**Solubility**

Silberberg 13.2, 13.3, 13.4, 19.3, 19.4

Problem book 8.63 - 8.82

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**Note on Units**

- **Concentrations of dissolved substances**

  1. **mass %** = \(\frac{\text{grams solute}}{\text{grams solution}} \times 100\)

     - e.g., 5.0 g sugar (teaspoon) in a cup (250 mL) = 2.0 %

     - 5.0 g salt in a cup = 2.0 %

  2. **molarity** = \(\frac{\text{moles solute}}{\text{litre of solution}}\)

     - \([\text{sugar}] = \frac{5.0 \text{ g}}{0.25 \text{ L}} = 0.058 \text{ M}\)

     - \([\text{NaCl}] = \frac{5.0 \text{ g}}{58.5 \text{ g mol}^{-1}} = 0.34 \text{ M}\)

  3. **ppm** = mass % \(\times 10^4\)

---

**Solubility Equilibria**

- **Amount dissolved** = Solubility

- **Saturated solution**:

  where Maximum amount of solute is dissolved

  \(\Rightarrow\) Equilibrium between solution and some undissolved solid

  \[\text{solute} \rightleftharpoons \text{solvent} \leftrightarrow \text{solution}\]

- **Molecular solutes**

  Amount dissolved equals solubility equilibrium constant \(K_{sp}\)

  - e.g., for sucrose at 25 °C:

    \(K_{sp} = \left[\text{products}\right] / \left[\text{reactants}\right]\)

    \(= \frac{[\text{sugar(aq)}]}{[\text{sugar(s)}]} = [\text{sugar(aq)}]\)

    \(K_{sp} = 6 \text{ M}\)

- **Ionic solutes**

  Amount dissolved does NOT equal \(K_{sp}\)

  \(\text{MX(s)} \rightleftharpoons \text{M}^+\text{(aq)} + \text{X}^-\text{(aq)}\)

  \(K_{sp} = [\text{M}^+][\text{X}^-]\)
**Example:** How much AgCl dissolves in water at 298 K?

\[ K_{sp} (\text{AgCl}) = 1.6 \times 10^{-10} \text{ M}^2 \]

every x moles of AgCl produces x moles of Ag\(^+\) and x moles of Cl\(^-\)

\[ \text{AgCl}(s) \rightarrow \text{Ag}^+(aq) + \text{Cl}^- (aq) \times \times \]

\[ K_{sp} = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10} \text{ M}^2 = x^2 \]

\[ \therefore x = 1.3 \times 10^{-5} \text{ M} \] (solubility in water)

**Question:** What is the solubility of AgI at 298 K?

\[ K_{sp} (\text{AgI}) = 8 \times 10^{-17} \text{ M}^2 \]

**Solubility Product of 2:1 Salts**

Solubility product equilibrium constants differ between 1:1 and 2:1 electrolytes

**Example:**

\[ \text{PbCl}_2(s) \rightarrow \text{Pb}^{2+}(aq) + 2 \text{Cl}^-(aq) \]

for x moles dissolved:

\[ x \quad 2x \]

\[ K_{sp} = [\text{Pb}^{2+}][\text{Cl}^-]^2 = [x][2x]^2 \text{ (units of } K_{sp} \text{ are M}^0) \]

\[ K_{sp} (\text{PbCl}_2) = 1.6 \times 10^{-5} \text{ M}^2 = x(2x)^2 = 4x^3 \]

\[ \therefore x = 1.6 \times 10^{-2} \text{ M} \]

**Relative Solubilities**

Care must be taken when comparing the relative solubilities of a group of salts using the \( K_{sp} \) values.

