

# Ionic Equilibria in Aqueous Systems

## 19.1 Acid-Base Buffers

- Resist changes in **pH** upon addition of acids ( $H^+$ ) or bases ( $OH^-$ )

### The Buffer Action

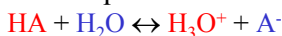
- Buffer solutions consist of two components
  - Acid component** – reacts with added bases ( $OH^-$ )
  - Base component** – reacts with added acids ( $H^+$ )
- The two components must be a **conjugate acid-base pair**
- The two components must be present in **high concentrations**

- Weak acid buffer** – a solution of the weak acid, HA, and its conjugate base,  $A^-$  ( $HF/F^-$ , ...)
  - Add  $H_3O^+$  (acid)  $\rightarrow$  ( $A^-$  consumes the added  $H_3O^+$ )
 
$$H_3O^+ + A^- \rightarrow H_2O + HA$$
  - Add  $OH^-$  (base)  $\rightarrow$  (HA consumes the added  $OH^-$ )
 
$$OH^- + HA \rightarrow H_2O + A^-$$
  - Weak base buffer** – a solution of the weak base, B, and its conjugate acid,  $HB^+$  ( $NH_4^+/NH_3$ , ...)
  - Add  $H_3O^+$  (acid)  $\rightarrow$  (B consumes the added  $H_3O^+$ )
 
$$H_3O^+ + B \rightarrow H_2O + HB^+$$
  - Add  $OH^-$  (base)  $\rightarrow$  ( $HB^+$  consumes the added  $OH^-$ )
 
$$OH^- + HB^+ \rightarrow H_2O + B$$
- $\Rightarrow$  The addition of  $H_3O^+$  and  $OH^-$  changes the relative amounts of the buffer components ( $HA/A^-$  or  $HB^+/B$ )

### The pH of a Buffer

- For a weak acid buffer ( $HA/A^-$ ),  $A^-$  can be supplied in solution by means of the salt, MA
 
$$MA \rightarrow M^+ + A^-$$

- HA and  $A^-$  reach equilibrium

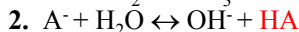
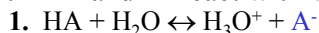


$$K_a = \frac{[H_3O^+][A^-]}{[HA]} \Rightarrow [H_3O^+] = K_a \frac{[HA]}{[A^-]}$$

$\Rightarrow$  The  $[H_3O^+]$  and **pH** depend on the ratio  $[HA]/[A^-]$

$\rightarrow$  If  $[HA]$  and  $[A^-]$  are relatively large, adding small amounts of  $H_3O^+$  or  $OH^-$  changes the ratio only slightly, so  $[H_3O^+] \approx \text{constant}$

- Both HA and  $A^-$  react with water



$\rightarrow$  Both equilibria are shifted to the left, so the amounts of HA and  $A^-$  produced are often very small compared to the total concentrations,  $C_{HA}$  and  $C_{A^-}$

$\Rightarrow$  Assume that  $[HA]_2$  and  $[A^-]_1 \ll C_{HA}$  and  $C_{A^-}$

$$[HA] = C_{HA} - [A^-]_1 + [HA]_2 \approx C_{HA} = C_a$$

$$[A^-] = C_{A^-} - [HA]_2 + [A^-]_1 \approx C_{A^-} = C_b$$

$\rightarrow C_a$  and  $C_b$  – total concentrations of the acid and base components of the buffer

$$[H_3O^+] = K_a \frac{[HA]}{[A^-]} \Rightarrow [H_3O^+] = K_a \frac{C_a}{C_b}$$

$\rightarrow$  Take a **-log()** of  $[H_3O^+] = K_a(C_a/C_b)$

$$-\log[H_3O^+] = -\log K_a - \log \frac{C_a}{C_b} = -\log K_a + \log \frac{C_b}{C_a}$$

$$\Rightarrow pH = pK_a + \log \frac{C_b}{C_a} \quad \text{Henderson-Hasselbalch Equation}$$

$\rightarrow$  The equation is valid only if  $C_a$  and  $C_b$  are large enough so that the assumptions  $[HA] \approx C_a$  and  $[A^-] \approx C_b$  are justified; If not,  $[HA]$  and  $[A^-]$  must be used

$\rightarrow$  Works if  $C_a > 100 \times K_a$  and  $C_b > 100 \times K_b$

$\rightarrow$  If  $C_a = C_b$ ,  $\log(C_a/C_b) = 0$  and **pH** = **pK<sub>a</sub>**

$\Rightarrow$  If  $C_a$  and  $C_b$  are comparable, the **pH** of the buffer is close to the **pK<sub>a</sub>** of the acid component

**Example:** What is the **pH** of a buffer that is **0.50 M** in HF and **0.50 M** in KF? ( $K_a = 6.8 \times 10^{-4}$  for HF)

- Use the **Hend.-Hass. Eq.** (HF – acid;  $F^-$  – base)

$$C_a = 0.50 \quad C_b = 0.50$$

$$pH = pK_a + \log(0.50/0.50) = pK_a + \log(1) = pK_a + 0$$

$$pH = pK_a = -\log(6.8 \times 10^{-4}) = \boxed{3.17}$$

- Or use an **ice table**

	HF + H <sub>2</sub> O $\leftrightarrow$ H <sub>3</sub> O <sup>+</sup> + F <sup>-</sup>	
i	0.50	0
c	-x	+x
e	0.50 - x	x

$$K_a = \frac{[H_3O^+][F^-]}{[HF]} =$$

$$\frac{x(0.50 + x)}{(0.50 - x)} \approx \frac{x(0.50)}{(0.50)}$$

$$x = K_a = 6.8 \times 10^{-4} = [H_3O^+] \Rightarrow pH = -\log(6.8 \times 10^{-4}) = \boxed{3.17}$$

**Example:** For **1.0 L** of the same buffer, calculate the **pH** after the addition of **5.0 mL 2.0 M HCl**.

→ HCl is a strong acid and converts to  $\text{H}_3\text{O}^+$  which reacts with  $\text{F}^-$  from the buffer

→ Calculate the starting moles of HF and  $\text{F}^-$  in the buffer and the added moles of  $\text{H}_3\text{O}^+$  from HCl

$$\text{HF} \rightarrow 1.0 \text{ L} \times 0.50 \text{ mol/L} = \mathbf{0.50 \text{ mol}}$$

$$\text{F}^- \rightarrow 1.0 \text{ L} \times 0.50 \text{ mol/L} = \mathbf{0.50 \text{ mol}}$$

$$\text{H}_3\text{O}^+ \rightarrow 0.0050 \text{ L} \times 2.0 \text{ mol/L} = \mathbf{0.010 \text{ mol}}$$

→ Use an “**srf**” table (*starting, reacted, final*) to calculate the final moles of HF and  $\text{F}^-$

	[ ]	$\text{F}^-$	$+$	$\text{H}_3\text{O}^+$	$\rightarrow$	$\text{H}_2\text{O}$	$+$	HF
moles	s	0.50		0.010		–		0.50
	r	-0.010		-0.010		–		+0.010
	f	0.49		0.00		–		0.51

