

Ionic Equilibria in Aqueous Solutions

- Equilibria of Acid-Base Buffer Systems
 - The Common Ion Effect
 - The Henderson-Hasselbalch Equation
 - Buffer Capacity and Range
 - Preparing a buffer
- Acid-Base Titration Curves
 - Acid-Base Indicators
 - Strong-Acid-Strong Base Titrations
 - Weak Acid-Strong Base Titrations
 - Weak Base-Strong Acid Titrations
 - Polyprotic Acid Titrations
 - Amino Acids as Polyprotic Acids

Ionic Equilibria in Aqueous Solutions

- Equilibria of Slightly Soluble Ionic Compounds
 - The Solubility-Product Constant
 - Calculations involving K_{sp}
 - The Effect of a Common Ion
 - The Effect of pH
 - Q_{sp} vs. K_{sp}
- Equilibria involving Complex Ions
 - Formation of Complex Ions
 - Complex Ions and Solubility
 - Amphoteric Hydroxides

Ionic Equilibria in Aqueous Solutions

- The simplest acid-base equilibria are those in which a single acid or base solute reacts with water
- In this chapter, we will look at:
 - solutions of weak **acids** and **bases** through acid/base ionization
 - The reactions of salts with water
 - Titration curves
- All of these processes involve equilibrium theory

Ionic Equilibria in Aqueous Solutions

■ Equilibria of Acid-Base Buffer Systems

➤ Buffer

- An Acid-Base Buffer is a species added to a solution to minimize the impact on pH from the addition of $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ ions
- Small amounts of acid or base added to an unbuffered solution can change the pH by several units
- Since pH is a logarithmic term, the change in $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ can be several orders of magnitude

Ionic Equilibria in Aqueous Solutions

■ The Common Ion Effect

- Buffers work through a phenomenon known as the:

Common Ion Effect

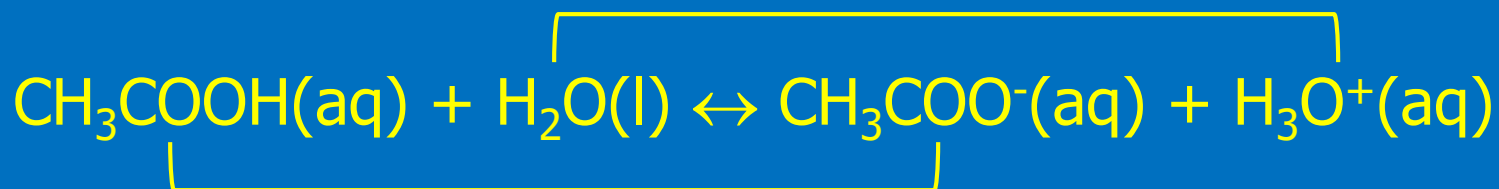
- The common ion effect occurs when a given ion is added to an "equilibrium mixture of a weak acid or weak base that already contains that ion
- The additional "common ion" shifts the equilibrium away from its formation to more of the undissociated form; i.e., the acid or base dissociation decreases
- A buffer must contain an "acidic" component that can react with the added OH^- ion, and a "basic" component that can react with the added $[\text{H}_3\text{O}^+]$

Ionic Equilibria in Aqueous Solutions

- The buffer components cannot be just any acid or base
- The components of a buffer are usually the conjugate acid-base pair of the weak acid (or base) being buffered

Ex: Acetic Acid & Sodium Acetate

Acetic acid is a weak acid, slightly dissociated



Acid

Base

Conjugate

Conjugate

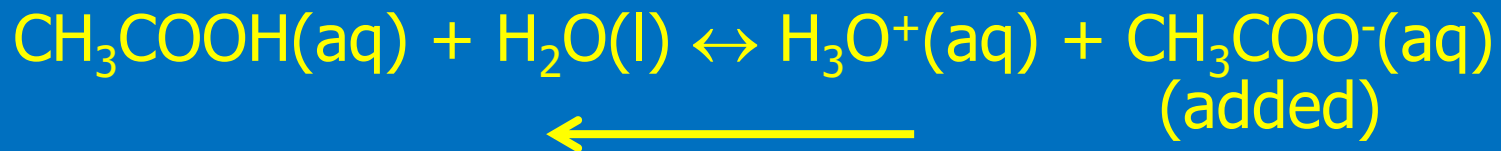
Base

Acid

Ionic Equilibria in Aqueous Solutions

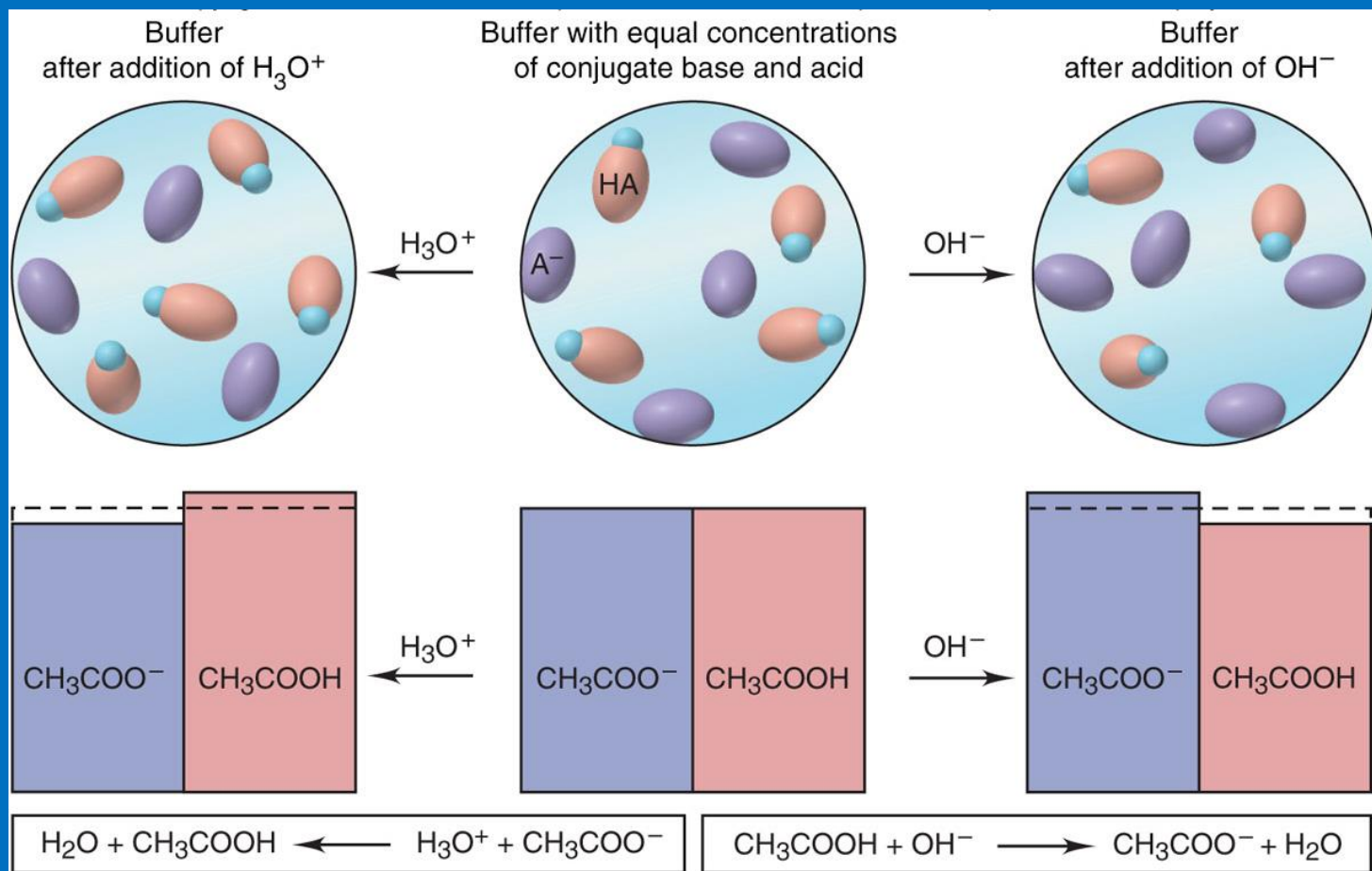
➤ Ex: Acetic Acid & Sodium Acetate (Con't)