\[ \text{AgI} \quad K_{sp} = 1.5 \times 10^{-9} \quad x = (K_{sp})^{1/2} = 1.2 \times 10^{-4} \text{M} \]

\[ \text{CuI} \quad K_{sp} = 5.0 \times 10^{-22} \quad x = (K_{sp})^{1/2} = 2.2 \times 10^{-6} \text{M} \]

\[ \text{CaSO}_4 \quad K_{sp} = 6.1 \times 10^{-5} \quad x = (K_{sp})^{1/2} = 7.8 \times 10^{-3} \text{M} \]

\[ K_{sp} = \text{[cation][anion]} \text{ if } x \text{ is the solubility in moles/litre then } x = (K_{sp})^{1/2} \]

\[ \text{CuS} \quad K_{sp} = 8.5 \times 10^{-40} \quad \]

\[ \text{Ag}_2\text{S} \quad K_{sp} = 1.6 \times 10^{-49} \quad \]

\[ \text{Bi}_2\text{S}_3 \quad K_{sp} = 1.1 \times 10^{-73} \quad \]

\[ K_{sp} \text{ of CuS is larger, but more Bi}_2\text{S}_3 \text{ dissolves} \]
**Common Ion Effect**

Example: How much AgCl dissolves in 0.1 M HCl?

Same equilibrium constant, but solubility is suppressed by the effect of common ion on equilibrium.

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq)
\]

\[
K_w = [\text{Ag}^+][\text{Cl}^-] = 1.6 \times 10^{-10} M = x(0.1 + x) = 0.1x
\]

\[
x = 1.6 \times 10^{-4} M \quad (\text{This is } \ll \text{ than } 10^{-5} M \text{ in pure H}_2\text{O})
\]

Question: What is the solubility of AgBr in 0.05 M sodium bromide solution at 298 K? \(K_{sp} (\text{AgBr}) = 5 \times 10^{-13} M\)

**pH and Solubility**

\[
\text{Mg(OH)}_2(s) \rightleftharpoons \text{Mg}^{2+} (aq) + 2\text{OH}^- (aq)
\]

\(K_{sp} = 2 \times 10^{-13} M^3\)

What is the solubility in water at pH = 2 (\text{-stomach acid})?

in water, \(K_{sp} = 2 \times 10^{-13} M^3 = 4x^3 \quad x = 3 \times 10^{-6} M\)

at pH = 2, \(pOH = 12, [\text{OH}^-] = 1 \times 10^{-12} M\)

\(K_{sp} = 2 \times 10^{-13} M^3 = x(1 \times 10^{-12})^2 \quad x = 2 \times 10^{11} M\)

Question: Al(OH)_3 is used to clarify drinking water - how much Al remains in water at pH 6.6? \(K_{sp} (\text{Al(OH)}_3) = 3 \times 10^{-34} M^4\)

**Ion Product, Q**

If \(Q > K_{sp}\) then a precipitate forms

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq)
\]

Example: Does a precipitate of AgCl(s) form if equal volumes of 1 mM HCl and 1 mM AgNO_3 solutions are mixed?

(NB: Concentration halved after mixing!)

\[
[\text{Ag}^+] = 5 \times 10^{-4} M \quad \text{and} \quad [\text{Cl}^-] = 5 \times 10^{-4} M \quad (\text{after mixing})
\]

\[
Q = [\text{Ag}^+][\text{Cl}^-] = 2.5 \times 10^{-7} M^2 \quad > \quad K_{sp} = 1.6 \times 10^{-10} M^2
\]

\(\therefore\) AgCl(s) precipitates, i.e., reaction moves to left toward equilibrium.

**Ion Product, Q**

If \(Q > K_{sp}\) then a precipitate forms

\[
\text{AgCl(s)} \rightleftharpoons \text{Ag}^+ (aq) + \text{Cl}^- (aq)
\]

Example: What about equal volumes of 2.0 \times 10^{-5} M solutions?

\[
[\text{Ag}^+] = 1.0 \times 10^{-5} M \quad \text{and} \quad [\text{Cl}^-] = 1.0 \times 10^{-5} M \quad (\text{after mixing})
\]

\[
Q = [\text{Ag}^+][\text{Cl}^-] = 1.0 \times 10^{-10} M^2 \quad < \quad K_{sp} = 1.6 \times 10^{-10} M^2
\]