→ Use the Hend.-Hass. Eq. (HF – acid;  $\text{F}^-$  – base)

→ Since the acid and base components of the buffer are in the same volume, the ratio of the concentrations is the same as the ratio of the moles →  $C_b/C_a = n_b/n_a$

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log \frac{n_b}{n_a} = -\log(6.8 \times 10^{-4}) + \log \frac{0.49}{0.51} \\ &= 3.17 + (-0.02) = \mathbf{3.15} \end{aligned}$$

⇒ The **pH** is reduced by only **0.02 pH-units**

- The addition of strong acids or bases to unbuffered solutions has a much greater effect on **pH**

**Example:** Calculate the **pH** after the addition of **5.0 mL 2.0 M HCl** to **1.0 L** of pure water.

→ The **pH** of pure water is **7.00**

→ After addition of the strong acid HCl:

$$[\text{H}_3\text{O}^+] = \frac{0.0050 \text{ L} \times \frac{2.0 \text{ mol}}{1 \text{ L}}}{(1.0 + 0.0050) \text{ L}} = \mathbf{0.010 \text{ M}}$$

$$\text{pH} = -\log(0.010) = \mathbf{2.00}$$

⇒ The **pH** is reduced by **5.00 pH-units** (a much larger change compared to the buffered solution)

### Buffer Capacity and Buffer Range

- Buffer capacity (BC)** – a measure of the ability of the buffer to resist **pH** changes

– BC is higher for more concentrated buffers

$$\uparrow\uparrow C_a \text{ and } C_b \Rightarrow \uparrow\uparrow \text{ Buffer capacity}$$

– BC is higher for buffers with similar component concentrations (BC is highest when  $C_a = C_b$ )

- Buffer range (BR)** – buffers act most efficiently when  $C_b/C_a$  is between **0.1** and **10**

$$\begin{aligned} \text{pH} &= \text{p}K_a + \log(0.1) = \text{p}K_a - 1 \\ \text{pH} &= \text{p}K_a + \log(10) = \text{p}K_a + 1 \end{aligned} \quad \Rightarrow \mathbf{BR = pK_a \pm 1}$$

### Preparing Buffers

- **Choose the conjugate acid-base pair** (select a pair with an acid component having  $\text{p}K_a$  close to the desired buffer **pH**)
- **Calculate the ratio of  $C_b/C_a$**  needed to achieve the desired buffer **pH** (use the Hend.-Hass. Eq.)
- **Determine the buffer concentration** and the amounts of the two components to be mixed
- **Mix the components and adjust the pH** (final **pH** may be slightly off and can be adjusted by adding strong acid or base)
- Buffers can also be prepared by **partial neutralization** of weak acids (or bases) with strong bases (or acids) (Ex: **HF** + KOH → **KF** +  $\text{H}_2\text{O}$ ; If only half of the HF is converted to KF → buffer)

**Example:** How many moles of  $\text{NH}_4\text{Cl}$  must be added to **1.0 L** of **0.20 M  $\text{NH}_3$**  solution to get a buffer with **pH = 9.35**? ( $K_b = 1.8 \times 10^{-5}$  for  $\text{NH}_3$ )

→ Conjugate pair  $\text{NH}_4^+/\text{NH}_3$

$$\rightarrow K_a = K_w/K_b = 10^{-14}/1.8 \times 10^{-5} = \mathbf{5.6 \times 10^{-10}}$$

$$\rightarrow \text{p}K_a = -\log(5.6 \times 10^{-10}) = \mathbf{9.25}$$

$$\rightarrow n_b = 1.0 \text{ L} \times 0.20 \text{ mol/L} = \mathbf{0.20 \text{ mol } \text{NH}_3} \quad n_a = ??$$

$$\text{pH} = \text{p}K_a + \log \frac{n_b}{n_a} \rightarrow 9.35 = 9.25 + \log \frac{0.20}{n_a}$$

$$\rightarrow 0.10 = \log(0.20/n_a) \rightarrow 10^{0.10} = 0.20/n_a$$

$$\rightarrow n_a = 0.20/10^{0.10} = \mathbf{0.16 \text{ mol } \text{NH}_4^+ = 0.16 \text{ mol } \text{NH}_4\text{Cl}}$$

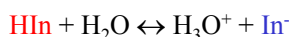
## 19.2 Acid-Base Titration Curves

- **Titration curves** – plots of **pH** versus the volume of titrant added during titration
- **Equivalence point (E)** – a point along the course of the titration at which the acid and the base are present in equivalent (stoichiometric) amounts and consume each other completely
  - Typically, the **pH changes sharply at the E-point** and this fact is used in the detection of the **E-point**
  - The titration is actually stopped at the **end point**
  - Ideally, the end point should be at the equivalence point, but in practice they can differ slightly due to imperfect detection of the **E-point**

## Acid-Base Indicators

- **Indicators** – used to estimate the **pH** of solutions and to detect the **E-point** in titrations
  - Weak organic acids with general formula **HIn**
  - Exhibit different colors at different **pH** values
  - The colors are quite intense so only small amounts are needed for detection
- **Indicator range** – a relatively narrow **pH** range over which the indicator changes color
  - If the **E-point** is within (or close to) the indicator range, the indicator changes color very close to **E**
 ⇒ The **pH** at the **E-point** must be known for the proper selection of an indicator

➤ The indicator is a weak B-L acid



- The acid form of the indicator, **HIn**, and its conjugate base, **In<sup>-</sup>**, have different colors
- If  $[\text{HIn}]/[\text{In}^-] > 10$ , the solution has the color of the acid form, **HIn**
- If  $[\text{HIn}]/[\text{In}^-] < 0.1$ , the solution has the color of the base form, **In<sup>-</sup>**

⇒ The color change is within  $0.1 < [\text{HIn}]/[\text{In}^-] < 10$

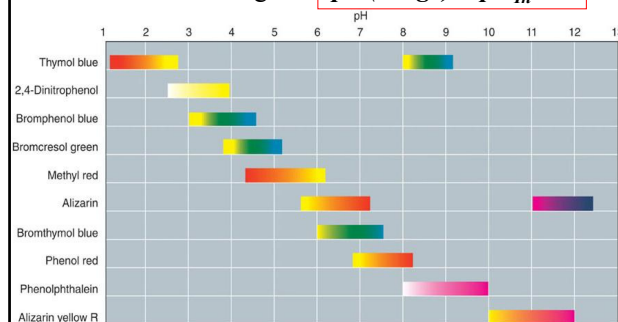
$$K_{\text{In}} = \frac{[\text{H}_3\text{O}^+][\text{In}^-]}{[\text{HIn}]} \Rightarrow \frac{[\text{HIn}]}{[\text{In}^-]} = \frac{[\text{H}_3\text{O}^+]}{K_{\text{In}}}$$