- Now add Sodium Acetate (CH_3COONa), a strong electrolyte (Acetate ion is the conjugate base)



- The added Acetate ions shift the equilibrium to the left forming more undissociated acetic acid
- This lowers the extent of acid dissociation, which lowers the acidity by reducing the $[\text{H}_3\text{O}^+]$ and increasing the pH
- Similarly, if Acetic Acid is added to a solution of Sodium Acetate, the Acetate ions already present act to suppress the dissociation of the acid

Ionic Equilibria in Aqueous Solutions



When a **small** amount of $[\text{H}_3\text{O}^+]$ is added to acetic acid/acetate buffer, that same amount of acetate ion (CH_3COO^-) combines with it, increasing the concentration of acetic acid (CH_3COOH). The change in the $[\text{HA}]/[\text{A}^-]$ ratio is small; the added $[\text{H}_3\text{O}^+]$ is effectively tied up; thus, the change in pH is also small

Ionic Equilibria in Aqueous Solutions

■ Essential Features of a Buffer

- A buffer consists of high concentrations of the undissociated acidic component $[HA]$ and the conjugate base $[A^-]$ component
- When small amounts of $[H_3O^+]$ or $[OH^-]$ are added to the buffer, they cause small amounts of one buffer component to convert to the other component

Ionic Equilibria in Aqueous Solutions

Ex. When a small amount of H_3O^+ is added to an Acetate buffer, that same amount of CH_3COO^- combines with it, increasing the amount of undissociated CH_3COOH tying up potential $[\text{H}_3\text{O}^+]$

Similarly, a small amount of OH^- added combines with undissociated CH_3COOH to form CH_3COO^- & H_2O tying up potential $[\text{OH}^-]$

In both cases, the relative changes in the amount of buffer components is small, but the added $[\text{H}_3\text{O}^+]$ or $[\text{OH}^-]$ ions are tied up as undissociated components; thus little impact on pH

Ionic Equilibria in Aqueous Solutions

- The equilibrium perspective



$$K_a = \frac{[\text{H}^+][\text{A}^-]}{\text{HA}} = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}_3\text{O}^+] = K_a \times \frac{[\text{HA}]}{[\text{A}^-]} = K_a \times \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

- The $[\text{H}_3\text{O}^+]$ (pH) of the solution depends directly on the buffer-component concentration ratio
- If the ratio $[\text{HA}]/[\text{A}^-]$ goes up, $[\text{H}_3\text{O}^+]$ goes up (pH down)
- If the ratio $[\text{HA}]/[\text{A}^-]$ goes down, $[\text{H}_3\text{O}^+]$ goes down ($[\text{OH}^-]$ goes up) and pH increases (less acidic)
- When a small amount of a strong acid is added, the increased amount of $[\text{H}_3\text{O}^+]$ reacts with a stoichiometric amount of acetate ion from the buffer to form more undissociated acetic acid

Ionic Equilibria in Aqueous Solutions

■ The Henderson-Hasselbalch Equation

- For any weak acid, HA, the dissociation equation and K_a expression are:



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The key variable that determines the $[\text{H}_3\text{O}^+]$ is the ratio of acid species (HA) to base species (A^-)

$$[\text{H}_3\text{O}^+] = k_a \times \frac{[\text{HA}] \text{ (acid species)}}{[\text{A}^-] \text{ (base species)}}$$

$$-\log[\text{H}_3\text{O}^+] = -\log K_a - \log \frac{[\text{HA}]}{[\text{A}^-]}$$

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

$$\text{pH} = \text{p}K_a + \log \frac{[\text{base}]}{[\text{acid}]}$$

Note the change in sign of "log" term and inversion of acid-base terms

Ionic Equilibria in Aqueous Solutions

■ Buffer Capacity

- A buffer resists a pH change as long as the concentration of buffer components are large compared with the amount of strong acid or base added
- Buffer Capacity is a measure of the ability to resist pH change
- Buffer capacity depends on both the absolute and relative component concentrations
 - Absolute - The more concentrated the components of a buffer, the greater the buffer capacity
 - Relative – For a given addition of acid or base, the buffer-component concentration ratio changes less when the concentrations are similar than when they are different

Ionic Equilibria in Aqueous Solutions

- Ex. Consider 2 solutions
 - Solution 1 – Equal volumes of 1.0M HAc and 1.0 M Ac⁻
 - Solution 2 – Equal volumes of 0.1M HAc and 0.1M Ac⁻
 - Same pH (4.74) but 1.0 M buffer has much larger buffer capacity

(Con't)

Ionic Equilibria in Aqueous Solutions

Ex. Buffer #1 $[HA] = [A^-] = 1.000 \text{ M}$

Add 0.010 mol of OH^- to 1.00 L of buffer

$[HA]$ changes to 0.990 M $[A^-]$ changes to 1.010 M

$$\frac{[A^-]_{\text{init}}}{[HA]_{\text{init}}} = \frac{1.000 \text{ M}}{1.000 \text{ M}} = 1.000 \quad \frac{[A^-]_{\text{final}}}{[HA]_{\text{final}}} = \frac{1.010 \text{ M}}{0.990 \text{ M}} = 1.020$$

$$\text{Percent change} = \frac{1.020 - 1.000}{1.000} \times 100 = 2\%$$

Ionic Equilibria in Aqueous Solutions

Buffer #2 $[HA] = 0.250 \text{ M}$ $[A^-] = 1.75 \text{ M}$

Add 0.010 mol of OH^- to 1.00 L of buffer

$[HA]$ changes to 0.240 M $[A^-]$ changes to 1.760 M

$$\frac{[A^-]_{\text{init}}}{[HA]_{\text{init}}} = \frac{1.750 \text{ M}}{0.250 \text{ M}} = 7.000$$

$$\frac{[A^-]_{\text{final}}}{[HA]_{\text{final}}} = \frac{1.760 \text{ M}}{0.240 \text{ M}} = 7.330$$

$$\text{Percent change} = \frac{7.330 - 7.000}{7.000} \times 100 = 4.7\%$$

Buffer-component concentration ratio is much larger when the initial concentrations of the components are very different

