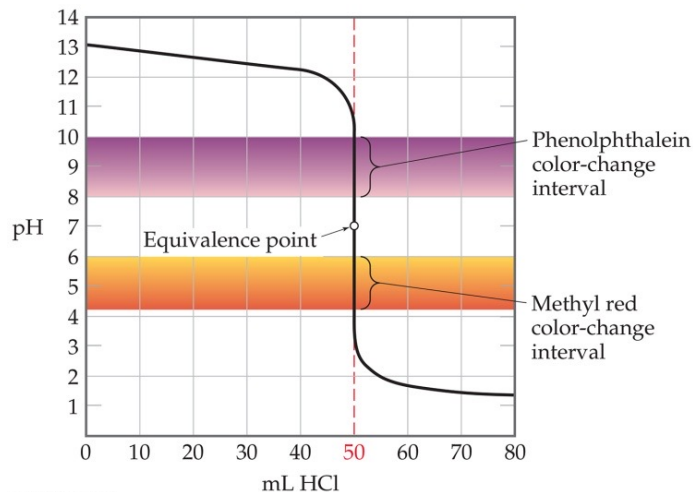
Ways That a Weak Acid Titration Differs from a Strong Acid Titration

1) A solution of **weak** acid has a **higher** initial pH than a **strong** acid.

2) The pH change is smaller

3) The pH midway to equivalence point = pK_a

4) pH at the equivalence point is **greater than 7** for a weak acid.

Equivalence point →

Initial pH increases as K_a decreases.

$K_a = 10^{-8}$

pH

$K_a = 10^{-6}$

$K_a = 10^{-4}$

pH at equivalence point (marked with circles) increases as K_a decreases.

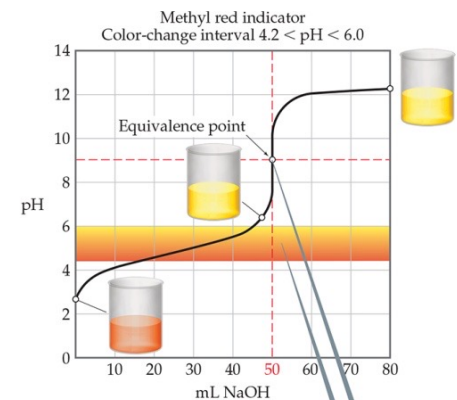$K_a = 10^{-2}$

Strong acid

mL NaOH

Titrations with an Acid–Base Indicator

- Indicators are weak acids that have a different color than their conjugate base form.

    – Each indicator has its own pH range over which it changes color.

    – Can be used to determine the equivalence point in a titration as long as it changes color at the pH of the equivalence point.

Let's calculate the pH at the equivalence point for a weak acid/strong base titration.

- Calculate the pH at the equivalence point in the titration of 50 mL of 0.1 M acetic acid with 0.1 M NaOH.

- $CH_3COOH(aq) + NaOH(aq) \longrightarrow CH_3COO^-(aq) + H_2O + Na^+(aq)$

- 50 mL 0.1M.   0.1 M

- .05L(0.1mole/L)=.   .005 moles/0.1M

- St. .005 moles   0.05 L   0

- Ch.   -.005 moles   -.005 moles   +0.005 moles

- Fin.   0   0   0.005 moles

$$K_b = K_w / K_a = \left(1.0 \times 10^{-14}\right) / \left(1.8 \times 10^{-5}\right) = 5.6 \times 10^{-10}.$$

$$K_b = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} = \frac{(x)(x)}{0.0500 - x} = 5.6 \times 10^{-10}$$

$x = [OH^-] = 5.3 \times 10^{-6}$ M, which gives pOH = 5.28 and pH = 8.72

Titrations of Polyprotic Acids

- There are multiple equivalence points.

- Treat each step separately with their corresponding polyanions and K_a.

- The halfway to each equivalence point gives the pK_a

- The concentration of the dianion is always equal to K_{a2}.
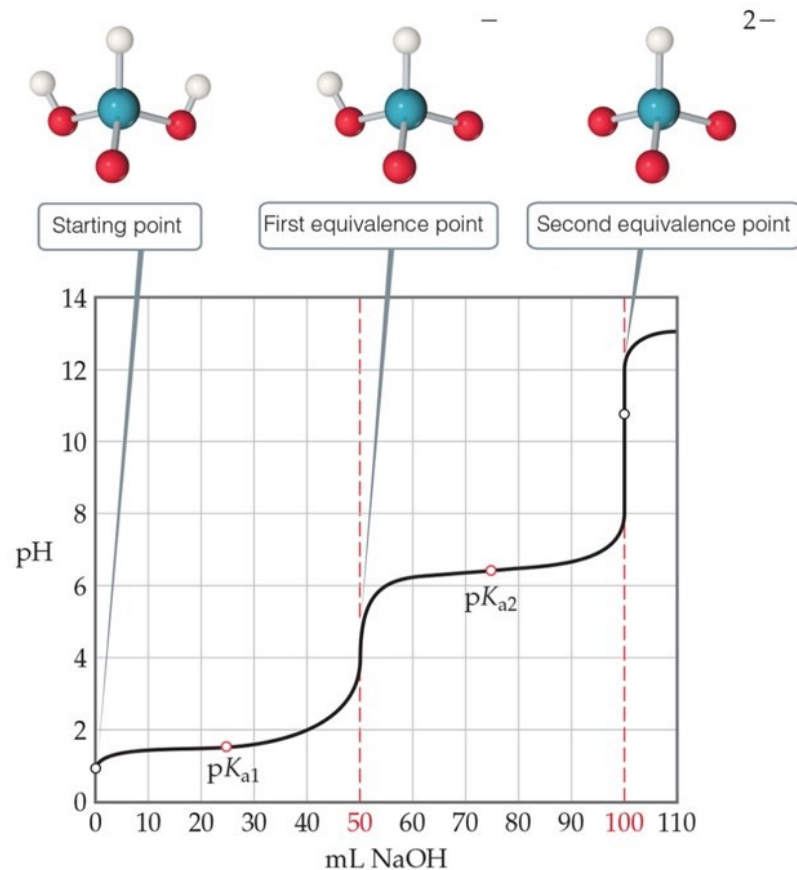
17.4 Solubility Equilibria