⇒ The ratio  $[\text{HIn}]/[\text{In}^-]$  depends on  $[\text{H}_3\text{O}^+]$

$$[\text{H}_3\text{O}^+] = K_{\text{In}} \frac{[\text{HIn}]}{[\text{In}^-]} \Rightarrow \text{pH} = \text{p}K_{\text{In}} - \log \frac{[\text{HIn}]}{[\text{In}^-]}$$

$$\rightarrow \log(0.1) = -1 \quad \rightarrow \log(10) = +1$$

⇒ The indicator range is:  **$\text{pH}(\text{range}) \approx \text{p}K_{\text{In}} \pm 1$**



## Strong Acid-Strong Base Titration Curves

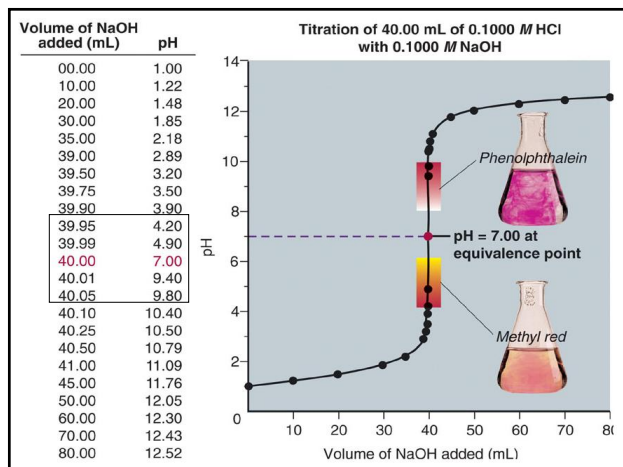
- Strong acids and bases are completely converted to  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in water solns.
- ⇒ The net ionic equation of the titration is:
- $$\text{H}_3\text{O}^+ + \text{OH}^- \rightarrow 2\text{H}_2\text{O}$$
- ⇒ At the **E-point**, **pH = 7.00** (neutral)
- To calculate the **pH** during the titration:
1. Calculate the **mmol of  $\text{H}_3\text{O}^+$**  from the acid
  2. Calculate the **mmol of  $\text{OH}^-$**  from the base
  3. Calculate the **excess mmol of  $\text{H}_3\text{O}^+$  or  $\text{OH}^-$**  from the difference between (1) and (2)
  4. Calculate  $[\text{H}_3\text{O}^+]$  or  $[\text{OH}^-]$  from the excess and the total volume of the solution ( $V_{\text{tot}}$ ) → convert to **pH**

**Example:** Calculate the **pH** during the titration of **40.0 mL 0.100 M HCl** with **0.100 M NaOH** after the addition of **25.0 mL NaOH**.

$$0.100 \text{ M HCl} \rightarrow 0.100 \text{ M H}_3\text{O}^+ = 0.100 \text{ mmol/mL}$$

$$0.100 \text{ M NaOH} \rightarrow 0.100 \text{ M OH}^- = 0.100 \text{ mmol/mL}$$

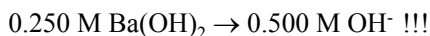
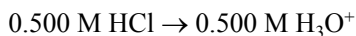
1.  $\text{H}_3\text{O}^+ \rightarrow 40.0 \text{ mL} \times 0.100 \text{ mmol/mL} = \mathbf{4.00 \text{ mmol}}$
2.  $\text{OH}^- \rightarrow 25.0 \text{ mL} \times 0.100 \text{ mmol/mL} = \mathbf{2.50 \text{ mmol}}$
3. **Excess acid** =  $4.00 - 2.50 = \mathbf{1.50 \text{ mmol H}_3\text{O}^+}$
4.  $V_{\text{tot}} = 40.0 + 25.0 = \mathbf{65.0 \text{ mL}}$   
 $1.50 \text{ mmol} / 65.0 \text{ mL} = \mathbf{0.0231 \text{ M H}_3\text{O}^+}$   
 $\text{pH} = -\log(0.0231) = \mathbf{1.64}$  (acidic, before E-point)



➤ A titration curve for the titration of a strong base with a strong acid looks like a mirror image of that for the titration of a strong acid with a strong base

- **Characteristics** of strong acid-strong base t-curves
    - Slow **pH** changes before and after the E-point
    - A sharp **pH** change at the E-point (**pH** = 7.00) → 1-2 drops cause a **pH** change of 5-6 pH units
    - The **vertical region** of the t-curve is quite long (from **pH** ≈ 4 to **pH** ≈ 10)
    - Any indicator having a range within the vertical region of the t-curve can be used (the indicator range does not have to be at 7.00)
- ⇒ Phenolphthalein (8.3-10), Methyl red (4.3-6.2), Phenol red (6.8-8.3), ... can all be used

**Example:** Calculate the **pH** during the titration of 20.0 mL 0.500 M HCl with 0.250 M Ba(OH)<sub>2</sub> after the addition of 21.0 mL Ba(OH)<sub>2</sub>

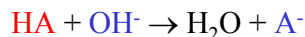


1. **H<sub>3</sub>O<sup>+</sup>** → 20.0 mL × 0.500 mmol/mL = **10.0 mmol**
2. **OH<sup>-</sup>** → 21.0 mL × 0.500 mmol/mL = **10.5 mmol**
3. **Excess base** = 10.5 – 10.0 = **0.50 mmol OH<sup>-</sup>**
4. **V<sub>tot</sub>** = 20.0 + 21.0 = **41.0 mL**  
 0.50 mmol / 41.0 mL = **0.012 M OH<sup>-</sup>**  
**pOH** = -log(0.012) = **1.91**  
**pH** = 14.00 – 1.91 = **12.09** (basic, after E-point)

### Weak Acid-Strong Base Titration Curves

➤ The strong base is completely converted to OH<sup>-</sup> in water solution

⇒ The net ionic equation of the titration is:



⇒ At the E-point, **pH** > 7.00 (basic) due to the presence of A<sup>-</sup> which is a weak base

➤ **Regions** of the titration curve:

1. **Initial point** → solution of the **weak acid HA**
2. **Before the E-point** → **buffer solution** of the weak acid, HA, and its conjugate base, A<sup>-</sup> (buffer region)
3. **At the E-point** → solution of the **weak base A<sup>-</sup>**
4. **After the E-point** → **excess of OH<sup>-</sup>** from base

**Example:** Calculate the **pH** during the titration of 20.0 mL 0.500 M HCOOH with 0.500 M NaOH after the addition of 0.0, 10.0, 19.0, 20.0 and 21.0 mL NaOH

1) **0.0 mL NaOH added (Initial point):**

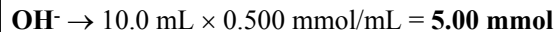
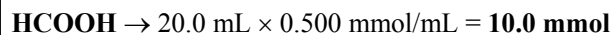
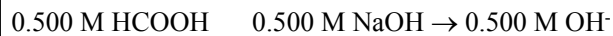
→ A 0.500 M solution of the **weak acid HCOOH**