Ionic Equilibria in Aqueous Solutions

- A buffer has the highest capacity when the component acid / base concentrations are equal:

$$\frac{[\text{Base}]}{[\text{Acid}]} = \frac{[\text{A}^-]}{[\text{HA}]} = 1$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right) = \text{pK}_a + \log 1 = \text{pK}_a + 0 = \text{pK}_a$$

A buffer whose pH is equal to or near the pK_a of its acid component has the highest buffer capacity

Ionic Equilibria in Aqueous Solutions

■ Buffer Range

- pH range over which the buffer acts effectively is related to the relative component concentrations
- The further the component concentration ratio is from 1, the less effective the buffering action
- If the $[A^-]/[HA]$ ratio is greater than 10 or less than 0.1 (or one component concentration is more than 10 times the other) the buffering action is poor

$$\text{pH} = \text{pK}_a + \log\left(\frac{10}{1}\right) = \text{pK}_a + 1 \quad \text{pH} = \text{pK}_a + \log\left(\frac{1}{10}\right) = \text{pK}_a - 1$$

- Buffers have a usable range within:

± 1 pH unit or pK_a value of the acid components

Ionic Equilibria in Aqueous Solutions

■ Equilibria of Acid-Base Systems

➤ Preparing a Buffer

- Choose the Conjugate Acid-Base pair

 - ◆ Driven by pH

 - ◆ Ratio of component concentrations close to 1 and $\text{pH} \approx \text{pK}_a$

Ionic Equilibria in Aqueous Solutions

Ex. Assume you need a biochemical buffer whose pH is 3.9

1. pK_a of acid component should be close to 3.9

$$K_a = 10^{-3.9} = 1.3 \times 10^{-4}$$

2. From a table of pK_a values select buffer possibilities

Lactic acid (pK_a = 3.86)

Glycolic acid (pK_a = 3.83)

Formic Acid (pK_a = 3.74)

3. To avoid common biological species, select Formic Acid

Buffer components of Formic Acid

Formic Acid – HCOOH (Acid)

Formate Ion – HCOO⁻ (Conjugate Base)

Obtain soluble Formate salt – HCOONa

Con't

Ionic Equilibria in Aqueous Solutions

4. Calculate Ratio of Buffer Component Concentrations ($[A^-]/[HA]$) that gives desired pH

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

$$3.9 = 3.74 + \log\left(\frac{[\text{HCOO}^-]}{[\text{HCOOH}]}\right)$$

$$\log\left(\frac{[\text{HCOO}^-]}{[\text{HCOOH}]}\right) = 3.9 - 3.74 = 0.16$$

$$\text{Thus: } \left(\frac{[\text{HCOO}^-]}{[\text{HCOOH}]}\right) = 10^{0.16} = 1.4$$

Con't

Ionic Equilibria in Aqueous Solutions

➤ Preparing a Buffer (Con't)

● Determine the Buffer Concentrations

- ◆ The higher the concentration of the components, the higher the buffer capacity
- ◆ Assume 1 Liter of buffer is required and you have a stock of 0.40 M Formic Acid (HCOOH)
- ◆ Compute moles and then grams of Sodium Formate (HCOONa) needed to produce 1.4/1.0 ratio

$$\text{Moles of HCOOH} = 1.0 \text{ L} \times \frac{0.40 \text{ mol HCOOH}}{1.0 \text{ L soln}} = 0.40 \text{ mol HCOOH}$$

$$\text{Moles of HCOONa} = 0.40 \text{ mol HCOOH} \times \frac{1.40 \text{ mol HCOONa}}{1.0 \text{ mol HCOOH}} = 0.56 \text{ mol HCOONa}$$

$$\text{Mass of HCOONa} = 0.56 \text{ mol HCOONa} \times \frac{68.01 \text{ g HCOONa}}{1 \text{ mol HCOONa}} = 38 \text{ g HCOONa}$$

Con't

Ionic Equilibria in Aqueous Solutions

➤ Preparing a Buffer (Con't)

- Mix the solution and adjust the pH
 - ◆ The prepared solution may not be an **ideal solution** (see Chapter 13, Section 6)

The desired pH (3.9) may not exactly match the actual value of the buffer solution

- ◆ The pH of the buffer solution can be adjusted by a few tenths of a pH unit by adding strong acid or strong base.

Ionic Equilibria in Aqueous Solutions

■ Acid-Base Titration Curves

➤ Acid-Base Indicators

- Weak organic acid (HIn) that has a different color than its conjugate base (In⁻)
- The color change occurs over a relatively narrow pH range
- Only small amounts of the indicator are needed; too little to affect the pH of the solution
- The color range of typical indicators reflects a 100 - fold range in the [HIn]/[In⁻] ratio
- This corresponds to a pH range of 2 pH units

Mixing Acids & Bases

- Acids and bases react through neutralization reactions
- The change in pH of an acid mixed with a base is tracked with an **Acid-Base Titration Curve**
- Titration:
 - Titration Curve: Plot of pH vs. the volume of the "Strong" acid or "Strong" base being added via buret
 - Solution in buret is called the "**titrant**"
- **Equivalence Point**: Point in a titration curve where **stoichiometric** amounts of acid and base have been mixed (point of complete reaction)
- 3 Important Cases:
 - Strong Acid + Strong Base (& vice versa)
 - Weak Acid + Strong Base
 - Weak Base + Strong Acid

Titration Curves

- Titration Curve: Plot of measured pH *versus* Volume of acid or base added during a “Neutralization” experiment

- All Titration Curves have a characteristic

“Sigmoid (S-shaped) profile

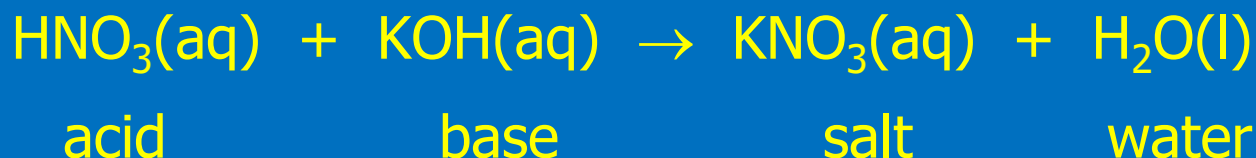
- Beginning of Curve: pH changes slowly
 - Middle of Curve: pH changes very rapidly
 - End of Curve: pH changes very slowly again
- pH changes very rapidly in the titration as the equivalence point (point of complete reaction) is reached and right after the equivalence point

Neutralization Reactions

- Acids and Bases react with each other to form salts (not always) and water (not always) through

Neutralization Reactions

- Neutralization reaction between a strong acid and strong base



- Neutralization of a strong acid and strong base reaction lies very far to the ***right*** (K_n is very large); reaction goes to completion; net ionic equation is

