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\(_3\)O\(^+\) (acid) \(\rightarrow\) (A\(^-\) consumes the added H\(_3\)O\(^+\))
  \[H_3O^+ + A^- \rightarrow H_2O + HA\]
- 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\(_3\)O\(^+\) (acid) \(\rightarrow\) (B consumes the added H\(_3\)O\(^+\))
  \[H_3O^+ + B \rightarrow H_2O + HB^+\]
- Add OH\(^-\) (base) \(\rightarrow\) (HB\(^+\) consumes the added OH\(^-\))
  \[OH^- + HB^+ \rightarrow H_2O + B\]

⇒ The addition of H\(_3\)O\(^+\) 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
- HA and A\(^-\) reach equilibrium
  \[HA + H_2O \leftrightarrow H_3O^+ + A^-\]
- 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
- Works if \( C_a > 100 \times K_a \) and \( C_b > 100 \times K_b \)
- If \( C_a = C_b, \log(C_a/C_b) = 0 \) and \( pH = pK_a \)
- If \( C_a \) and \( C_b \) are comparable, the \( pH \) of the buffer is close to the \( pK_a \) of the acid component
- Take a -log() of \([H_3O^+] = K_a(C_a/C_b)\)
  \[\log[H_3O^+] = -\log K_a - \log \frac{C_a}{C_b} = -\log K_a + \log \frac{C_b}{C_a}\]
  \[pH = pK_a + \log \frac{C_b}{C_a}\]
  \[\text{Henderson-Hasselbalch Equation}\]
  \[\Rightarrow \text{The equation is valid only if } C_a \text{ and } C_b \text{ are large enough so that the assumptions } [HA] \approx C_a \text{ and } [A^-] \approx C_b \text{ are justified; If not, } [HA] \text{ and } [A^-] \text{ must be used}\]
  \[\Rightarrow \text{Works if } C_a > 100 \times K_a \text{ and } C_b > 100 \times K_b\]
  \[\Rightarrow \text{If } C_a = C_b, \log(C_a/C_b) = 0 \text{ and } pH = pK_a\]
  \[\Rightarrow \text{If } C_a \text{ and } C_b \text{ are comparable, the } pH \text{ of the buffer is close to the } pK_a \text{ of the acid component}\]

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)

1. Use the Hend.-Hass. Eq. (HF – acid; F\(^-\) – base)
  \( C_a = 0.50 \quad C_b = 0.50\)
  \[pH = pK_a + \log(0.50/0.50) = pK_a + \log(1) = pK_a + 0\]
  \[pH = pK_a = -\log(6.8 \times 10^{-4}) = 3.17\]

2. Or use an ice table

\[
\begin{array}{c|c|c|c}
| i & [HF + H_2O] & [H_3O^+] & [F^-] \\
|---|---|---|---|
| 1 & 0.50 & 0.50 & 0.50 \\
| 2 & 0.50 - x & x & 0.50 + x \\
\end{array}
\]

\[K_a = \frac{[H_3O^+] [F^-]}{[HF]} = \frac{x(0.50 + x)}{(0.50 - x)} \approx \frac{x(0.50)}{(0.50)}\]

\[x = K_a = 6.8 \times 10^{-4} = [H_3O^+] \Rightarrow pH = -\log(6.8 \times 10^{-4}) = 3.17\]
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 H3O+ which reacts with F- from the buffer

→Calculate the starting moles of HF and F- in the buffer and the added moles of H3O+ from HCl

\[ \text{HF} \rightarrow 1.0 \text{ L} \times 0.50 \text{ mol/L} = 0.50 \text{ mol} \]

\[ \text{F}^- \rightarrow 1.0 \text{ L} \times 0.50 \text{ mol/L} = 0.50 \text{ mol} \]