- Many Ionic compounds are not very soluble in water.

- The equilibrium constant expression is called the **solubility-product constant**. It is represented as
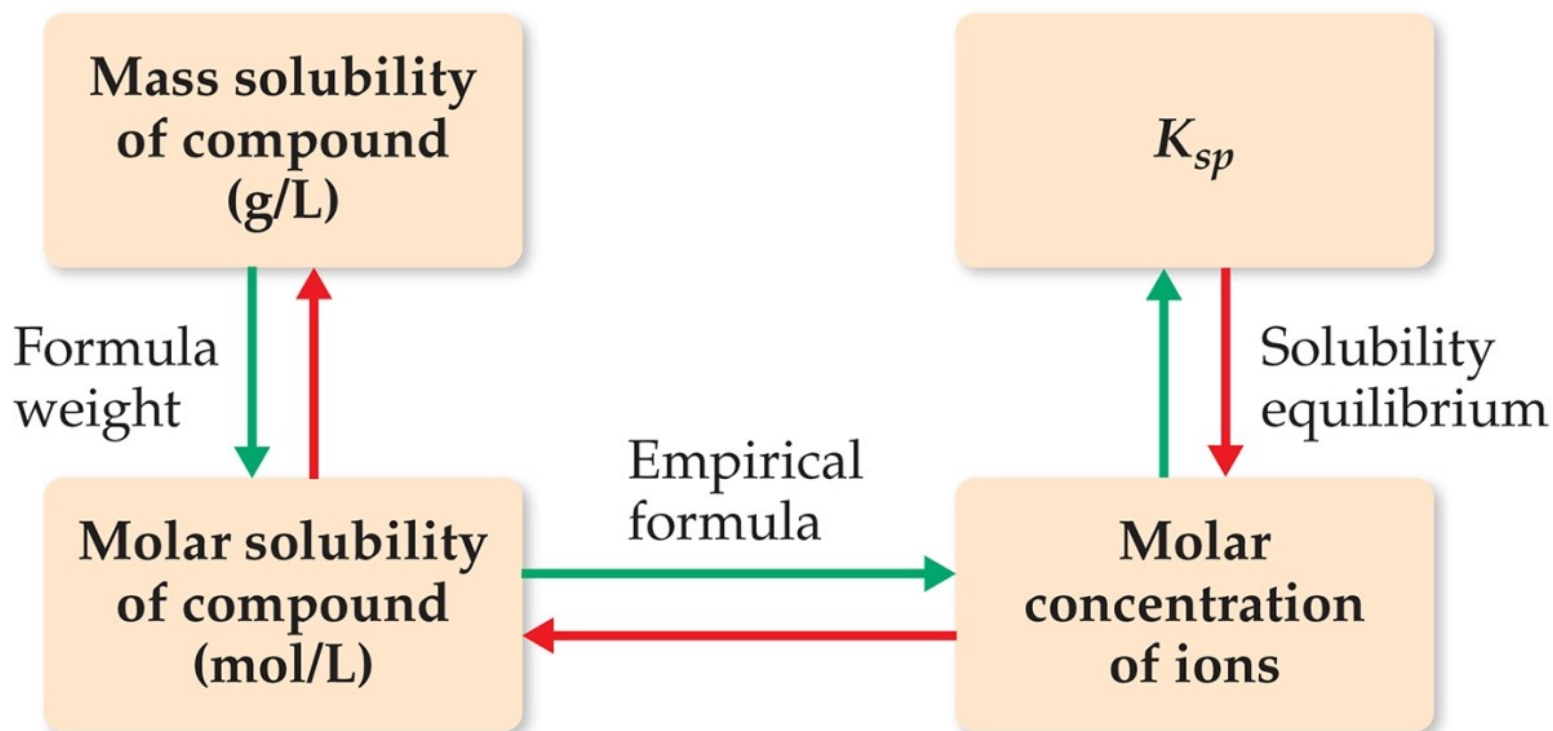
- K_{sp}