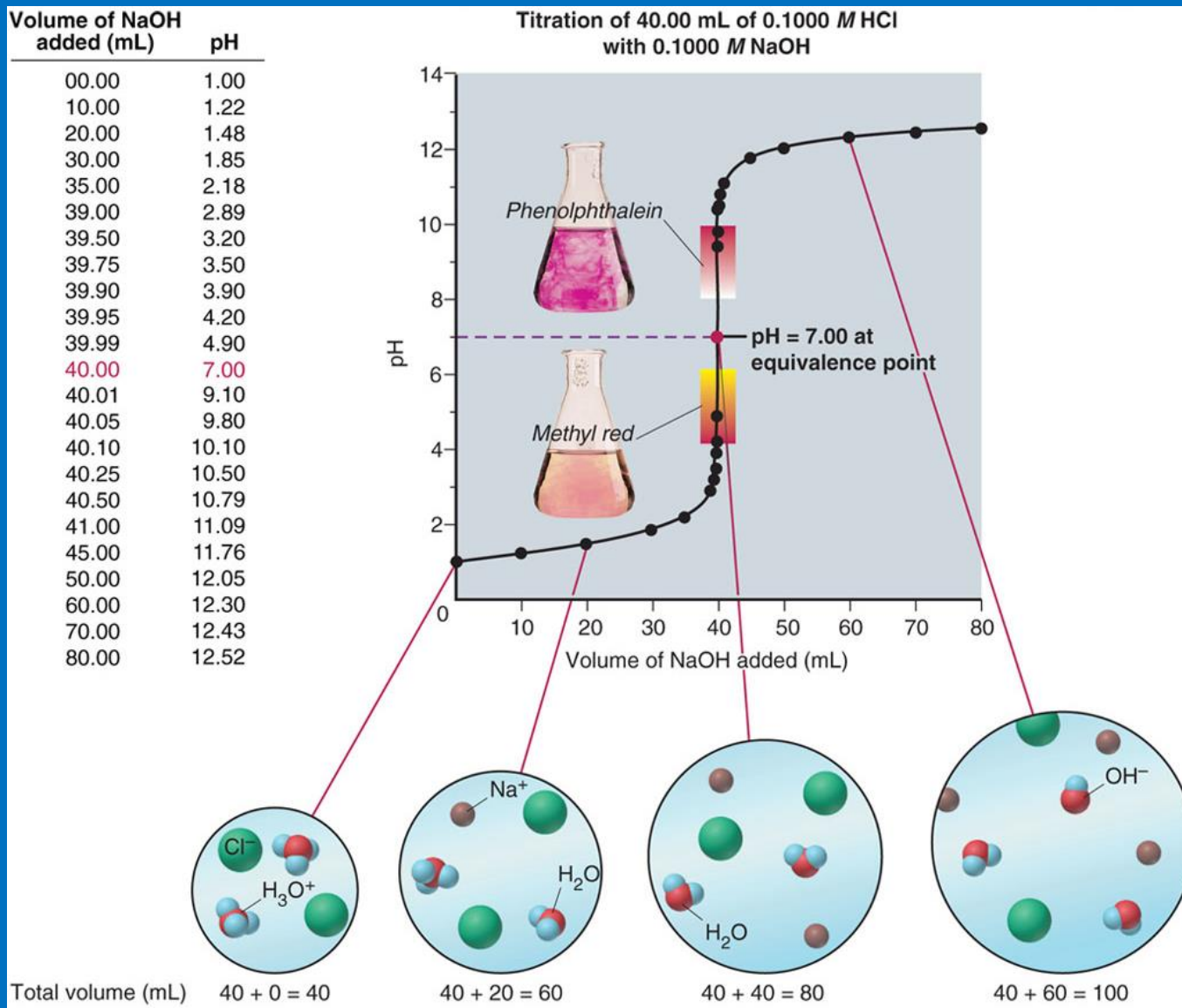


$$K_n = \frac{[\text{H}_2\text{O}]^2}{[\text{H}_3\text{O}^+][\text{OH}^-]} = \frac{1}{[\text{H}_3\text{O}^+][\text{OH}^-]} = \frac{1}{K_w} = 1 \times 10^{14}$$

- H_3O^+ and OH^- efficiently react with each other to form water

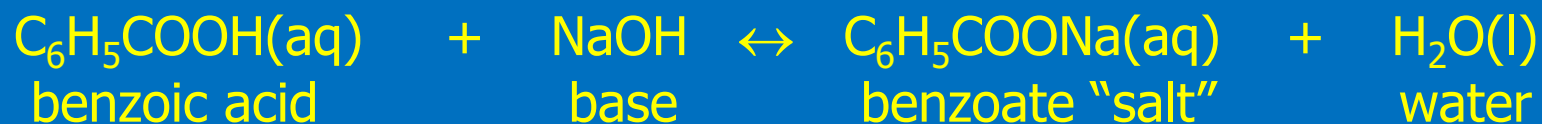
Titration Curves

Curve for Titration of a Strong Acid by a Strong Base



Neutralization Reactions

- Neutralization reactions between **weak acids** and **strong bases** (net ionic equation shown below)



- The above equilibrium lies very far to the right

The two equilibria below can be added together to provide the overall neutralization reaction shown above



$$K_a = 1.7 \times 10^{-5} \quad (\text{from Appendix C})$$



$$\text{Recall: } K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

$$1/K_w = (1 \times 10^{-14})^{-1} = 1 \times 10^{14}$$

Neutralization Reactions

- The overall neutralization equilibrium constant (K_n) is the product of the two intermediate equilibrium constants