\(\therefore\) AgCl(s) does not precipitate.
Application: Barium Sulfate for X-Ray Imaging

**Ba**^{2+} is very toxic

\[ K_{sp} \text{ of } BaSO_4 = 1.1 \times 10^{-10} \]

How much is soluble:
(a) in pure water?
(b) in 0.1 M Na_2SO_4?

\[ [Ba^{2+}] = (1.1 \times 10^{-10})^{1/2} \sim 1 \times 10^{-5} \text{ M} \]

\[ [Ba^{2+}][SO_4^{2-}] = 1.1 \times 10^{-10} \]

∴ \[ [Ba^{2+}] = 1.1 \times 10^{-5} \]

Application: Calcium Oxalate in Kidney Stones

\[ K_{sp} \text{ of } Ca(C_2O_4) = 1.96 \times 10^8 \]

\[ [Ca^{2+}][C_2O_4^{2-}] = 1.96 \times 10^8 \]

\[ C_2(OOH)_2 \rightarrow C_2(OO)(OO^-) \quad (pK_a = 1.23) \]

\[ C_2(OO)(OO^-) \rightarrow C_2(OO)O_2^{2-} \quad (pK_a = 4.12) \]

• Drink lots of water
• Avoid dairy products (calcium)
• Avoid antacids (calcium)
• Don’t take huge quantities of vitamin C
• Avoid foods rich in oxalic acid (tea, chocolate, rhubarb)

Why is it so?

- **Enthalpy of Hydration**
  - The smaller the ionic radius, the more energy is released by surrounding an ion with water molecules...
  - The more highly charged the ion, the more energy is released...
  - \( \Delta H_{hyd} \) - Always favours dissolution

- **Lattice Energy (Silberberg 9.6)**
  - Energy released when crystal is formed from free ions
  - \( \Delta H_{lat} = \text{cation charge} \times \text{anion charge} \times r^2 \)
  - cation radius + anion radius
  - \( \Delta H_{lat} \) – Always opposes dissolution

- **Entropy of Hydration**
  - Solid \( \rightarrow \) Dissolved ions
  - \( \Delta G_{hyd} = \Delta H_{hyd} - \Delta H_{lat} - T\Delta S_{hyd} \)
  - \( \Delta S_{hyd} \) – Almost Always favours dissolution

Relation Between Solubility and Temperature

Silberberg, p.499
### Trends in Ionic Heats of Hydration

<table>
<thead>
<tr>
<th>Ion</th>
<th>Radius (pm)</th>
<th>$\Delta H_{\text{hyd}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$^+$</td>
<td>76</td>
<td>$-510$</td>
</tr>
<tr>
<td>Na$^+$</td>
<td>102</td>
<td>$-410$</td>
</tr>
<tr>
<td>K$^+$</td>
<td>138</td>
<td>$-336$</td>
</tr>
<tr>
<td>Cs$^+$</td>
<td>167</td>
<td>$-282$</td>
</tr>
<tr>
<td>Mg$^{2+}$</td>
<td>72</td>
<td>$-1903$</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>100</td>
<td>$-1591$</td>
</tr>
<tr>
<td>Ba$^{2+}$</td>
<td>135</td>
<td>$-1317$</td>
</tr>
</tbody>
</table>

### Trends in Ionic Heats of Hydration

<table>
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<tr>
<th>Ion</th>
<th>Radius (pm)</th>
<th>$\Delta H_{\text{hyd}}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>F$^-$</td>
<td>133</td>
<td>$-431$</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>181</td>
<td>$-313$</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>196</td>
<td>$-284$</td>
</tr>
<tr>
<td>I$^-$</td>
<td>220</td>
<td>$-247$</td>
</tr>
</tbody>
</table>

### Important Things to Know:

- How to do solubility product calculations
- What the Common Ion Effect is
- How to convert from one unit of solubility to another
- Why milk chocolate is worse for you than dark chocolate