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

→Use an “srf” table (starting, reacted, final) to calculate the final moles of HF and F-

\[
\begin{array}{c|ccc}
\text{moles} & s & r & f \\
0.50 & 0.010 & - & 0.50 \\
-0.010 & -0.010 & +0.010 \\
0.49 & 0.00 & - & 0.51 \\
\end{array}
\]

→Use the Hend.-Hass. Eq. (HF – acid; F- – base)

\[
\text{pH} = pK_a + \log \frac{n_b}{n_a} = -\log(6.8 \times 10^{-1}) + \log \frac{0.49}{0.51} = 3.17 + (-0.02) = 3.15
\]

⇒ 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:

\[
\text{pH} = -\log(0.010) = 2.00
\]

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

Preparing Buffers

➢ Choose the conjugate acid-base pair (select a pair with an acid component having \( pK_a \) 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 + H2O; If only half of the HF is converted to KF → buffer)

Example: How many moles of NH4Cl must be added to 1.0 L of 0.20 M NH3 solution to get a buffer with \( pH = 9.35 \)? (\( K_b = 1.8 \times 10^{-5} \) for NH3)

→ Conjugate pair NH4+/NH3

\[
K_a = \frac{K_b}{K_w} = \frac{1.8 \times 10^{-5}}{1.0 \times 10^{-14}} = 1.8 \times 10^{9.5}
\]

\[
pK_a = -\log(1.8 \times 10^{9.5}) = 9.25
\]

\[
\text{pH} = pK_a + \log \frac{n_b}{n_a} = 9.25 + \log \frac{0.20}{n_a} \Rightarrow 9.35 = 9.25 + \log \frac{0.20}{n_a}
\]

\[
0.10 = \log \left( \frac{0.20}{n_a} \right) \Rightarrow 10^{0.10} = \frac{0.20}{n_a} \Rightarrow n_a = 0.20/10^{0.10} = 0.16 \text{ mol NH}_4^+ = 0.16 \text{ mol NH}_4\text{Cl}
\]

Buffer Capacity and Buffer Range

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

\[ \uparrow \uparrow C_a \text{ and } C_b \Rightarrow \uparrow \uparrow \text{Buffer capacity} \]

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

\[
pH = pK_a + \log(0.1) = pK_a - 1
\]

\[
pH = pK_a + \log(10) = pK_a + 1 \Rightarrow \text{BR} = pK_a \pm 1
\]
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

Strong Acid-Strong Base Titration Curves

- Strong acids and bases are completely converted to H₃O⁺ and OH⁻ in water solns.
  - The net ionic equation of the titration is: H₃O⁺ + OH⁻ → 2H₂O
  - At the E-point, pH = 7.00 (neutral)
  - To calculate the pH during the titration:
    1. Calculate the mmol of H₃O⁺ from the acid
    2. Calculate the mmol of OH⁻ from the base
    3. Calculate the excess mmol of H₃O⁺ or OH⁻ from the difference between (1) and (2)
    4. Calculate [H₃O⁺] or [OH⁻] from the excess and the total volume of the solution (Vₜot) → 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 M HCl → 0.100 M H₂O⁺ = 0.100 mmol/mL
0.100 M NaOH → 0.100 M OH⁻ = 0.100 mmol/mL

1. H₃O⁺ → 40.0 mL × 0.100 mmol/mL = 4.00 mmol
2. OH⁻ → 25.0 mL × 0.100 mmol/mL = 2.50 mmol
3. Excess acid = 4.00 – 2.50 = 1.50 mmol H₂O⁺
4. Vₜot = 40.0 + 25.0 = 65.0 mL
   1.50 mmol / 65.0 mL = 0.0231 M H₃O⁺

pH = -log(0.0231) = 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)₂ after the addition of 21.0 mL Ba(OH)₂ 0.500 M HCl

1. H₃O⁺ → 20.0 mL × 0.500 mmol/mL = 10.0 mmol
2. OH⁻ → 21.0 mL × 0.500 mmol/mL = 10.5 mmol
3. Excess base = 10.5 – 10.0 = 0.50 mmol OH⁻
4. Vₜₒₜ = 20.0 + 21.0 = 41.0 mL