$$(K_a \text{ \& } 1/K_w)$$

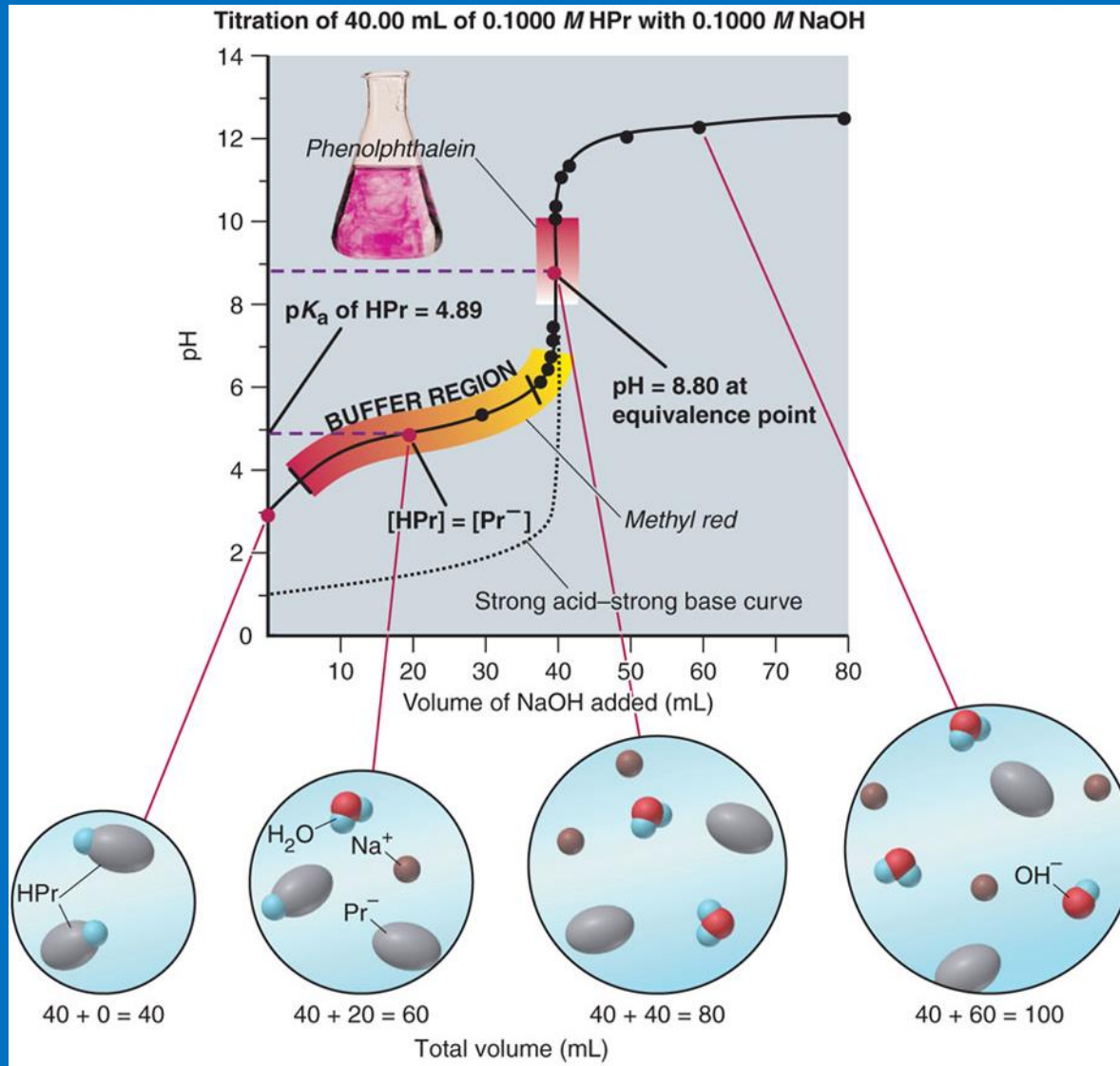
$$K_N = K_a \times 1/K_w = (1.7 \times 10^{-5})(1 \times 10^{14}) = 1.9 \times 10^9$$

(very large!)

- Weak acids react *completely* with strong bases

Titration Curves

Curve for Titration of a Weak Acid by a Strong Base



Weak Acid-Strong Base Titration Curve

- Consider the reaction between Propanoic Acid (weak acid) and Sodium Hydroxide (NaOH) (strong base)
- K_a for $\text{CH}_3\text{CH}_2\text{COOH}$ (HPr) - 1.3×10^{-5}
- The Titration Curve (see previous slide)
 - The bottom dotted curve corresponds to the strong acid-strong base titration
 - The Curve consists of 4 regions, the first 3 of which differ from the strong acid case
 - The initial pH is "Higher"
 - ★ The weak acid dissociates only slightly producing less $[\text{H}_3\text{O}^+]$ than with a strong acid
 - The gradually arising portion of the curve before the steep rise to the equivalence point is called the "buffer region"

Weak Acid-Strong Base Titration Curve

- ◆ As HPr reacts with the strong base, more and more of the conjugate base (Pr^-) forms creating an (HPr/ Pr^-) buffer
- ◆ At the midpoint of the "Buffer" region, half the original HPr has reacted

$$[\text{HPr}] = [\text{Pr}^-] \quad \text{or} \quad \frac{[\text{Pr}^-]}{[\text{HPr}]} = 1$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{Pr}^-]}{[\text{HPr}]}\right) = \text{pK}_a + \log(1) = \text{pK}_a$$

pH at midpoint of "Buffer" region is common method of estimating pK_a of an "unknown" acid

Weak Acid-Strong Base Titration Curve

- The pH at the “equivalence point” is greater than 7.00
 - ◆ The weak-acid anion (Pr^-) acts as a weak base to accept a proton from H_2O forming OH^-
 - ◆ The additional $[\text{OH}^-]$ raises the pH
- Beyond the equivalence point, the pH increases slowly as excess OH^- is added

Weak Base-Strong Acid Titration

- Neutralization reactions between weak bases and strong acids (net ionic equation shown below)



- Above equilibrium also lies very far to the right; the two equilibria below can be added together to provide the overall neutralization reaction shown above