- $\qquad$ $Ba_3(PO_4)(s) \rightleftharpoons 3Ba^{2+}(aq) + 2PO_4^{-3}(aq)$
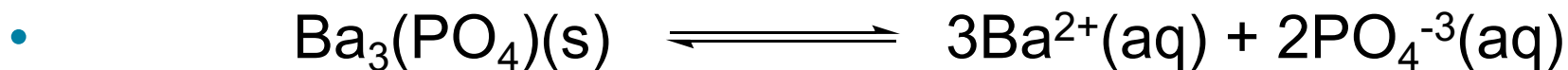
$$K_{sp} = \left[Ba^{2+} \right]^3 \left[PO_4^{3-} \right]^2$$
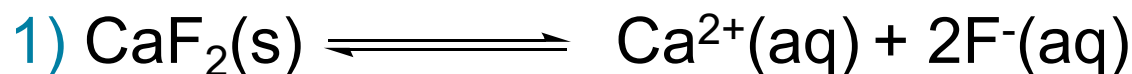
Solubility and K_{sp}

- K_{sp} is **not** the same as solubility.

- **Solubility:** *Maximum amount* that can dissolve.

- Common units for solubility:

  - Grams per liter (g/L)

  - Moles per liter (mol/L)
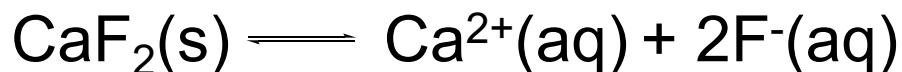
Solubility and K_{sp}

Calculating Solubility from K_{sp}

- The K_{sp} for CaF_2 is 3.9×10^{-11} at $25\,°C$. What is its molar solubility?

1) $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

2) $K_{sp} = \left[Ca^{2+} \right]\left[F^- \right]^2 = 3.9 \times 10^{-11}$

3)

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

Initial concentration (M)	-	0	0
Change (M)	-	+x	+2x
Equilibrium concentration (M)	-	X	2x

- Substitute the equilibrium concentration values from the table into the solubility-product equation:
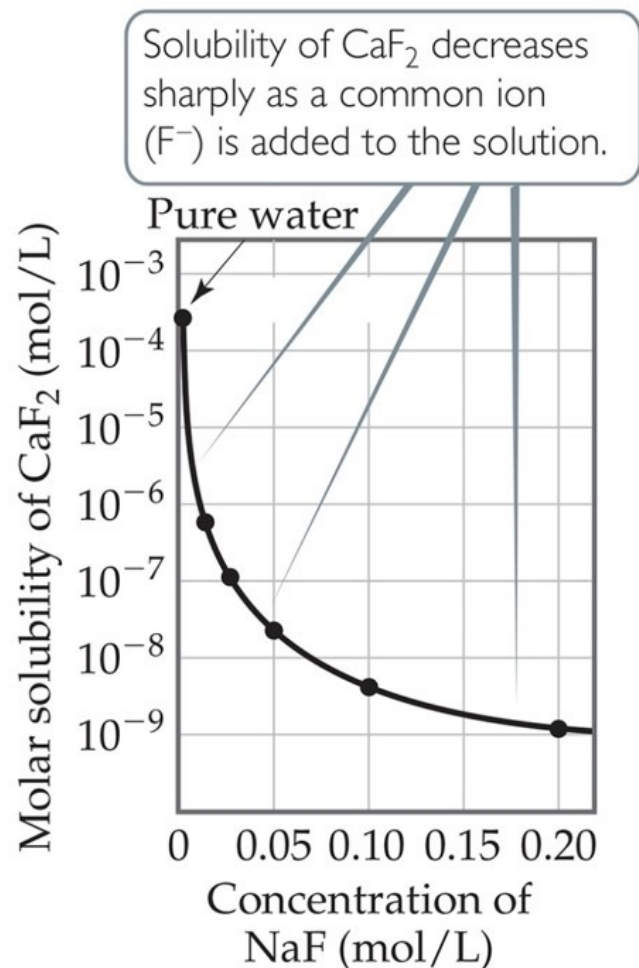
$$3.9 \times 10^{-11} = (x)(2x)^2 = 4x^3$$

$$x = 2.1 \times 10^{-4} \ M$$

For g/mol: multiply by molar mass.

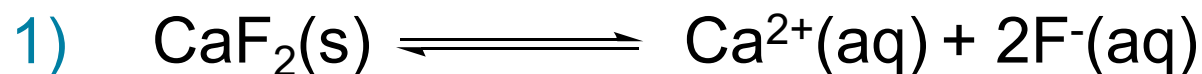2.1x10^{-4} mol/L(78.1g/mol) = 0.0164 g/L

17.5 Factors That Affect Solubility

- **The common-ion effect**:
  - If one of the ions is added
    - *Independently*
  - *The salt will be even less soluble.*

  - For CaF_2,
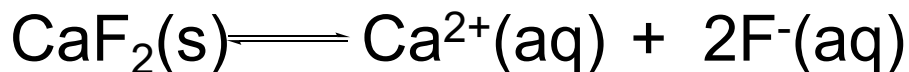   - Add either Ca^{2+} or F^-
    - CaF_2 less soluble.

Solubility of CaF_2 decreases sharply as a common ion (F^-) is added to the solution.

Calculating Solubility with a Common Ion (1 of 2)

- What is the molar solubility CaF_2 in $0.010\ M\ Ca(NO_3)_2$?