	HCOOH + H <sub>2</sub> O ↔ H <sub>3</sub> O <sup>+</sup> + HCOO <sup>-</sup>		$K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]}$
i	0.500	0	0
c	-x	+x	+x
e	0.500 - x	x	x

$$x = (0.500K_a)^{1/2} = (1.8 \times 10^{-4} \times 0.500)^{1/2} = 9.5 \times 10^{-3} = [\text{H}_3\text{O}^+]$$

$$\Rightarrow \text{pH} = -\log[\text{H}_3\text{O}^+] = -\log(9.5 \times 10^{-3}) = \mathbf{2.02}$$

2) **10.0 mL NaOH added (Half-way to the E-point):**



		$\text{HCOOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCOO}^-$			
mmol	s	10.0	5.00	–	0.00
	r	-5.00	-5.00	–	+5.00
	f	5.00	0.00	–	5.00

→ The system is a **buffer** (HCOOH → a, HCOO<sup>-</sup> → b)

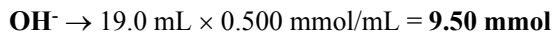
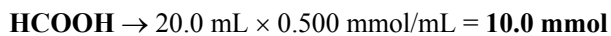
$$\text{pH} = \text{p}K_a + \log(n_b/n_a) = \text{p}K_a + \log(5.00/5.00) = \text{p}K_a + 0$$

$$\Rightarrow \text{pH} = \text{p}K_a = -\log(1.8 \times 10^{-4}) = \mathbf{3.74}$$

⇒ Half-way to the E-point → **pH** = **pK<sub>a</sub>** !!!

**Cont:** Titration of 20.0 mL 0.500 M HCOOH with 0.500 M NaOH

**3) 19.0 mL NaOH added (Before the E-point):**



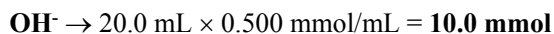
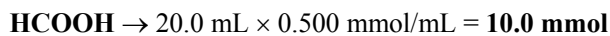
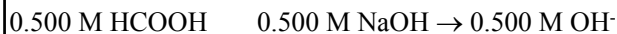
	$\text{HCOOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCOO}^-$			
<b>mmol</b>	<i>s</i>	<b>10.0</b>	<b>9.50</b>	<b>0.00</b>
	<i>r</i>	<b>-9.50</b>	<b>-9.50</b>	<b>+9.50</b>
	<i>f</i>	<b>0.50</b>	<b>0.00</b>	<b>9.50</b>

→ The system is a **buffer** ( $\text{HCOOH} \rightarrow a$ ,  $\text{HCOO}^- \rightarrow b$ )

$$\text{pH} = \text{p}K_a + \log(n_b/n_a) = -\log(1.8 \times 10^{-4}) + \log(9.50/0.50)$$

$$\Rightarrow \text{pH} = 3.74 + 1.28 = \mathbf{5.02}$$

**4) 20.0 mL NaOH added (E-point):**



	$\text{HCOOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCOO}^-$			
<b>mmol</b>	<i>s</i>	<b>10.0</b>	<b>10.0</b>	<b>0.00</b>
	<i>r</i>	<b>-10.0</b>	<b>-10.0</b>	<b>+10.0</b>
	<i>f</i>	<b>0.00</b>	<b>0.00</b>	<b>10.0</b>

→ A solution of the **weak base**  $\text{HCOO}^-$

$$V_{\text{tot}} = 20.0 + 20.0 = \mathbf{40.0 \text{ mL}}$$

$$10.0 \text{ mmol} / 40.0 \text{ mL} = \mathbf{0.250 \text{ M HCOO}^-}$$

	$\text{HCOO}^- + \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{HCOOH}$		
<i>i</i>	<b>0.250</b>	<b>0</b>	<b>0</b>
<i>c</i>	<b>-x</b>	<b>+x</b>	<b>+x</b>
<i>e</i>	<b>0.250 - x</b>	<b>x</b>	<b>x</b>

$$K_b = \frac{[\text{OH}^-][\text{HCOOH}]}{[\text{HCOO}^-]}$$

$$K_b = \frac{x^2}{0.250 - x} \approx \frac{x^2}{0.250}$$

$$K_b(\text{HCOO}^-) = K_w/K_a(\text{HCOOH}) = 1.0 \times 10^{-14}/1.8 \times 10^{-4}$$

$$K_b(\text{HCOO}^-) = 5.6 \times 10^{-11}$$

$$x = (K_b \times 0.250)^{1/2} = (5.6 \times 10^{-11} \times 0.250)^{1/2} = 3.7 \times 10^{-6} = [\text{OH}^-]$$

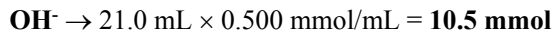
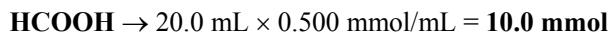
$$[\text{Check assumption: } (3.7 \times 10^{-6}/0.250) \times 100 = 0.0015\% < 5\%]$$

$$\Rightarrow \text{pOH} = -\log[\text{OH}^-] = -\log(3.7 \times 10^{-6}) = 5.43$$

$$\Rightarrow \text{pH} = 14.00 - \text{pOH} = 14.00 - 5.43 = \mathbf{8.57}$$

⇒ At the **E-point** → **pH > 7 (basic solution!!!)**

**5) 21.0 mL NaOH added (After the E-point):**



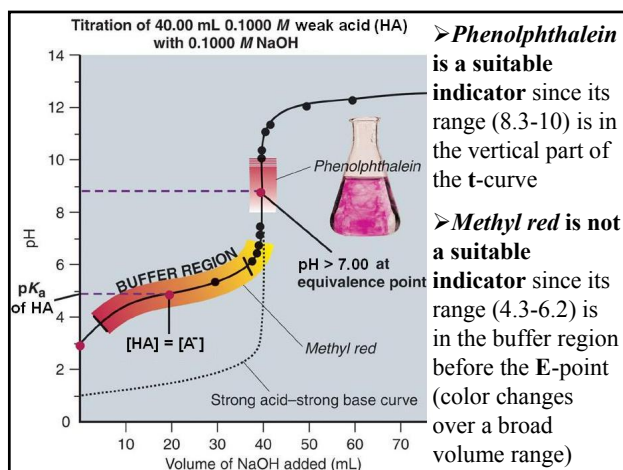
	$\text{HCOOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCOO}^-$			
<b>mmol</b>	<i>s</i>	<b>10.0</b>	<b>10.5</b>	<b>0.00</b>
	<i>r</i>	<b>-10.0</b>	<b>-10.0</b>	<b>+10.0</b>
	<i>f</i>	<b>0.00</b>	<b>0.50</b>	<b>10.0</b>