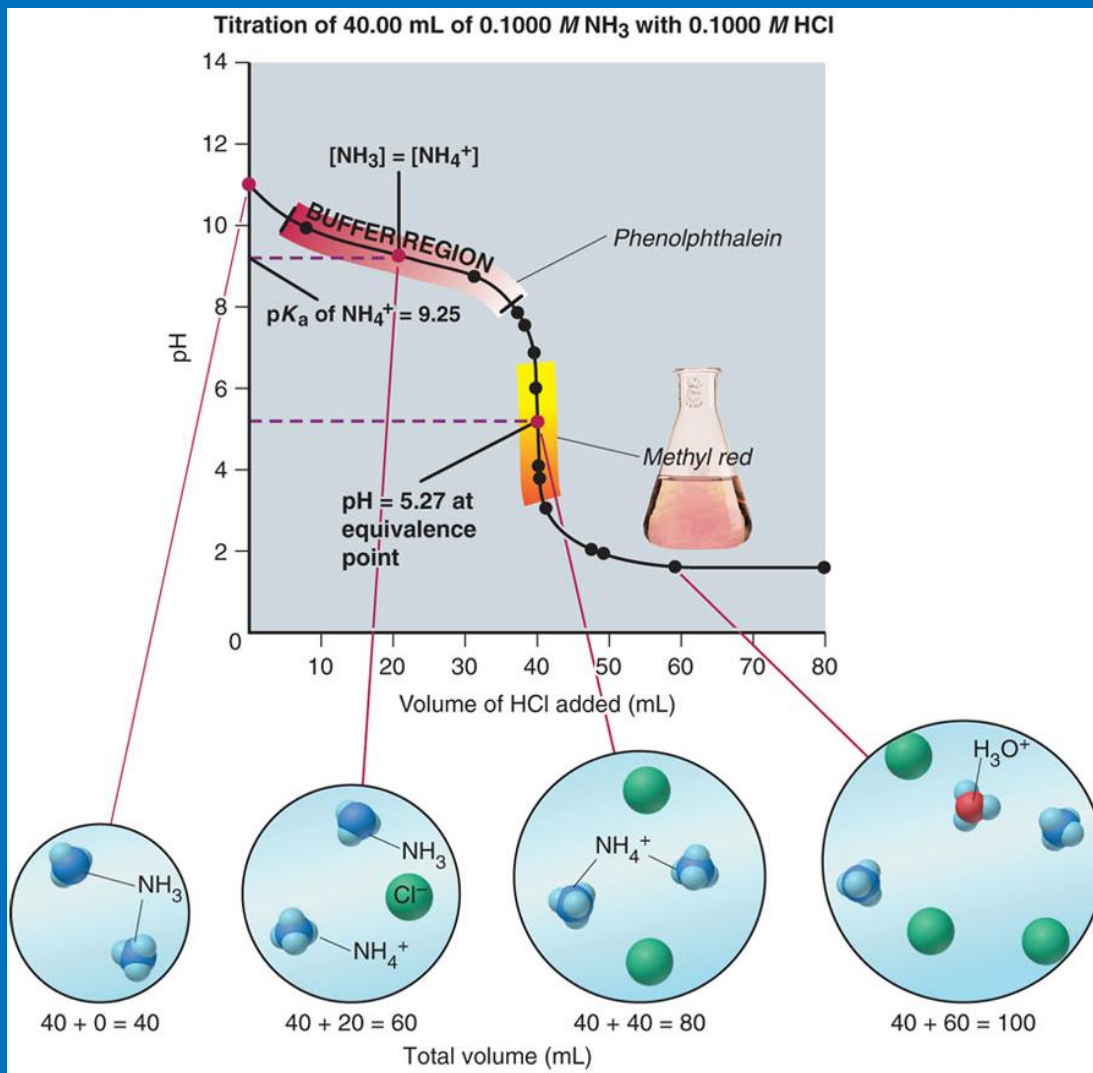


$$K_{\text{N}} = K_{\text{b}} \times 1/K_{\text{w}} = (1.8 \times 10^{-5})(1 \times 10^{14}) = 1.8 \times 10^9 \text{ (very large!)}$$

- Weak bases react *completely* with strong acids

Weak Base-Strong Acid Titration

Curve for Titration of a Weak Base by a Strong Acid



Polyprotic Acid Titrations

- Polyprotic Acids have more than one ionizable proton
- Except for Sulfuric Acid (H_2SO_4), the common polyprotic acids are all weak acids
- Successive K_a values for a polyprotic acid differ by several orders of magnitude
- The first H^+ is lost much more easily than subsequent ones
- All "1st" protons (H^+) are removed before any of the "2nd" protons



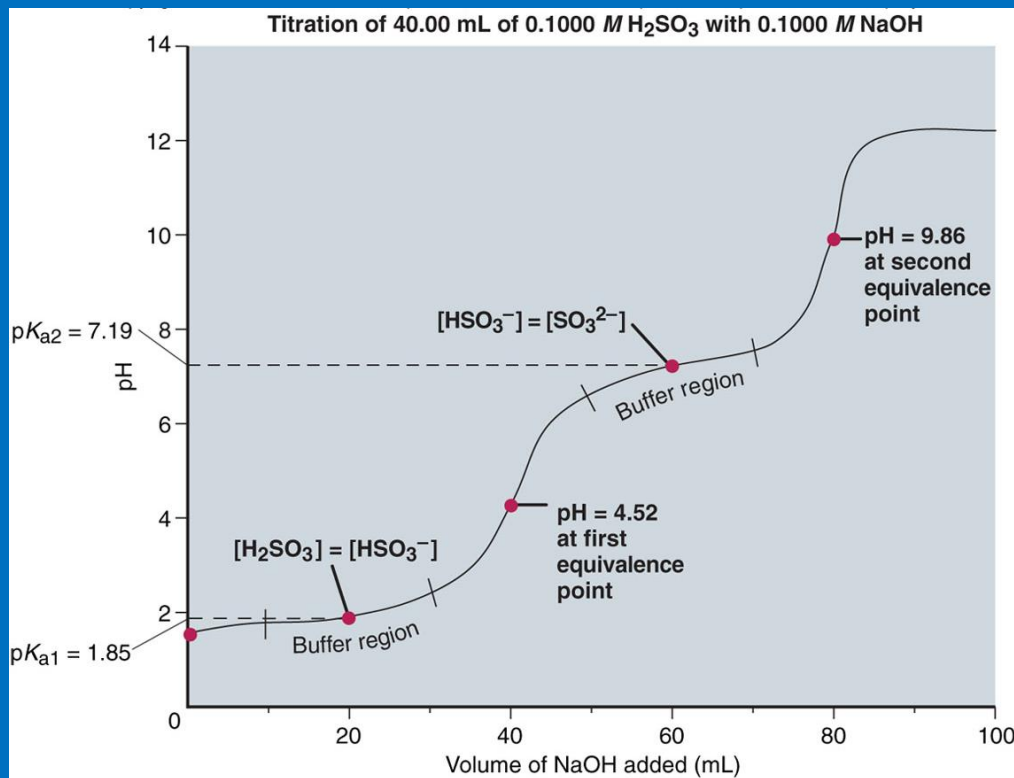
$$K_{a1} = 1.4 \times 10^{-2} \quad \text{and} \quad \text{p}K_{a1} = 1.85$$



$$K_{a2} = 6.5 \times 10^{-8} \quad \text{and} \quad \text{p}K_{a2} = 7.19$$

Polyprotic Acid Titrations

- Each mole of H^+ is titrated separately
- In a diprotic acid two OH^- ions are required to completely remove both H^+ ions
- All H_2SO_3 molecules lose one H^+ before any HSO_3^- ions lose a H^+ to form SO_3^{2-}



Titration curves look like two weak acid-strong base curves joined end-to-end

HSO_3^- is the conjugate base of H_2SO_3 ($K_b = 7.1 \times 10^{-13}$)

HSO_3^- is also an acid ($K_a = 6.5 \times 10^{-8}$) dissociating to form its conjugate base SO_3^{2-}

Slightly Soluble Compounds

- Most solutes, even those called “soluble,” have a limited solubility in a particular solvent
- In a saturated solution, at a particular temperature, equilibrium exists between the dissolved and undissolved solute
- Slightly soluble ionic compounds, normally called “insoluble,” reach equilibrium with very little of the solute dissolved
- Slightly soluble compounds can produce complex mixtures of species
- Discussion here is to assume that the small amount of a slightly soluble solute that does dissolve, dissociates completely

Equilibria - Slightly Soluble Ionic Compounds

Solubility Rules for Ionic Compounds in Water

Soluble Ionic Compounds

1. All common compounds of Group 1A(1) ions (Li^+ , Na^+ , K^+ , etc.) and ammonium ion (NH_4^+) are soluble.
2. All common nitrates (NO_3^-), acetates (CH_3COO^- or $\text{C}_2\text{H}_3\text{O}_2^-$), and most perchlorates (ClO_4^-) are soluble.
3. All common chlorides (Cl^-), bromides (Br^-), and iodides (I^-) are soluble, *except* those of Ag^+ , Pb^{2+} , Cu^+ , and Hg_2^{2+} . All common fluorides (F^-) are soluble, *except* those of Pb^{2+} and Group 2A(2).
4. All common sulfates (SO_4^{2-}) are soluble, *except* those of Ca^{2+} , Sr^{2+} , Ba^{2+} , Ag^+ , and Pb^{2+} .

Insoluble Ionic Compounds

1. All common metal hydroxides are insoluble, *except* those of Group 1A(1) and the larger members of Group 2A(2) (beginning with Ca^{2+}).
2. All common carbonates (CO_3^{2-}) and phosphates (PO_4^{3-}) are insoluble, *except* those of Group 1A(1) and NH_4^+ .
3. All common sulfides are insoluble *except* those of Group 1A(1), Group 2A(2), and NH_4^+ .