1) $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$

2) $K_{sp} = \left[Ca^{2+}\right]\left[F^-\right]^2 = 3.9 \times 10^{-11}$

3)

$$CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2F^-(aq)$$

		$CaF_2(s)$	$Ca^{2+}(aq)$	$2F^-(aq)$
Initial concentration (M)		-	0.010	0
Change (M)		-	+x	+2x
Equilibrium concentration (M)		-	(0.010 + x)	2x

Calculating Solubility with a Common Ion

4) Substitute the equilibrium concentration values from the table into the solubility-product equation:

$$3.9 \times 10^{-11} = (0.010 + x)(2x)^2$$

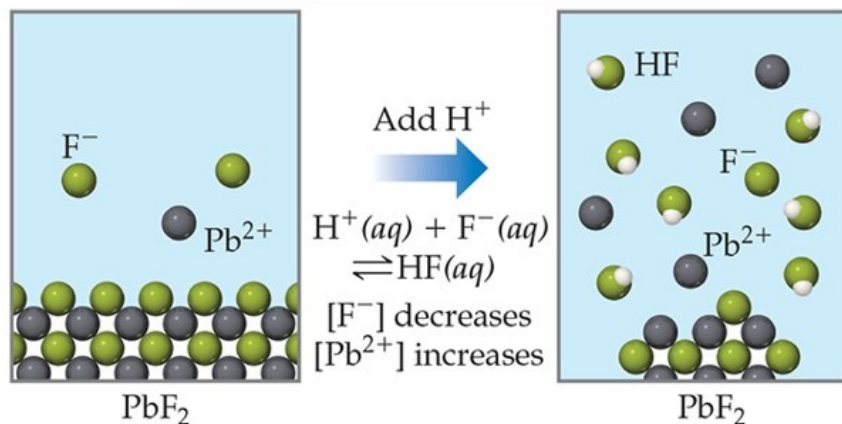(We assume that $x \ll 0.010$, so that $0.010 + x = 0.010$!)

$$3.9 \times 10^{-11} = (0.010)(2x)^2$$

$$x = 3.1 \times 10^{-5} M$$

Solubility can be effected by pH

- When?
  - When the **anion** is a weak base…(conj. of weak acid)
    - Adding acid reduces anion.
    - $F^- + HA \rightleftharpoons HF + A^-$

Salt whose anion is conjugate base of weak acid:
Solubility increases as pH decreases

$H^+(aq) + F^-(aq) \rightleftharpoons HF(aq)$

$[F^-]$ decreases
$[Pb^{2+}]$ increases

Add H^+

PbF_2 PbF_2

(a)

Salt whose anion is conjugate base of strong acid:
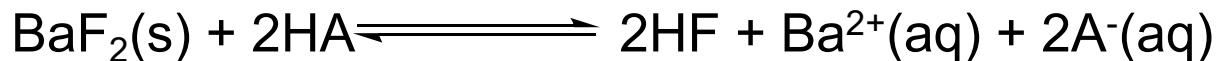*Solubility unaffected by changes in pH*

Add H^+

No reaction

PbI_2 PbI_2
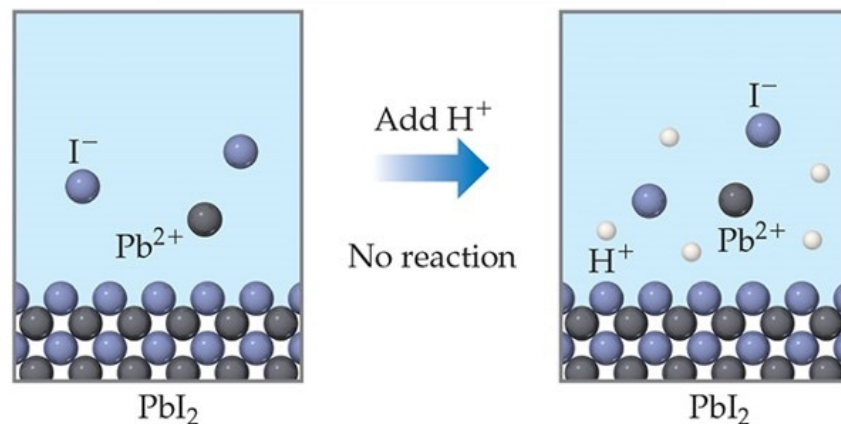
(b)

Sample Exercise 17.15 Predicting the Effect of Acid on Solubility

Which of these substances are more soluble in acidic solution than in basic solution?   **(a)** $Ni(OH)_2(s)$ **(b)** $CaCO_3(s)$ **(c)** $BaF_2(s)$ **(d)** $AgCl(s)$