→ A solution of the **excess strong base** ( $\text{OH}^-$ ) and the weak base ( $\text{HCOO}^-$ ) → the weak base is neglected

$$V_{\text{tot}} = 20.0 + 21.0 = \mathbf{41.0 \text{ mL}}$$

$$0.50 \text{ mmol} / 41.0 \text{ mL} = \mathbf{0.012 \text{ M OH}^-}$$

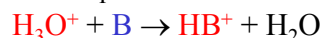
$$\text{pOH} = -\log(0.012) = 1.91 \Rightarrow \text{pH} = 14.00 - 1.91 = \mathbf{12.09}$$



**Weak base-Strong Acid Titration Curves**

➤ The strong acid is completely converted to  $\text{H}_3\text{O}^+$  in water solution

⇒ The net ionic equation of the titration is:

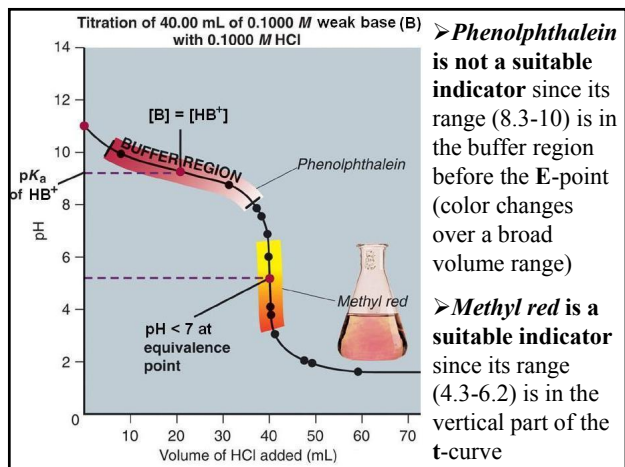


⇒ At the **E-point**, **pH < 7.00** (acidic) due to the presence of  $\text{HB}^+$  which is a weak acid

➤ **Regions of the titration curve:**

1. **Initial point** → solution of the **weak base B**
2. **Before the E-point** → **buffer solution** of the weak base, B, and its conjugate acid,  $\text{HB}^+$  (buffer region)
3. **At the E-point** → solution of the **weak acid  $\text{HB}^+$**
4. **After the E-point** → **excess of  $\text{H}_3\text{O}^+$**  from acid



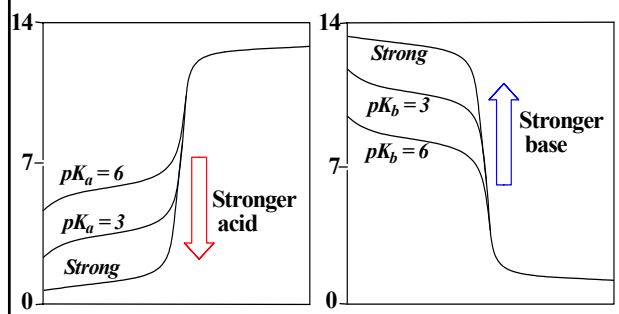


➤ A titration curve for the titration of a weak base with a strong acid looks like a mirror image of that for the titration of a weak acid with a strong base

- **Characteristics of t-curves involving weak acids/bases**
  - Slow **pH** changes before and after the E-point and a sharp **pH** change at the E-point
  - At the E-point
    - $pH > 7.00$  for titration of weak acids
    - $pH < 7.00$  for titration of weak bases
  - Half-way to the E-point, **pH** equals  $pK_a$  of the weak acid (or the conjugate acid of the weak base)
  - The **vertical region** of the t-curve is shorter than the vertical region for strong acid-strong base titrations
  - A careful selection of the indicator is necessary

### Dependence of the Titration Curve on the Strength of the Acid or Base

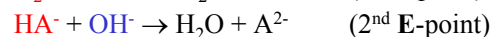
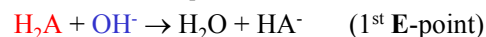
- Weaker acids and bases have shorter vertical **pH** ranges at the E-point (more difficult to detect)



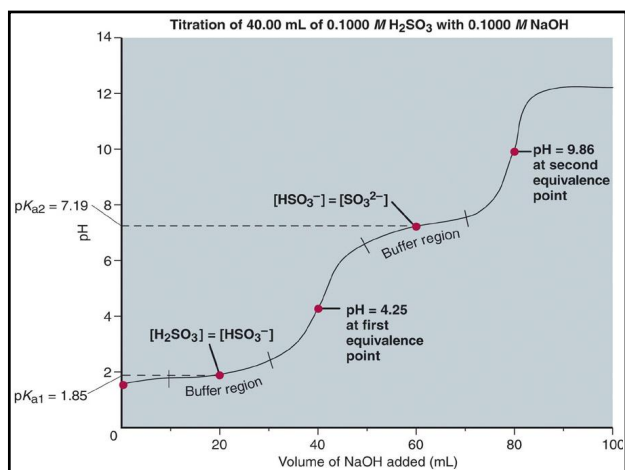
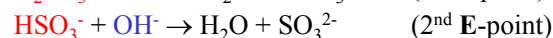
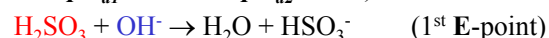
### Titration Curves for Polyprotic Acids

- The loss of each proton results in a separate E-point and a separate buffer region
- For a diprotic acid,  $H_2A$ , titrated with a strong base there are two E-points and two buffer regions

➤ The net ionic equations of the titration are:



**Example:** Titration of  $H_2SO_3$  (a diprotic acid with  $pK_{a1} = 1.85$  and  $pK_{a2} = 7.19$ ) with NaOH

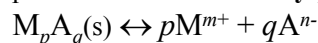


### 19.3 Equilibria of Slightly Soluble Ionic Compounds

- Slightly soluble ionic solids reach equilibrium with their saturated solutions at very low concentrations of the dissolved solute
- The **dissolved portion** of the ionic solid is assumed to be **completely dissociated to ions** (not always the case)

#### The Solubility-Product Constant ( $K_{sp}$ )

- For an ionic solid,  $M_pA_q$ , in equilibrium with its saturated solution, the equilibrium constant of the dissolution process is called **solubility-product**



$$K_{sp} = [M^{m+}]^p [A^{n-}]^q$$

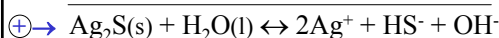
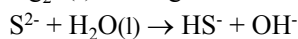
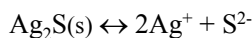
**Example:** Write the solubility-product expression for  $\text{Al}(\text{OH})_3$ .