Equilibria - Slightly Soluble Ionic Compounds

- Equilibrium exists between solid solute and the aqueous ions



- Set up "Reaction Quotient"

$$Q_c = \frac{[\text{Pb}^{2+}][\text{SO}_4^{2-}]}{[\text{PbSO}_4(\text{s})]}$$

$$Q_c [\text{PbSO}_4(\text{s})] = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

Note: concentration of a solid - $[\text{PbSO}_4(\text{s})] = 1$

- Define Solubility Product

$$Q_{sp} = Q_c [\text{PbSO}_4(\text{s})] = [\text{Pb}^{2+}][\text{SO}_4^{2-}]$$

- When solid PbSO_4 reaches equilibrium with Pb^{2+} and SO_4^{2-} at saturation, the numerical value of Q_{sp} attains a constant value called the solubility-product constant (K_{sp})

Q_{sp} at saturation = K_{sp} = solubility - product constant

Equilibria - Slightly Soluble Ionic Compounds

- The Solubility Product Constant (K_{sp})
 - Value of K_{sp} depends only on temperature, not individual ion concentrations
 - Saturated solution of a slightly soluble ionic compound, M^pX^q , composed of ions M^{n+} and X^{z-} , the equilibrium condition is:

$$Q_{sp} = [M^{n+}]^p [X^{z-}]^q = K_{sp}$$

Equilibria - Slightly Soluble Ionic Compounds

➤ Single-Step Process



$$K_{\text{sp}} = [\text{Cu}^{2+}][\text{OH}^-]^2$$

➤ Multi-Step Process



$$K_{\text{sp}} = [\text{Mn}^{2+}][\text{HS}^-][\text{OH}^-]$$

Equilibria - Slightly Soluble Ionic Compounds

Solubility-Product Constants (K_{sp}) of Selected Ionic Compounds at 25°C

Name, Formula	K_{sp}
Aluminum hydroxide, Al(OH) ₃	3×10^{-34}
Cobalt(II) carbonate, CoCO ₃	1.0×10^{-10}
Iron(II) hydroxide, Fe(OH) ₂	4.1×10^{-15}
Lead(II) fluoride, PbF ₂	3.6×10^{-8}
Lead(II) sulfate, PbSO ₄	1.6×10^{-8}
Mercury(I) iodide, Hg ₂ I ₂	4.7×10^{-29}
Silver sulfide, Ag ₂ S	8×10^{-48}
Zinc iodate, Zn(IO ₃) ₂	3.9×10^{-6}

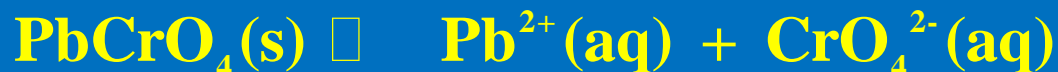
Relationship Between K_{sp} and Solubility at 25°C

No. of Ions	Formula	Cation/Anion	K_{sp}	Solubility (M)
2	MgCO ₃	1/1	3.5×10^{-8}	1.9×10^{-4}
2	PbSO ₄	1/1	1.6×10^{-8}	1.3×10^{-4}
2	BaCrO ₄	1/1	2.1×10^{-10}	1.4×10^{-5}
3	Ca(OH) ₂	1/2	6.5×10^{-6}	1.2×10^{-2}
3	BaF ₂	1/2	1.5×10^{-6}	7.2×10^{-3}
3	CaF ₂	1/2	3.2×10^{-11}	2.0×10^{-4}
3	Ag ₂ CrO ₄	2/1	2.6×10^{-12}	8.7×10^{-5}

Equilibria - Slightly Soluble Ionic Compounds

■ The Effect of the Common Ion

- The presence of a "Common Ion" decreases the solubility of a slightly soluble ionic compound



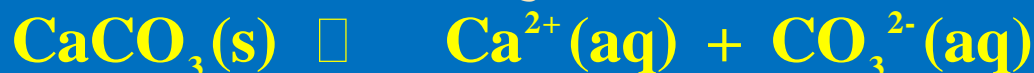
$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = 2.3 \times 10^{-13}$$

- Add some Na_2CrO_4 , a soluble salt, to the saturated PbCrO_4 solution
 - Concentration of CrO_4^{2-} increases
 - Some of excess CrO_4^{2-} combines with Pb^{2+} to form $\text{PbCrO}_4(\text{s})$
 - Equilibrium shifts to the "Left"
 - This shift "reduces" the solubility of PbCrO_4

Equilibria - Slightly Soluble Ionic Compounds

■ The Effect of pH on Solubility

- The Hydronium Ion (H_3O^+) of a strong acid increases the solubility of a solution containing the anion of a weak acid (HA^-)
- Adding some strong acid to a saturated solution of Calcium Carbonate (CaCO_3) introduces large amount of H_3O^+ ion, which reacts immediately with the CaCO_3 to form the weak acid HCO_3^-

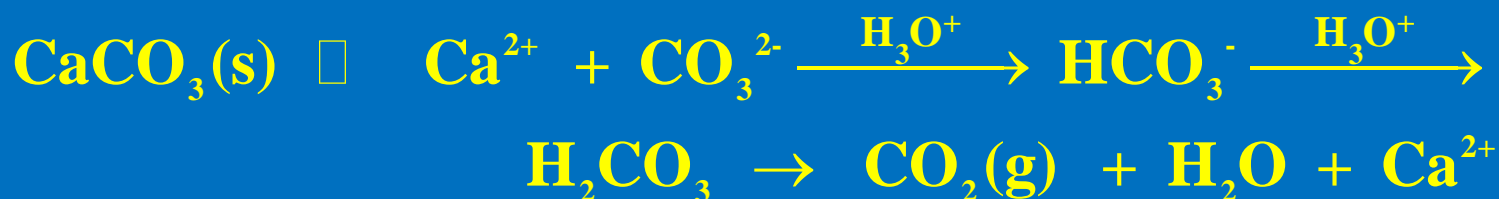


- Additional H_3O^+ reacts with the HCO_3^- to form carbonic acid, H_2CO_3 , which immediately decomposes to H_2O and CO_2



Equilibria - Slightly Soluble Ionic Compounds

- The equilibrium shifts to the "Right" and more CaCO_3 dissolves – increased solubility
- The overall reaction is:



- Adding H_3O^+ to a saturated solution of a compound with a strong acid anion – AgCl
 - Chloride ion, Cl^- , is the conjugate base of a strong acid (HCl)
 - It coexists with water, i.e. does not react with water
 - There is "No" effect on the equilibrium

Equilibria - Slightly Soluble Ionic Compounds

■ Predicting Formation of a Precipitate

- $Q_{sp} = K_{sp}$ when solution is "saturated"
- $Q_{sp} > K_{sp}$ solution momentarily "supersaturated"
 - Additional solid precipitates until $Q_{sp} = K_{sp}$ again
- $Q_{sp} < K_{sp}$ solution is "unsaturated"
 - No precipitate forms at that temperature
 - More solid dissolves until $Q_{sp} = K_{sp}$