(a) $Ni(OH)_2(s)$ is more soluble in acidic solution because of the basicity of OH^-; the H^+ reacts with the OH^- ion, forming water:

$$Ni(OH)_2 \ (s) \rightleftharpoons Ni^{2+}(aq) + 2OH^-(aq)$$

$$2OH^- + 2HA \rightleftharpoons 2H_2O(l) + 2A^-(aq)$$

$$Ni(OH)_2(s) + 2HA(aq) \rightleftharpoons Ni^{2+} + 2H_2O(l) + 2A^-(aq)$$

(b) $CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$

$CO_3^{2-}(aq) + 2H^+ \rightleftharpoons H_2CO_3$

$H_2CO_3(aq) \rightleftharpoons CO_2(g) + H_2O(l)$

$CaCO_3(s) + 2H^+(aq) \quad\quad CO_2(g) + H_2O(l) + Ca^{2+}(aq)$

(c) $BaF_2(s) \rightleftharpoons Ba^{2+}(aq) + 2F^-(aq)$

$2F^-(aq) + 2HA \rightleftharpoons 2HF + 2A^-(aq)$

$BaF_2(s) + 2HA \rightleftharpoons 2HF + Ba^{2+}(aq) + 2A^-(aq)$

(d) $Cl^-(aq) + H^+(aq) \rightleftharpoons Cl^-(aq) + H^+(aq)$ *acid does nothing.*

Complex Ion Formation

- Metal ions can act as Lewis acids and form **complex ions** with Lewis bases in the solvent.

- The formation of these complex ions can increase the solubility of these salts.

NH_3 reacts with Ag^+, forming $Ag(NH_3)_2^+$

Addition of sufficient NH_3 leads to complete dissolution of AgCl

Reaction with NH_3 reduces concentration of free Ag^+ and increases solubility of AgCl

Ag^+

Cl^-

AgCl

Cl^-

$Ag(NH_3)_2^+$

NH_3

$$AgCl(s) + 2\,NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)$$
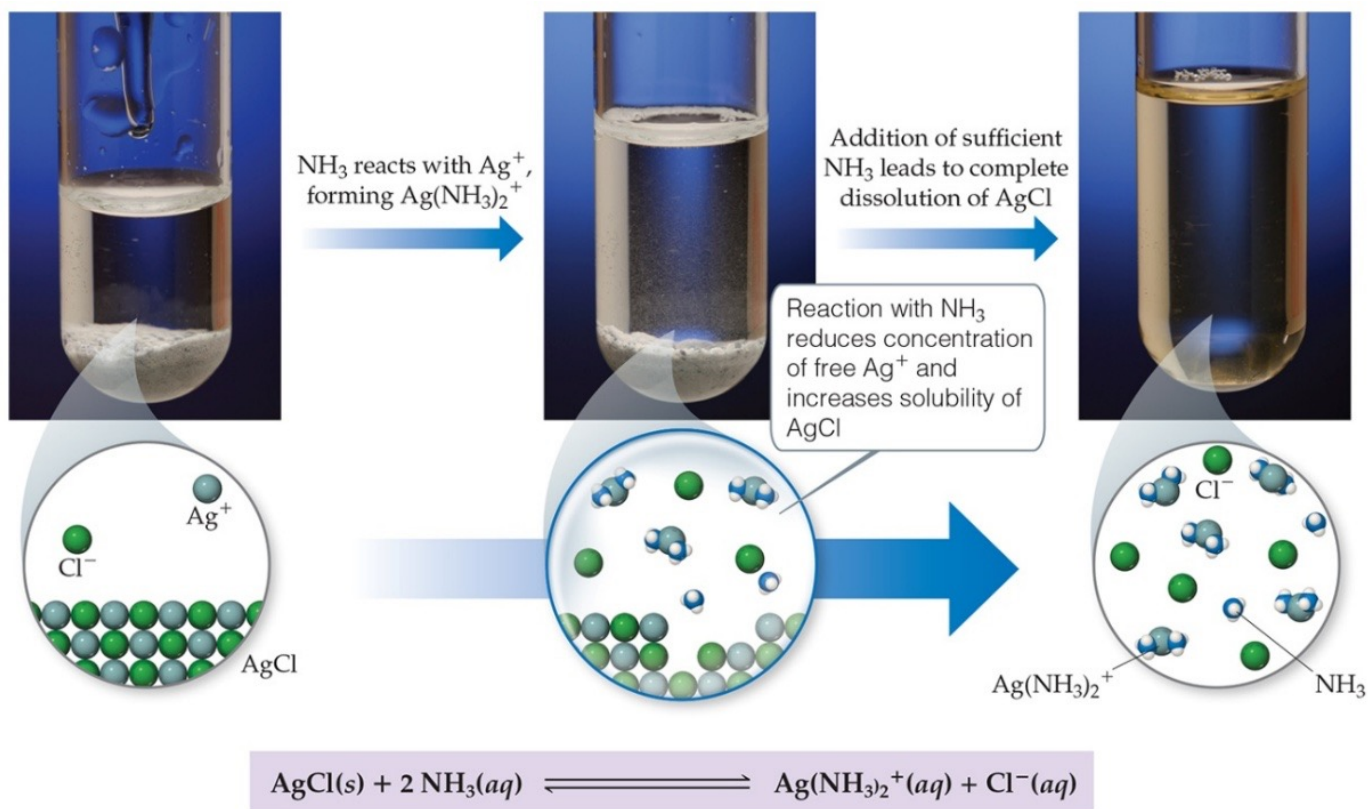
- Silver chloride is insoluble. It has a K_{sp} of 1.6×10^{-10}.