→ The subscripts in the formula become powers in the solubility-product expression

$$\Rightarrow K_{sp} = [\text{Al}^{3+}][\text{OH}^-]^3$$

➤ Sulfides are slightly different since  $\text{S}^{2-}$  acts as a strong base in water and converts entirely to  $\text{OH}^-$

**Example:**  $\text{Ag}_2\text{S}$



$$\Rightarrow K_{sp} = [\text{Ag}^+][\text{HS}^-][\text{OH}^-]$$

•  $K_{sp}$  is a measure of the extent to which the solubility equilibrium proceeds to the right

$$\uparrow K_{sp} \leftrightarrow \uparrow \text{Solubility}$$

–  $K_{sp}$  depends on temperature

### Calculations Involving $K_{sp}$

• **Molar solubility ( $s$ )** – the molarity of the saturated solution (mol/L)

– The solubility is often expressed in g/L or grams/100 mL of solution → can be easily converted to mol/L

–  $K_{sp}$  can be experimentally determined by measuring the molar solubility,  $s$

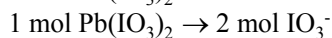
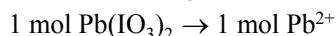
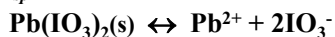
–  $s$  can be calculated if  $K_{sp}$  is known

**Example:** The solubility of  $\text{Pb}(\text{IO}_3)_2$  is 0.022 g/L at 25°C. Calculate  $K_{sp}$  of  $\text{Pb}(\text{IO}_3)_2$ .

→ Convert the solubility to molar solubility,  $s$

$$s = 0.022 \frac{\text{g Pb}(\text{IO}_3)_2}{\text{L}} \times \frac{1 \text{ mol Pb}(\text{IO}_3)_2}{557 \text{ g Pb}(\text{IO}_3)_2} = 3.9 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

→ Express  $K_{sp}$  through the molar solubility,  $s$



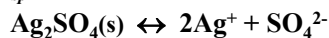
$$\Rightarrow [\text{Pb}^{2+}] = s \quad \text{and} \quad [\text{IO}_3^-] = 2s$$

$$\Rightarrow K_{sp} = [\text{Pb}^{2+}][\text{IO}_3^-]^2 = s(2s)^2 = 4s^3$$

$$\Rightarrow K_{sp} = 4 \times (3.9 \times 10^{-5})^3 = \boxed{2.5 \times 10^{-13}}$$

**Example:** The  $K_{sp}$  of  $\text{Ag}_2\text{SO}_4$  is  $1.4 \times 10^{-5}$  at 24°C. Calculate the molar solubility of  $\text{Ag}_2\text{SO}_4$ .

→ Express  $K_{sp}$  through the molar solubility,  $s$



$$\Rightarrow [\text{Ag}^+] = 2s \quad \text{and} \quad [\text{SO}_4^{2-}] = s$$

$$\Rightarrow K_{sp} = [\text{Ag}^+]^2[\text{SO}_4^{2-}] = (2s)^2s = 4s^3$$

$$\Rightarrow s^3 = K_{sp}/4 \quad \Rightarrow \quad s = (K_{sp}/4)^{1/3}$$

$$\Rightarrow s = (1.4 \times 10^{-5}/4)^{1/3} = \boxed{1.5 \times 10^{-2} \text{ M}}$$

**Note:** The problem can be solved using an *ice* table:

$$\Rightarrow K_{sp} = (2s)^2s = 4s^3$$

	$\text{Ag}_2\text{SO}_4(\text{s}) \leftrightarrow 2\text{Ag}^+ + \text{SO}_4^{2-}$		
<i>i</i>	excess	0	0
<i>c</i>	-s	+2s	+s
<i>e</i>	excess	2s	s

➤  $K_{sp}$  can be used as a guide in comparing molar solubilities of different ionic compounds (works only if the compounds have the same number of ions in the formula)

$$\uparrow K_{sp} \leftrightarrow \uparrow s$$

**Table 19.3** Relationship Between  $K_{sp}$  and Solubility at 25°C

No. of Ions	Formula	Cation:Anion	$K_{sp}$	Solubility (M)
2	$\text{MgCO}_3$	1:1	$3.5 \times 10^{-8}$	$1.9 \times 10^{-4}$
2	$\text{PbSO}_4$	1:1	$1.6 \times 10^{-8}$	$1.3 \times 10^{-4}$
2	$\text{BaCrO}_4$	1:1	$2.1 \times 10^{-10}$	$1.4 \times 10^{-5}$
3	$\text{Ca}(\text{OH})_2$	1:2	$6.5 \times 10^{-6}$	$1.2 \times 10^{-2}$
3	$\text{BaF}_2$	1:2	$1.5 \times 10^{-6}$	$7.2 \times 10^{-3}$
3	$\text{CaF}_2$	1:2	$3.2 \times 10^{-11}$	$2.0 \times 10^{-4}$
3	$\text{Ag}_2\text{CrO}_4$	2:1	$2.6 \times 10^{-12}$	$8.7 \times 10^{-5}$

### The Common Ion Effect

➤ For a slightly soluble ionic solid, MA



– If  $\text{M}^{n+}$  is added by means of the soluble salt (MB), the equilibrium shifts to the left toward formation of more MA(s)

– MA and MB have a **common ion** ( $\text{M}^{n+}$ )

– Similarly, if  $\text{A}^{n-}$  is added to the solution, the equilibrium also shifts to the left toward formation of more MA(s)

⇒ **The molar solubility decreases in the presence of common ions**

**Example:** At a given temperature,  $K_{sp}$  of AgBr is  $7.7 \times 10^{-13}$ . Estimate the solubility of AgBr in:

- a) Pure  $H_2O$       b) 0.10 M  $CaBr_2$  solution

**a) In pure  $H_2O$**

→ Express  $K_{sp}$  through the molar solubility,  $s$

	AgBr(s) $\leftrightarrow$ Ag <sup>+</sup> + Br <sup>-</sup>		
<i>i</i>	excess	0	0
<i>c</i>	-s	+s	+s
<i>e</i>	excess	s	s

$$\Rightarrow [Ag^+] = s \quad \text{and} \quad [Br^-] = s$$

$$\Rightarrow K_{sp} = [Ag^+][Br^-] = s^2$$

$$\Rightarrow s = (K_{sp})^{1/2} = (7.7 \times 10^{-13})^{1/2} = \boxed{8.8 \times 10^{-7} \text{ M}}$$

**b) In 0.10 M  $CaBr_2$  solution**

0.10 M  $CaBr_2 \rightarrow 0.20 \text{ M } Br^-$  ( $Br^-$  is the common ion)

→ Express  $K_{sp}$  through the molar solubility,  $s$

	AgBr(s) $\leftrightarrow$ Ag <sup>+</sup> + Br <sup>-</sup>		
<i>i</i>	excess	0	0.20
<i>c</i>	-s	+s	+s
<i>e</i>	excess	s	0.20 + s

$$\Rightarrow K_{sp} = [Ag^+][Br^-] = s(0.20 + s)$$

→ Assume  $s \ll 0.20 \Rightarrow K_{sp} = s(0.20)$

$$\Rightarrow s = K_{sp}/0.20 = 7.7 \times 10^{-13}/0.20 = \boxed{3.8 \times 10^{-12} \text{ M}}$$

→ Check assumption → OK

⇒ The solubility is much lower in 0.1 M  $CaBr_2$

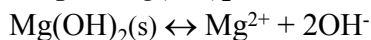
**The Effect of pH on Solubility**

➤ The solubility of some ionic solids in water is greatly affected by the **pH**

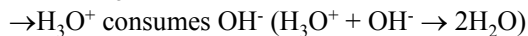
– **Metal hydroxides** ( $Fe(OH)_3$ ,  $Mg(OH)_2$ , ...) – the anion ( $OH^-$ ) reacts with added  $H_3O^+$