Equilibria - Slightly Soluble Ionic Compounds

■ Selective Precipitation of Ions

- Separation of one ion in a solution from another
- Exploit differences in the solubility of their compounds
- The K_{sp} of the less soluble compound is much smaller than the K_{sp} of the more soluble compound
- Add solution of precipitating ion until the Q_{sp} value of the more soluble compound is almost equal to its K_{sp} value
- The less soluble compound continues to precipitate while the more soluble compound remains dissolved, i.e., the K_{sp} of the less soluble compound is always being exceeded, i.e. precipitation is occurring
- At equilibrium, most of the ions of the less soluble compound have been removed as the precipitate

Equilibria - Slightly Soluble Ionic Compounds

■ Equilibria Involving Complex Ions

- The product of any Lewis acid-base reaction is called an "Adduct", a single species that contains a new covalent bond



- A complex ion consists of a central metal ion covalently bonded to two or more anions or molecules, called ligands

Ionic ligands – OH^- Cl^- CN^-

Molecular ligands – H_2O CO NH_3



Cr^{3+} is the central metal ion

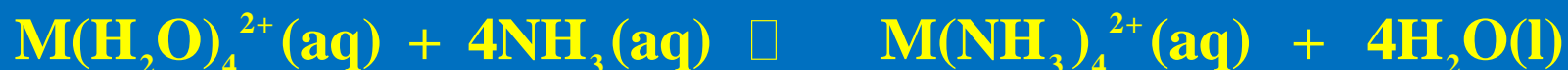
NH_3 molecules are molecular ligands

- Metal acts as Lewis Acid by accepting electron pair; ligands acts as Lewis base by donating electron pair
- **All complex ions are Lewis adducts**

Equilibria - Slightly Soluble Ionic Compounds

■ Complex Ions

- Acidic Hydrated metal ions are complex ions with water molecules as ligands
- When the hydrated cation is treated with a solution of another ligand, the bound water molecules exchange for the other ligand



- At equilibrium

$$\mathbf{K_c = \frac{[M(NH_3)_4^{2+}][H_2O]^4}{[M(H_2O)_4^{2+}][NH_3]^4}}$$

- Water is constant in aqueous reactions
- Incorporate in K_c to define K_f (formation constant)

$$\mathbf{K_f = \frac{K_c}{[H_2O]^4} = \frac{[M(NH_3)_4^{2+}]}{[M(H_2O)_4^{2+}][NH_3]^4}}$$

Equilibria - Slightly Soluble Ionic Compounds

■ Complex Ions (Con't)

- The actual process is stepwise, with ammonia molecules replacing water molecules one at a time to give a series of intermediate species, each with its own formation constant (K_f)



$$K_{f1} = \frac{[\text{M(H}_2\text{O)}_3(\text{NH}_3)^{2+}]}{[\text{M(H}_2\text{O)}_4^{2+}][\text{NH}_3]}$$

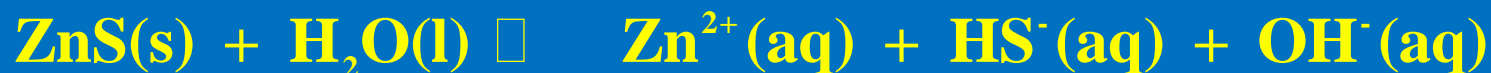
- The sum of the 4 equations gives the overall equation
- The product of the individual formation constants gives the overall formation constant
- The K_f for each step is much larger than "1" because "ammonia" is a stronger Lewis base than H_2O

$$K_f = K_{f1} \times K_{f2} \times K_{f3} \times K_{f4}$$

- Adding excess NH_3 replaces all H_2O and all M^{2+} exists as $\text{M(NH}_3)_4^{2+}$

Complex Ions – Solubility of Precipitates

- Increasing $[\text{H}_3\text{O}^+]$ increases solubility of slightly soluble ionic compounds if the anion of the compound is that of a weak acid
- A Ligand increases the solubility of a slightly soluble ionic compound if it forms a complex ion with the cation



$$K_{\text{sp}} = 2.0 \times 10^{-22}$$

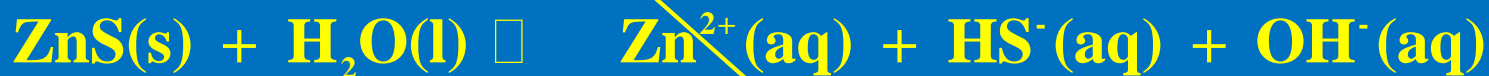
- When 1.0 M NaCN is added to the above solution, the CN^- ions act as ligands and react with the small amount of $\text{Zn}^{2+}(\text{aq})$ to form a complex ion



$$K_{\text{f}} = 4.2 \times 10^{19}$$

Complex Ions – Solubility of Precipitates

- Add the two reactions and compute the overall K



$$K_{\text{overall}} = K_{\text{sp}} \times K_{\text{f}} = (2.0 \times 10^{-22}) (4.2 \times 10^{19}) = 8.4 \times 10^{-3}$$

- The overall equilibrium constant, K_{overall} , is more than a factor of 10^{19} larger than the original K_{sp} (2.0×10^{-22})
- This reflects the increased amount of ZnS in solution as Zn(CN)_4^{2-}

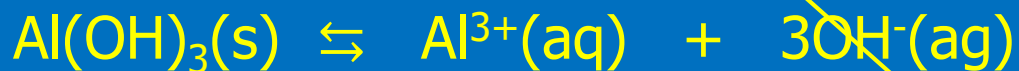
Ionic Equilibria in Aqueous Solutions

■ Equilibria Involving Complex Ions

➤ Amphoteric Oxides & Hydroxides (Recall Chapter 8)

- Some metals and many metalloids form oxides or hydroxides that are amphoteric; they can act as acids or bases in water
- These compounds generally have very little solubility in water, but they do dissolve more readily in acids or bases

◆ Ex. Aluminum Hydroxide



$$K_{\text{sp}} = 3 \times 10^{-34} \text{ (very insoluble in water)}$$

- ◆ In acid solution, the OH^- reacts with H_3O^+ to form water



Ionic Equilibria in Aqueous Solutions

■ Equilibria Involving Complex Ions

- ◆ Aluminum Hydroxide in basic solution



- ◆ The above reaction is actually a much more complex situation, involving multiple species
- ◆ When dissolving an aluminum salt, such as $\text{Al(NO}_3)_3$, in a strong base (NaOH), a precipitate forms initially and then dissolves as more base is added
- ◆ The formula for hydrated Al^{3+} is $\text{Al(H}_2\text{O)}_6^{3+}$
- ◆ $\text{Al(H}_2\text{O)}_6^{3+}$ acts as a “weak polyprotic acid and reacts with added OH^- in a stepwise removal of the H_2O ligands attached to the hydrated Al

Ionic Equilibria in Aqueous Solutions

- Amphoteric Aluminum Hydroxide in basic solution



- $\text{Al}(\text{H}_2\text{O})_3(\text{OH})_3(\text{s})$ is more simply written $\text{Al}(\text{OH})_3(\text{s})$
- As more base is added, a 4th H^+ is removed from a H_2O ligand and the soluble ion $\text{Al}(\text{H}_2\text{O})_2(\text{OH})_4^-(\text{aq})$ forms



The ion is normally written as $\text{Al}(\text{OH})_4^-(\text{aq})$