### Complexes, aka Coordination Compounds

- **Silberberg** 18.9, 19.4, 23.4
- **Problem book** 8.83 - 8.91

**Reaction of a metal ion (Lewis acid) with anions or molecules (Lewis base ~ ligands) forms complex species (coordination compounds)**

\[ \text{e.g., } \text{Ag}^+ + 2\text{NH}_3 \rightarrow \text{Ag(NH}_3)_2^+ \]
**Complexes, aka Coordination Compounds**

- Reaction of a metal ion with anions or molecules (ligand(s)) forms complex species (coordination compound)
  - e.g., $\text{Ag}^+ + 2 \text{NH}_3 \rightarrow \text{Ag(NH}_3)_2^+$
- A complex is a chemical species whose components are capable of separate existence:
  - e.g., $\text{Ag(NH}_3)_2^+$ distinct from $\text{Ag}^+$ and $\text{NH}_3$;
  - (not $\text{CO}_3^{2-}$ because $\text{O}^{2-}$ and $\text{C}^{4+}$ do not exist independently)
- Metals are usually transition metals (but remember we had Mg$^{2+}$)
- Ligands have at least one atom with a lone (loan) pair:
  - e.g., $\text{H}_2\text{O}$, $\text{NH}_3$, $\text{Cl}^-$, $\text{CN}^-$

**Coordination Number and Geometry**

- The number of ligands attached to the metal is called the coordination number

<table>
<thead>
<tr>
<th>COORD. NO.</th>
<th>GEOMETRY</th>
<th>COMMENTS/EXAMPLES</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>LINEAR</td>
<td>uncommon $[\text{Ag(NH}_3)_2^+]$</td>
</tr>
<tr>
<td>4</td>
<td>PLANAR</td>
<td>electronic cause $^*$ $\text{d}_8$ $[\text{Cu(NH}_3)_4]^2^+$</td>
</tr>
<tr>
<td>4</td>
<td>TETRAHEDRAL</td>
<td>common $[\text{Zn(NH}_3)_4]^2^+$</td>
</tr>
<tr>
<td>6</td>
<td>OCTAHEDRAL</td>
<td>common $[\text{Cr(NH}_3)_6]^3^+$</td>
</tr>
</tbody>
</table>

**Ligands**

- Some ligands have more than one atom with lone pairs that can be bonded to the metal ion – these are CHELATES (‘chee-lates’ = claw)

  - Monodentate ligands (‘den’ = tooth) e.g. $\text{H}_2\text{O}$, $\text{NH}_3$, $\text{Cl}^-$
  - Bidentate ligands can form 2 bonds e.g. ethylenediamine (en)
  - Polyydentate ligands can form more than two bonds – some can form as many as 6, e.g. EDTA – ethylenediaminetetraacetic acid (hexadentate) - forms very stable complexes with most metal ions and is used as a “scavenger” to remove TOXIC heavy metals such as lead from the human body.

<table>
<thead>
<tr>
<th>Isomers</th>
<th>Coordination isomerism (which ligands are in coordination sphere and which outside)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example: $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$</td>
<td></td>
</tr>
<tr>
<td>$[\text{Cr(H}_2\text{O})_3]^2^+\text{Cl}_2$ hexaaquachromium(III) chloride</td>
<td></td>
</tr>
<tr>
<td>$[\text{Cr(H}_2\text{O})_5]\text{Cl}_2\cdot \text{H}_2\text{O}$ pentaaquachlorochromium(III) chloride—water (1/1)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Cr(H}_2\text{O})_4]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ tetraaquachlorochromium(III) chloride—water (1/2)</td>
<td></td>
</tr>
<tr>
<td>$[\text{Cr(H}_2\text{O})_3]\text{Cl}_2\cdot 3\text{H}_2\text{O}$ triaquachlorochromium(III) chloride—water (1/3)</td>
<td></td>
</tr>
</tbody>
</table>
Isomers