⇒ The solubility can be improved by adding acids

**Example:  $Mg(OH)_2$**



→ If acid ( $H_3O^+$ ) is added:

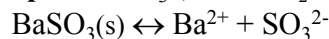


→ The equilibrium shifts to the right and the **solubility increases**

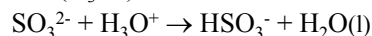
– **Salts of weak acids** ( $CaCO_3$ ,  $BaSO_3$ ,  $PbF_2$ ,  $ZnS$ , ...) – the anion of the salt is a weak base which reacts with added  $H_3O^+$

⇒ The solubility can be improved by adding acids

**Example:  $BaSO_3$  (a salt of  $H_2SO_3$ )**



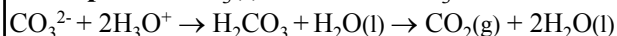
→ If acid ( $H_3O^+$ ) is added:



→  $H_3O^+$  consumes  $SO_3^{2-}$

→ The equilibrium shifts to the right and the **solubility increases**

**Example:  $CaCO_3(s) \leftrightarrow Ca^{2+} + CO_3^{2-}$**



**Predicting Precipitation –  $Q_{sp}$  versus  $K_{sp}$**

➤ The reaction quotient of the dissolution process ( $Q_{sp}$ ) is defined in the same way as  $K_{sp}$  and at equilibrium  $Q_{sp} = K_{sp}$

➤ To predict precipitation, compare  $Q_{sp}$  to  $K_{sp}$

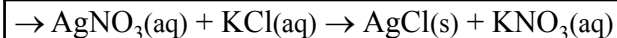
→ If  $Q_{sp} > K_{sp}$ , precipitation occurs

→ If  $Q_{sp} < K_{sp}$ , dissolution occurs (no precipitation)

→ If  $Q_{sp} = K_{sp}$ , no change occurs

**Example:** Does a precipitate form after mixing of 200. mL  $1.0 \times 10^{-4}$  M  $AgNO_3$  with 900. mL  $1.0 \times 10^{-6}$  M  $KCl$ ?

( $K_{sp} = 1.8 \times 10^{-10}$  for  $AgCl$ )



→ Net ionic equation:  $Ag^+ + Cl^- \rightarrow AgCl(s)$

→ Reverse:  $AgCl(s) \rightarrow Ag^+ + Cl^-$

$$K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$$

$$V_{tot} = 0.200 + 0.900 = 1.100 \text{ L}$$

→ Initial concentrations after mixing:

$$[Ag^+] = \frac{1.0 \times 10^{-4} \frac{\text{mol}}{\text{L}} \times 0.200 \text{ L}}{1.100 \text{ L}} = 1.8 \times 10^{-5} \frac{\text{mol}}{\text{L}}$$

$$[Cl^-] = \frac{1.0 \times 10^{-6} \frac{\text{mol}}{\text{L}} \times 0.900 \text{ L}}{1.100 \text{ L}} = 8.2 \times 10^{-7} \frac{\text{mol}}{\text{L}}$$



→ Calculate  $Q_{sp}$ :

$$Q_{sp} = [Ag^+][Cl^-] = (1.8 \times 10^{-5}) \times (8.2 \times 10^{-7})$$

$$Q_{sp} = 1.5 \times 10^{-11}$$

$$K_{sp} = 1.8 \times 10^{-10}$$

$$\Rightarrow Q_{sp} < K_{sp}$$

⇒ No precipitation occurs

## 19.4 Equilibria Involving Complex Ions

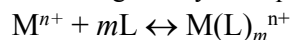
– **Complex ions** – consist of a metal cation surrounded by anions or neutral molecules called ligands

– Complex ions are **Lewis acid-base complexes** (adducts)

- The **metal cation** is a **Lewis acid**
- The **ligands** are **Lewis bases**

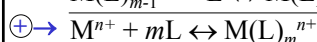
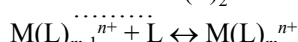
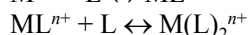
### Formation of Complex Ions

➤ For a metal cation,  $M^{n+}$ , and a neutral ligand,  $L$ , the complex formation is given by the equilibrium:



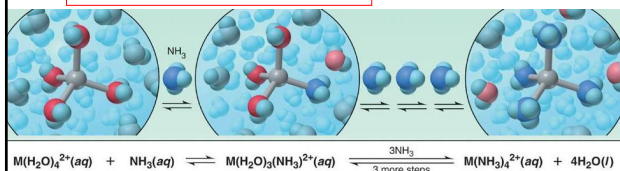
$$K_f = \frac{[M(L)_m^{n+}]}{[M^{n+}][L]^m} \quad K_f \rightarrow \text{formation constant of the complex}$$

➤ In reality, the metal cation,  $M^{n+}$ , is hydrated by several water molecules and the ligand,  $L$ , gradually replaces them one at a time in stepwise manner



Note: Water has been omitted from the expressions

$$K_f = K_{f1} \times K_{f2} \times \dots \times K_{fm}$$

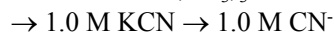
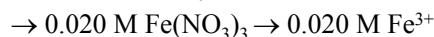


- Complexes between good Lewis acids (such as highly charged and transition metal cations) and good Lewis bases (such as  $NH_3$ ,  $CN^-$ ,  $OH^-$ , ...) are extremely stable

– Their  $K_f$  values are very large ( $>10^5$ )

⇒ If enough ligand is present in the solution, almost the entire amount of the cation is converted to the complex →  $C_M \approx [M(L)_m^{n+}]$

**Example:** What is the concentration of  $Fe^{3+}$  after mixing of **25 mL 0.020 M**  $Fe(NO_3)_3$  solution with **25 mL 1.0 M**  $KCN$  solution? ( $K_f = 4.0 \times 10^{43}$  for the complex  $Fe(CN)_6^{3-}$ )



→ After mixing, the total volume is  $25 + 25 = 50$  mL

$$\Rightarrow C_{Fe} = (0.020 \text{ M} \times 25 \text{ mL} / 50 \text{ mL}) = 0.010 \text{ M}$$

$$\Rightarrow C_{CN} = (1.0 \text{ M} \times 25 \text{ mL} / 50 \text{ mL}) = 0.50 \text{ M}$$

	$Fe^{3+}$	$6CN^-$	$Fe(CN)_6^{3-}$	
<i>i</i>	0.010	0.50	0	$K_f = \frac{[Fe(CN)_6^{3-}]}{[Fe^{3+}][CN^-]^6}$
<i>c</i>	-x	-6x	+x	
<i>e</i>	0.010 - x	0.50 - 6x	x	
<i>e'</i>	y	0.44	0.010	

→  $K_f$  is very large so almost the entire amount of  $Fe^{3+}$  is converted to the complex

$$\Rightarrow x \approx C_{Fe} \Rightarrow x \approx 0.010$$

$$\Rightarrow (0.50 - 6x) \approx (0.50 - 6 \times 0.010) = 0.44$$

→ Define a new variable,  $y = 0.010 - x = [Fe^{3+}]$

$$K_f = \frac{0.010}{y(0.44)^6} \Rightarrow y = \frac{0.010}{K_f(0.44)^6}$$

$$y = \frac{0.010}{4.0 \times 10^{43} (0.44)^6} = 3.4 \times 10^{-44} \text{ M} = [Fe^{3+}]$$

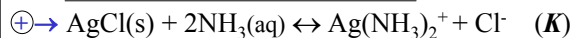
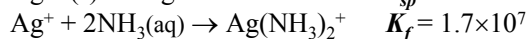
### Complex Ions and Solubility of Precipitates

➤ The solubility of some ionic solids in water can be improved by the addition of an appropriate ligand (such as  $NH_3$ ,  $CN^-$ , ...)