⇒ pH = 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⁻ in water solution
  ⇒ The net ionic equation of the titration is:

  \[ \text{HA} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{A}^- \]

  ⇒ At the E-point, pH > 7.00 (basic) due to the presence of A⁻ 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⁻ (buffer region)
  3. At the E-point → solution of the weak base A⁻
  4. After the E-point → excess of OH⁻ 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

  \[ \text{HCOOH} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{HCOO}^- \]

  \[ K_a = \frac{[\text{H}_3\text{O}^+][\text{HCOO}^-]}{[\text{HCOOH}]} \]

  \[ x = (0.500K_a)^{0.5} = (1.8 \times 10^{-4} \times 0.500)^{0.5} = 9.5 \times 10^{-3} = [\text{H}_3\text{O}^+] \]

  ⇒ pH = -log[H₃O⁺] = -log(9.5 × 10⁻³) = 2.02

2) 10.0 mL NaOH added (Half-way to the E-point):
  0.500 M HCOOH 0.500 M NaOH → 0.500 M OH⁻
  HCOOH → 20.0 mL × 0.500 mmol/mL = 10.0 mmol
  OH⁻ → 10.0 mL × 0.500 mmol/mL = 5.00 mmol

  \[ \text{HCOOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCOO}^- \]

  \[ \begin{array}{c|c|c|c|c}
  \text{mmol} & \text{HCOOH} & \text{OH}^- & \text{H}_2\text{O} & \text{HCOO}^- \\
  \hline
  s & 10.0 & 5.00 & - & 0.00 \\
  r & -5.00 & -5.00 & - & +5.00 \\
  f & 5.00 & 0.00 & - & 5.00 \\
  \end{array} \]

  ⇒ The system is a buffer (HCOOH → a, HCOO⁻ → b)

  \[ pH = pK_a + \log(n_b/n_a) = pK_a + \log(5.00/5.00) = pK_a + 0 \]

  ⇒ pH = pKₐ = -log(1.8 × 10⁻⁴) = 3.74

  ⇒ Half-way to the E-point → pH = pKₐ !!!
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):

0.500 M HCOOH + 0.500 M NaOH → 0.500 M OH⁻

\[ \text{HCOOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCOO}^- \]

\[ \begin{array}{ccc} \text{mmol} \\ \text{s} & 10.0 & 9.50 \\ \text{r} & -9.50 & -9.50 \\ \text{f} & 0.50 & 0.00 \end{array} \]

The system is a buffer (HCOOH → \( a \), HCOO⁻ → \( b \))

\[ \text{pH} = \text{pK}_a + \log\left(\frac{[b]}{[a]}\right) \]

\[ \Rightarrow \text{pH} = 3.74 + 1.28 = 5.02 \]

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

0.500 M HCOOH + 0.500 M NaOH → 0.500 M OH⁻

\[ \text{HCOOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCOO}^- \]

\[ \begin{array}{ccc} \text{mmol} \\ \text{s} & 10.0 & 10.0 \\ \text{r} & -10.0 & -10.0 \\ \text{f} & 0.00 & 0.00 \end{array} \]

\[ \Rightarrow \text{A solution of the weak base HCOO}^- \]

\[ V_{\text{tot}} = 20.0 + 20.0 = 40.0 \text{ mL} \]

⇒ \[ \frac{10.0 \text{ mmol}}{40.0 \text{ mL}} = 0.250 \text{ M HCOO}^- \]