- In the presence of NH_3, the solubility greatly increases because Ag^+ will form a complex ion with NH_3.

$$K_f = 1.7 \times 10^7$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$

$$\frac{Ag^+(aq) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq)}{AgCl(s) + 2NH_3(aq) \rightleftharpoons Ag(NH_3)_2^+(aq) + Cl^-(aq)}$$
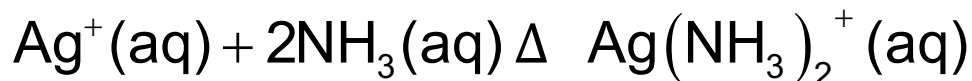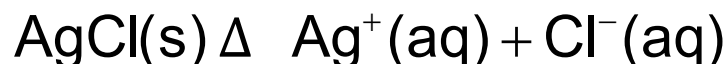
$$K_f\left(Ag(NH_3)_2^+\right) = \frac{\left[Ag(NH_3)_2\right]^+}{\left[Ag^+\right]\left[NH_3\right]^2} = 1.7 \times 10^7$$

Table 17.1 Formation Constants for Some Metal Complex Ions in Water at 25 $^\circ$C

Complex Ion	K_f	Chemical Equation
$Ag(NH_3)_2^+$	1.7×10^7	
$Ag(CN)_2^-$	1×10^{21}	
$Ag(S_2O_3)_2^{3-}$	2.9×10^{13}	
$Ag(OH)_4^-$	1.1×10^{33}	
$CdBr_4^{2-}$	5×10^3	
$Cr(OH)_4^-$	8×10^{29}	
$Co(SCN)_4^{2-}$	1×10^3	

Complex Ion Formation (4 of 4)

Table 17.1 [continued]

Complex Ion	K_f	
$Cu(NH_3)_4{}^{2+}$	5×10^{12}	
$Cu(CN)_4{}^{2-}$	1×10^{25}	
$Ni(NH_3)_6{}^{2+}$	1.2×10^9	
$Fe(CN)_6{}^{4-}$	1×10^{35}	
$Fe(CN)_6{}^{3-}$	1×10^{42}	
$Zn(OH)_4{}^{2-}$	4.6×10^{17}	

Calculate the concentration of free Ag^+ in a solution that is 0.01 M $AgNO_3$ and 0.20 M NH_3

This concerns the $AgNH_3^+$ formation:

$Ag^+ + NH_3(aq) \rightleftharpoons AgNH_3^+(aq)$ K = $1/K_f$ = $(1.7 \times 10^7)^{-1}$ = 5.9×10^{-8}
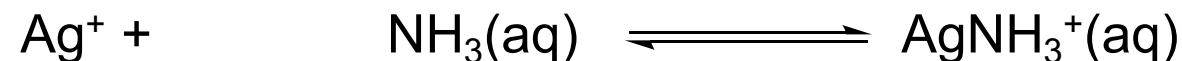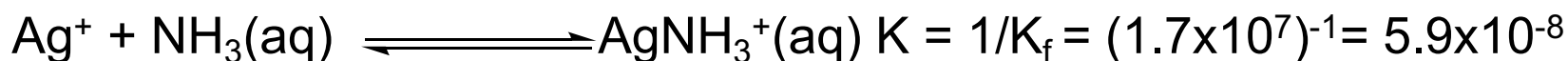
	Ag^+ +	$NH_3(aq) \rightleftharpoons$	$AgNH_3^+(aq)$
Initial (M)	0.010	0	-
Change (M)	$-x$	$+x$	-
Equilibrium (M)	$(0.010 - x)$	x	0.20

$$\frac{\left[Ag^+\right]\left[NH_3\right]^2}{\left[Ag(NH_3)_2^+\right]} = \frac{(x)(0.20)^2}{0.010} = 5.9 \times 10^{-8}$$

$$x = 1.5 \times 10^{-8}\ M = \left[Ag^+\right]$$

Amphoterism

- **Amphoteric oxides and hydroxides**
  - soluble in strong acids or base, because they can act either as acids or bases.
- Examples: Al^{3+}, Cr^{3+}, Zn^{2+}, and Sn^{2+}.

$$Al(OH)_3(s) + OH^-(aq) \rightleftharpoons Al(OH)_4^-(aq)$$

Al(OH)₃ dissolves in strongly acidic solutions due to an acid–base reaction.

Add H⁺

Add OH⁻

Al(OH)₃ dissolves in strongly basic solutions due to complex ion formation.