– The ligand (L) forms a complex with the cation of the slightly soluble salt and the solubility equilibrium shifts toward further dissolution



**Example:** The solubility of AgCl can be improved by addition of ammonia, NH<sub>3</sub>.



$$\rightarrow K = K_{sp} \times K_f = 1.8 \times 10^{-10} \times 1.7 \times 10^7 = \boxed{3.1 \times 10^{-3}}$$

→ The overall equilibrium constant,  $K$ , is much larger than  $K_{sp}$

⇒ The addition of NH<sub>3</sub> shifts the equilibrium to the right and the **solubility increases**

**Example:** Calculate the molar solubility of AgCl in **0.10 M** NH<sub>3</sub> solution.

	$\text{AgCl(s)} + 2\text{NH}_3(\text{aq}) \leftrightarrow \text{Ag}(\text{NH}_3)_2^+ + \text{Cl}^-$			
<i>i</i>	<i>excess</i>	<b>0.10</b>	<b>0</b>	<b>0</b>
<i>c</i>	<b>-s</b>	<b>-2s</b>	<b>+s</b>	<b>+s</b>
<i>e</i>	<i>excess</i>	<b>0.10 - 2s</b>	<b>s</b>	<b>s</b>

$$K = \frac{[\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]}{[\text{NH}_3]^2} = \frac{s^2}{(0.10 - 2s)^2}$$

$$\frac{s}{0.1 - 2s} = \sqrt{K} \Rightarrow s = \frac{0.10\sqrt{K}}{1 + 2\sqrt{K}} = \frac{0.10\sqrt{3.1 \times 10^{-3}}}{1 + 2\sqrt{3.1 \times 10^{-3}}} \Rightarrow \boxed{s = 5.0 \times 10^{-3}}$$

**Note:** The solubility of AgCl in 0.10 M NH<sub>3</sub> is higher than that in **pure water** which is:

$$s = (K_{sp})^{1/2} = (1.8 \times 10^{-10})^{1/2} = \mathbf{1.3 \times 10^{-5} \text{ M}}$$

## Complex Ions of Amphoteric Hydroxides

➤ Metals that form amphoteric oxides also form **amphoteric hydroxides** which react with both acids and bases

➤ Have low solubility in pure water

➤ Dissolve well in aqueous acids or bases

→ The solubility in acids is due to a reaction with H<sub>3</sub>O<sup>+</sup> which shifts the solubility equilibrium toward dissolution (as discussed in 19.3)

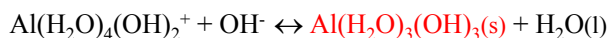
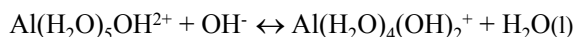
→ The solubility in bases is due to the formation of soluble complexes of the metal ions with OH<sup>-</sup>

➤ The solubility of amphoteric hydroxides can be explained as a complex formation process

**Example:** Al(OH)<sub>3</sub>

→ In acidic solution OH<sup>-</sup> ions are scarce so Al<sup>3+</sup> is completely hydrated as Al(H<sub>2</sub>O)<sub>6</sub><sup>3+</sup>

→ As the solution becomes less acidic and more basic, the OH<sup>-</sup> ions gradually accept H<sup>+</sup> from the hydrating water molecules



→ The neutral complex of Al is insoluble

⇒ A precipitate forms → **Al(H<sub>2</sub>O)<sub>3</sub>(OH)<sub>3</sub>(s)** → usually written without the water as **Al(OH)<sub>3</sub>(s)**

→ As the solution becomes even more basic, the OH<sup>-</sup> ions accept H<sup>+</sup> from one of the 3 remaining water molecules



⇒ The precipitate dissolves due to the formation of the soluble negative complex ion

➤ Zn<sup>2+</sup>, Sn<sup>2+</sup>, Pb<sup>2+</sup>, ... exhibit similar behavior

➤ Other metals such as Fe<sup>2+</sup>, Fe<sup>3+</sup>, ... only form the neutral insoluble hydroxide complex which can not be dissolved in basic solution

## 19.5 Applications of Ionic Equilibria

### Selective Precipitation

➤ Mixtures of cations can be separated by selective precipitation with an anion if the solubilities of the precipitates are significantly different

➤ The concentration of the anion is selected in a way so that  $Q_{sp}$  is above  $K_{sp}$  for the less soluble ion and just below  $K_{sp}$  for the more soluble ion

**Example:** What is the maximum concentration of Cl<sup>-</sup> that would precipitate only one of the ions in a solution that is **0.0010 M** in Ag<sup>+</sup> and **0.020 M** in Pb<sup>2+</sup>?  $K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}$ ;  $K_{sp}(\text{PbCl}_2) = 1.7 \times 10^{-5}$



→ Calculate the concentrations of  $\text{Cl}^-$  at which precipitation of each ion begins:

$$[\text{Cl}^-] = \frac{K_{sp}}{[\text{Ag}^+]} = \frac{1.8 \times 10^{-10}}{0.0010} = 1.8 \times 10^{-7} \text{ M}$$

$$[\text{Cl}^-] = \sqrt{\frac{K_{sp}}{[\text{Pb}^{2+}]}} = \sqrt{\frac{1.7 \times 10^{-5}}{0.020}} = 2.9 \times 10^{-2} \text{ M}$$

→  $\text{AgCl}$  will precipitate first at  $[\text{Cl}^-] > 1.8 \times 10^{-7} \text{ M}$

→ If  $[\text{Cl}^-] < 2.9 \times 10^{-2} \text{ M}$ ,  $\text{PbCl}_2$  will not precipitate

⇒ The maximum  $[\text{Cl}^-]$  is just below  **$2.9 \times 10^{-2} \text{ M}$**

**Note:** The concentration of unprecipitated  $\text{Ag}^+$  is:

$$[\text{Ag}^+] = K_{sp}/[\text{Cl}^-] = 1.8 \times 10^{-10}/2.9 \times 10^{-2} = 6.2 \times 10^{-9} \text{ M}$$