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

0.500 M HCOOH + 0.500 M NaOH → 0.500 M OH⁻

\[ \text{HCOOH} + \text{OH}^- \rightarrow \text{H}_2\text{O} + \text{HCOO}^- \]

\[ \begin{array}{ccc} \text{mmol} \\ \text{s} & 10.0 & 10.5 \\ \text{r} & -10.0 & -10.0 \\ \text{f} & 0.00 & 0.50 \end{array} \]

\[ \Rightarrow \text{A solution of the excess strong base (OH⁻) and the weak base (HCOO⁻)} \]

\[ V_{\text{tot}} = 20.0 + 21.0 = 41.0 \text{ mL} \]

0.50 mmol / 41.0 mL = 0.012 M OH⁻

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

Phenolphthalein is a suitable indicator since its range (8.3-10) is in the vertical part of the t-curve

Methyl red is not a suitable indicator since its range (4.3-6.2) is in the buffer region before the E-point (color changes over a broad volume range)

Weak base-Strong Acid Titration Curves

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

\[ \text{H}_3\text{O}^+ + \text{B} \rightarrow \text{HB}^- + \text{H}_2\text{O} \]

⇒ At the E-point, \( \text{pH} < 7.00 \) (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
Phenolphthalein is not a suitable indicator since its range (8.3-10) is in the buffer region before the E-point (color changes over a broad volume range).

Methyl red is a suitable indicator since its range (4.3-6.2) is in the vertical part of the t-curve.

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

Titrations 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:
  \[
  H_2A + OH^- \rightarrow H_2O + HA^- \quad (1\text{st E-point})
  \]
  \[
  HA^- + OH^- \rightarrow H_2O + A^{2-} \quad (2\text{nd E-point})
  \]

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

\[
H_2SO_3 + OH^- \rightarrow H_2O + HSO_3^- \quad (1\text{st E-point})
\]
\[
HSO_3^- + OH^- \rightarrow H_2O + SO_3^{2-} \quad (2\text{nd E-point})
\]

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, \( M_nA_m \), in equilibrium with its saturated solution, the equilibrium constant of the dissolution process is called solubility-product

\[
M_nA_m(s) \leftrightarrow nM^{m+} + mA^{n-} \\
K_{sp} = [M^{m+}]^n[A^{n-}]^m
\]
**Example:** Write the solubility-product expression for Al(OH)₃.

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

⇒ $K_{sp} = [Al^{3+}][OH^-]^3$

- Sulfides are slightly different since S²⁻ acts as a strong base in water and converts entirely to OH⁻

**Example:** Ag₂S

$Ag_2S(s) \leftrightarrow 2Ag^+ + S^{2-}$

$S^{2-} + H_2O(l) \leftrightarrow HS^- + OH^-$

$Ag_2S(s) + H_2O(l) \leftrightarrow 2Ag^+ + HS^- + OH^-$

⇒ $K_{sp} = [Ag^+]^2[HS^-][OH^-]$

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

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

- $K_{sp}$ 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 Pb(IO₃)₂ is 0.022 g/L at 25°C. Calculate $K_{sp}$ of Pb(IO₃)₂.

→ Convert the solubility to molar solubility, s

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

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

$Pb(IO}_3)_2(s) \leftrightarrow Pb^{2+} + 2IO_3^{-}$

1 mol Pb(IO₃)₂ → 1 mol Pb²⁺ + 2 mol IO₃⁻

$\Rightarrow [Pb^{2+}] = s$ and $[IO_3^-] = 2s$

$\Rightarrow K_{sp} = [Pb^{2+}][IO_3^-]^2 = s(2s)^2 = 4s^3$

$\Rightarrow K_{sp} = 4(3.9 \times 10^{-5})^3 = 2.5 \times 10^{-15}$

- $K_{sp}$ 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)

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

**The Common Ion Effect**

- For a slightly soluble ionic solid, MA

$MA(s) \leftrightarrow M^{n+} + A^{m-}$

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

- If $M^{n+}$ 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 (M⁻)