$$Al^{3+}(aq) + 3\,H_2O(l) \rightleftharpoons 3\,H^+(aq) + Al(OH)_3(s)$$
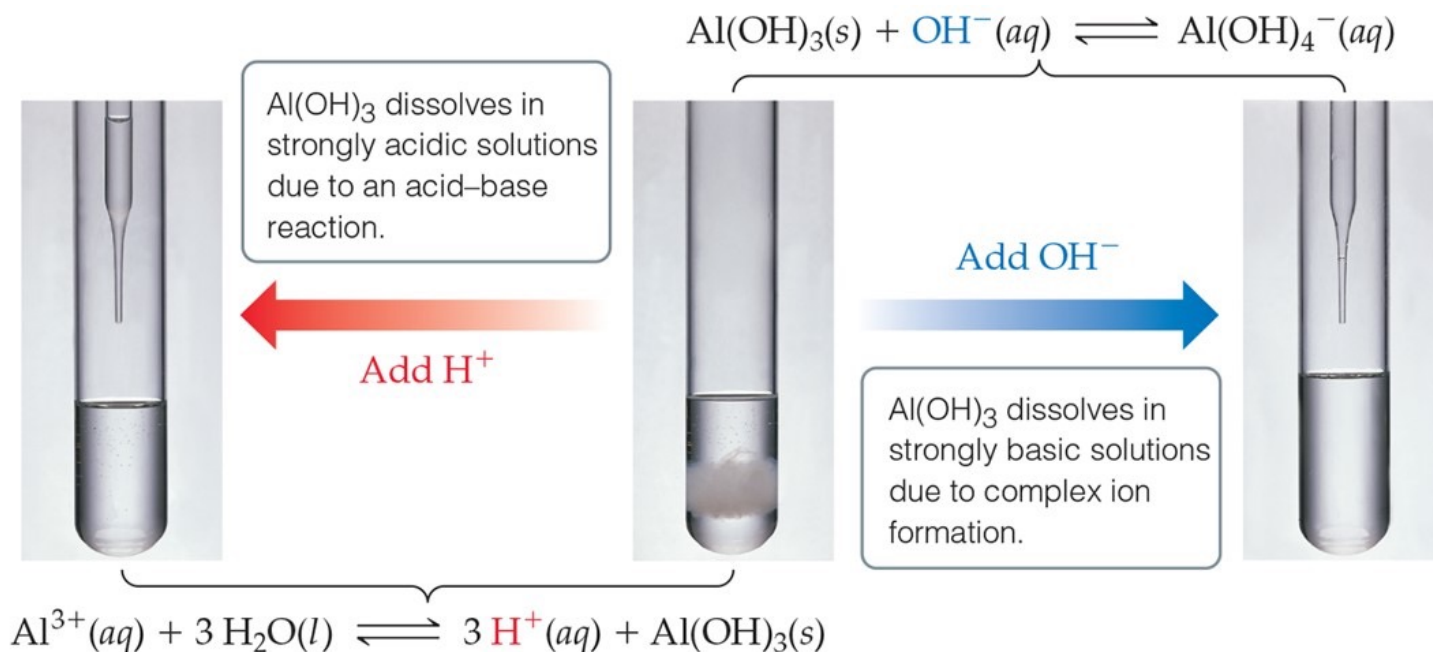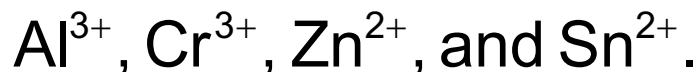
17.6 Precipitation and Ion Separation

- To decide if precipitation will occur, calculate the reaction quotient, Q, and compare it to K_{sp}.

- Q uses the given conditions and has the same form as the K expression.

  - If $Q = K_{sp}$, the system is at equilibrium and the solution is saturated.

  - If $Q < K_{sp}$, more solid can dissolve, no precipitate forms.

  - If $Q > K_{sp}$, a precipitate will form.

Does a precipitate form when 0.10 L of $8.0 \times 10^{-3} \, M \, Pb(NO_3)_2$ is added to $5.0 \times 10^{-3} \, M \, Na_2SO_4$?

Solution

Analyze The problem asks us to determine whether a precipitate forms when two salt solutions are combined.

Plan We should determine the concentrations of all ions just after the solutions are mixed and compare the value of Q with K_{sp} for any potentially insoluble product. The possible metathesis products are $PbSO_4$ and $NaNO_3$. Like all sodium salts, $NaNO_3$ is soluble, but $PbSO_4$ has a K_{sp} of 6.3×10^{-7} (Appendix D) and will precipitate if the Pb^{2+} and SO_4^{2-} concentrations are high enough for Q to exceed K_{sp}.

Sample Exercise 17.17

Solve

When the two solutions are mixed, the volume is 0.10 L + 0.40 L = 0.50 L. The number of moles of Pb^{2+} in 0.10 L of 8.0×10^{-3} M $Pb(NO_3)_2$ is:

$$(0.10 \, \cancel{L}) \left(\frac{8.0 \times 10^{-3} \, \text{mol}}{\cancel{L}} \right) = 8.0 \times 10^{-4} \, \text{mol}$$

The concentration of Pb^{2+} in the 0.50-L mixture is therefore:

$$\left[Pb^{2+} \right] = \frac{8.0 \times 10^{-4} \, \text{mol}}{0.50 \, \text{L}} = 1.6 \times 10^{-3} \, M$$

The number of moles of SO_4^{2-} in 0.40 L of 5.0×10^{-3} M Na_2SO_4 is:

$$(0.40 \, \cancel{L}) \left(\frac{5.0 \times 10^{-3} \, \text{mol}}{\cancel{L}} \right) = 2.0 \times 10^{-3} \, \text{mol}$$

Sample Exercise 17.17 Predicting Whether a Precipitate Forms (3 of 3)