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

$\Rightarrow$ The molar solubility decreases in the presence of common ions

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

<table>
<thead>
<tr>
<th>No. of Ions</th>
<th>Formula</th>
<th>Cation:Anion</th>
<th>$K_{sp}$</th>
<th>Solubility (M)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>MgCO₃</td>
<td>1:1</td>
<td>$3.5 \times 10^{-8}$</td>
<td>1.9×10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>PbSO₄</td>
<td>1:1</td>
<td>$1.6 \times 10^{-8}$</td>
<td>1.3×10⁻⁴</td>
</tr>
<tr>
<td>2</td>
<td>BaCrO₄</td>
<td>1:1</td>
<td>$2.1 \times 10^{-10}$</td>
<td>1.4×10⁻⁵</td>
</tr>
<tr>
<td>3</td>
<td>Ca(OH)₂</td>
<td>1:2</td>
<td>$6.5 \times 10^{-6}$</td>
<td>1.2×10⁻²</td>
</tr>
<tr>
<td>3</td>
<td>BaF₂</td>
<td>1:2</td>
<td>$1.5 \times 10^{-6}$</td>
<td>7.2×10⁻³</td>
</tr>
<tr>
<td>3</td>
<td>CaF₂</td>
<td>1:2</td>
<td>$3.2 \times 10^{-11}$</td>
<td>2.0×10⁻⁴</td>
</tr>
<tr>
<td>3</td>
<td>Ag₂CrO₄</td>
<td>2:1</td>
<td>$2.6 \times 10^{-12}$</td>
<td>8.7×10⁻⁵</td>
</tr>
</tbody>
</table>
**Example:** At a given temperature, $K_{sp}$ of AgBr is $7.7 \times 10^{-13}$. Estimate the solubility of AgBr in:

a) Pure H$_2$O

b) 0.10 M CaBr$_2$ solution

a) In pure H$_2$O

- Express $K_{sp}$ through the molar solubility, $s$:
  