Therefore:

$$\left[SO_4^{2-}\right] = \frac{2.0 \times 10^{-3}\, mol}{0.50\, L} = 4.0 \times 10^{-3}\, M$$

and:

$$Q = \left[Pb^{2+}\right]\left[SO_4^{2-}\right] = \left(1.6 \times 10^{-3}\right)\left(4.0 \times 10^{-3}\right) = 6.4 \times 10^{-6}$$
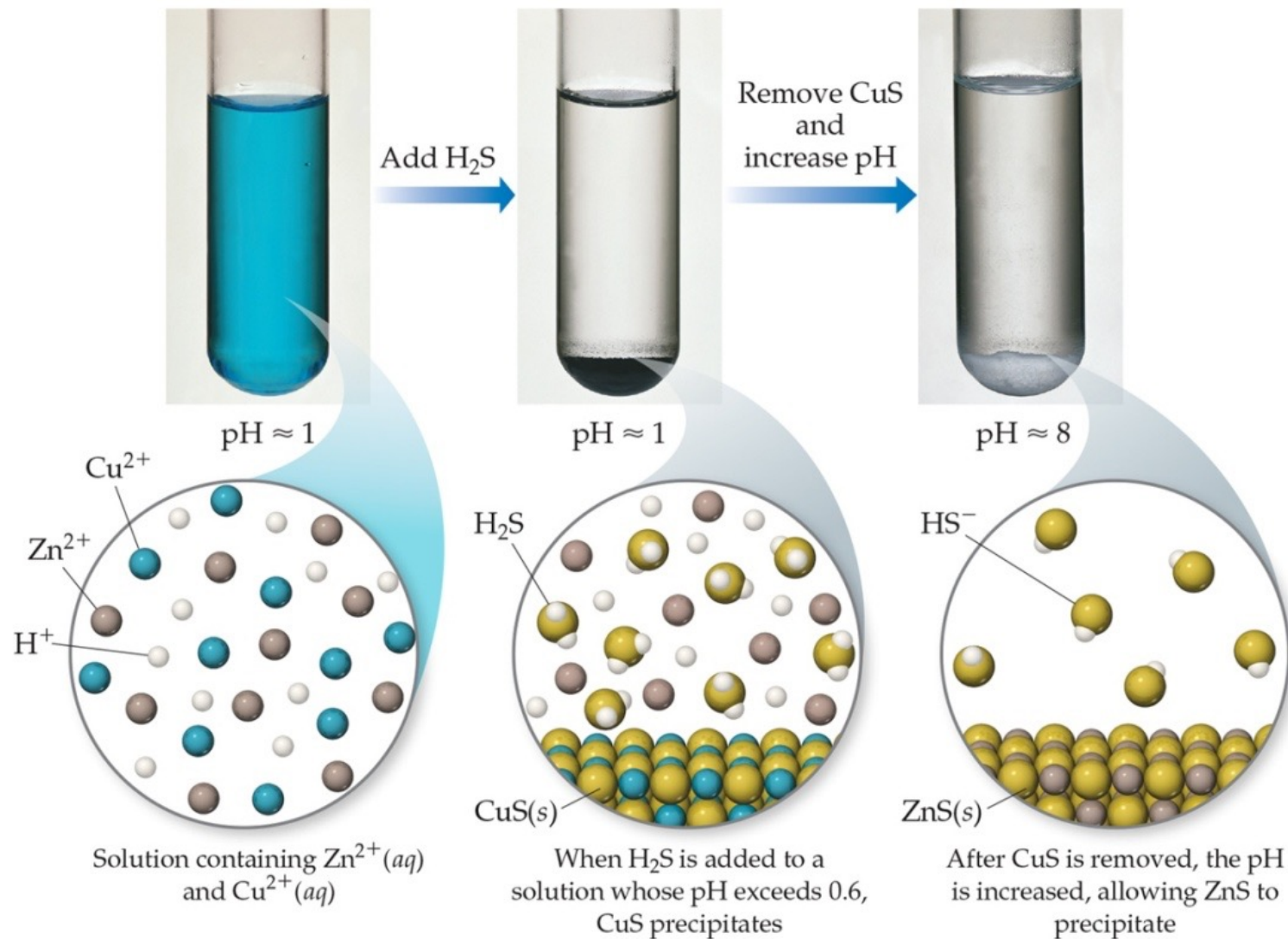
Because $Q > K_{sp}$, $PbSO_4$ precipitates.

Practice Exercise

Does a precipitate form when 0.050 L of $2.0 \times 10^{-2}\, M$ NaF is mixed with 0.010 L of $1.0 \times 10^{-2}\, M$ $Ca(NO_3)_2$?

Selective Precipitation of Ions

- Ions can be separated from solution based on their solubilities in the presence of different ions.

pH ≈ 1

Cu²⁺
Zn²⁺
H⁺

Solution containing $Zn^{2+}(aq)$ and $Cu^{2+}(aq)$

Add H₂S

pH ≈ 1

H₂S

$CuS(s)$

When H₂S is added to a solution whose pH exceeds 0.6, CuS precipitates

Remove CuS and increase pH

pH ≈ 8

HS⁻

$ZnS(s)$

After CuS is removed, the pH is increased, allowing ZnS to precipitate

17.7 Qualitative Analysis of Ions

One can use differences in solubilities of salts to separate ions in a mixture. This has been used for qualitative analysis of the presence of ions in a solution. A new application is recovery of metal ions from batteries used in electric vehicles.