  $[Ag^+] = s$ and $[Br^-] = s$  
  $K_{sp} = [Ag^+][Br^-] = s^2$

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

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<table>
<thead>
<tr>
<th></th>
<th>$i$</th>
<th>$e$ excess</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgBr(s)</td>
<td>+s</td>
<td>$s$</td>
</tr>
<tr>
<td>Ag^+ + Br-</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
```

$\Rightarrow [Ag^+] = s$ and $[Br^-] = s$

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

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

**b) In 0.10 M CaBr$_2$ solution**

- 0.10 M CaBr$_2$ solution
- $0.20 M$ Br$^-$ (Br$^-$ is the common ion)

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

- Assume $s << 0.20$  
  
  $K_{sp} = s(0.20)$

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

- Check assumption → OK

$\Rightarrow$ 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$_3$O$^+$
  
  $\Rightarrow$ The solubility can be improved by adding acids

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

  - Mg(OH)$_2$(s) $\leftrightarrow$ Mg$^{2+}$ + 2OH$^-$
  - If acid (H$_3$O$^+$) is added:
    
    $\Rightarrow$ H$_3$O$^+$ consumes OH$^-$ (H$_3$O$^+$ + OH$^-$ $\rightarrow$ 2H$_2$O)
  
  $\Rightarrow$ 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$_3$O$^+$

  $\Rightarrow$ The solubility can be improved by adding acids

  **Example:** BaSO$_3$ (a salt of H$_2$SO$_3$)

  - BaSO$_3$(s) $\leftrightarrow$ Ba$^{2+}$ + SO$_3^{2-}$
  - If acid (H$_3$O$^+$) is added:
    
    SO$_3^{2-}$ + H$_3$O$^+$ $\rightarrow$ HSO$_3^-$ + H$_2$O(l) (solubility increases)
  
  $\Rightarrow$ H$_3$O$^+$ consumes SO$_3^{2-}$

  $\Rightarrow$ The equilibrium shifts to the right and the solubility increases

  **Example:** CaCO$_3$(s) $\leftrightarrow$ Ca$^{2+}$ + CO$_3^{2-}$

  - CO$_3^{2-}$ + 2H$_3$O$^+$ $\rightarrow$ H$_2$CO$_3$ + H$_2$O(l) $\rightarrow$ CO$_2$(g) + 2H$_2$O(l)

---

**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 1.0×10$^{-4}$ M AgNO$_3$ with 900. mL 1.0×10$^{-6}$ KCl?

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

> AgNO$_3$(aq) + KCl(aq) $\rightarrow$ AgCl(s) + KNO$_3$(aq)

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

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

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

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

  Initial concentrations after mixing:

  $\frac{1.0 \times 10^{-4} \text{mol}}{L} \times \frac{0.200 \text{L}}{} = \frac{1.8 \times 10^{-5} \text{mol}}{L}$

  $\frac{1.0 \times 10^{-6} \text{mol}}{L} \times \frac{0.900 \text{L}}{} = \frac{8.2 \times 10^{-7} \text{mol}}{L}$
→ Calculate \( Q_{sp} \):
\[
Q_{sp} = [Ag^+][Cl^-] = (1.8 \times 10^{-5}) \times (8.2 \times 10^{-7})
\]
\[
Q_{sp} = 1.5 \times 10^{-11}
\]
⇒ \( Q_{sp} < K_{sp} \)
⇒ 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:

\[
M^{n+} + mL \leftrightarrow M(L)^{m+n}
\]

- \( K_f \) is very large so almost the entire amount of \( Fe^{3+} \) is converted to the complex

\[
x \approx C_{Fe} \Rightarrow x \approx 0.010
\]

\[
(0.50 - 6x) \approx (0.50 - 6 \times 0.010) = 0.44
\]

Define a new variable, \( y = 0.010 - x = [Fe^{3+}] \)
Example: The solubility of AgCl can be improved by addition of ammonia, NH₃.

\[ \text{AgCl(s)} \rightleftharpoons \text{Ag}^+ + \text{Cl}^- \quad K_{sp} = 1.8 \times 10^{-10} \]

\[ \text{Ag}^+ + 2\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ag(NH}_3)_2^+ \quad K_f = 1.7 \times 10^7 \]

Using the expression for the overall equilibrium constant, \( K = K_{sp} \times K_f \):

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

The solubility of AgCl in 0.10 M NH₃ is higher than that in pure water.

Example: Calculate the molar solubility of AgCl in 0.10 M NH₃ solution.

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 \( \text{H}_3\text{O}^+ \) 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 \( \text{OH}^- \)

The neutral complex of Al is insoluble
- A precipitate forms \( \text{Al(H}_2\text{O)}_3(\text{OH})_2(\text{s}) \rightarrow \text{Al(H}_2\text{O)}_3(\text{OH})_2(\text{s}) \)
- As the solution becomes even more basic, the \( \text{OH}^- \) ions accept \( \text{H}^+ \) from one of the 3 remaining water molecules

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⁻ that would precipitate only one of the ions in a solution that is 0.0010 M in Ag⁺ and 0.020 M in Pb²⁺?

\[ K_{sp}(\text{AgCl}) = 1.8 \times 10^{-10}; \quad K_{sp}(\text{PbCl}_2) = 1.7 \times 10^{-5} \]
AgCl(s) → Ag⁺ + Cl⁻  \[K_{sp} = [Ag^+][Cl^-]\]
PbCl₂(s) → Pb²⁺ + 2Cl⁻  \[K_{sp} = [Pb^{2+}][Cl^-]^2\]

→ Calculate the concentrations of Cl⁻ at which precipitation of each ion begins:

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

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

→ AgCl will precipitate first at [Cl⁻] > 1.8×10⁻⁷ M

→ If [Cl⁻] < 2.9×10⁻² M, PbCl₂ will not precipitate

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

**Note:** The concentration of unprecipitated Ag⁺ is:

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