Geometric isomers:

Four coordinate: cis- and trans- [Pt(NH$_3$)$_2$Cl$_2$]

Six coordinate: cis- and trans- [Co(NH$_3$)$_4$Cl$_2$]$^+$

Optical isomers:

compare cis-[Cr(NH$_3$)$_4$Cl$_2$]$^+$ and cis-[Cr(en)$_2$Cl$_2$]$^+$

[M(en)$_3$]$^{3+}$ complexes have optical isomers

Types of Isomerism

- Coordination
- Geometric
- Optical

- Know what they are!
- Know at least one example of each!
- Know how to name them (more on naming to come...)
Stability Constant \( (K_{\text{stab}}) \)

\[
K_{\text{stab}} = \frac{[\text{Complex}]}{[\text{Metal Ion}] [\text{Ligand}]^n}
\]

e.g., \([\text{AlF}_6^{3-}] \)

\[
K_{\text{stab}} = \frac{[\text{AlF}_6^{3-}]}{[\text{Al}^{3+}][\text{F}^-]^6} = 4 \times 10^{19}
\]

### Example
A solution is prepared by dissolving \( \text{AgNO}_3 \) (0.01 mol) in a 1.00 M aqueous solution of KCN (500 mL) and adding enough water to make 1.00 L of solution.

Calculate the equilibrium \([\text{Ag}^+]\) given \( K_{\text{stab}} [\text{Ag(CN)}_2^-] = 10^{20.0} \text{ M}^{-2} \).

\[
\begin{align*}
\text{Ag}^+ + 2\text{CN}^- &\rightleftharpoons \text{Ag(CN)}_2^- \\
\text{initial / M} &\quad 0.01 & 0.500 \\
\text{change} &\quad -0.01 & -0.02 & 0.01 \\
\text{equilibrium / M} &\quad x & 0.480 & 0.01 \\
\end{align*}
\]

\[
K_{\text{stab}} = \frac{[\text{Ag(CN)}_2^-]}{[\text{Ag}^+][\text{CN}]^2} = 10^{20.0}
\]

\[
[\text{Ag}^+] = \frac{[\text{Ag(CN)}_2^-]}{10^{20.0}[\text{CN}]^2} = \frac{0.01}{10^{20.0} \times (0.48)^2} = 4 \times 10^{-22} \text{ M}
\]

### Question
A solution is prepared by dissolving \( \text{Zn(NO}_3)_2 \) (0.10 mol) and ammonia (3.00 mol) in water and making 1.00 L of solution.

Calculate the equilibrium concentration of \( \text{Zn}^{2+} \) (aq) given \( K_{\text{stab}} [\text{Zn(NH}_3)_4^{2+}] = 1 \times 10^9 \text{ M}^{-4} \).

\[
K_{\text{stab}} = \frac{[\text{Zn(NH}_3)_4^{2+}]}{[\text{Zn}^{2+}][\text{NH}_3]^4} = 1 \times 10^9
\]

\[
[\text{Zn}]^{2+} = \frac{[\text{Zn(NH}_3)_4^{2+}]}{1 \times 10^9[\text{NH}_3]^4} = \frac{0.1}{45.7 \times 10^7} = 2.2 \times 10^{11} \text{ M}
\]

### Biologically Important Complexes
We have already had haemoglobin (Fe\(^{2+}\)) and chlorophyll (Mg\(^{2+}\)).

Also:
- Zinc – many enzymes including carbonic anhydrase, carboxypeptidase A, alcohol dehydrogenase
- Cobalt – xylose isomerase, cobalamin (vitamin B\(_{12}\))
- Manganese, Chromium, Vanadium...
Biologically Important Complexes

**Purple Acid Phosphatase**

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**Nomenclature**

- Name cation, then anion, as separate words
- Ligands, then metal, in same word
- Number of ligands as Greek prefixes (di-, tri-, tetra-, penta-, hexa-)
- Oxidation state in Roman numeral in parentheses after name of metal
  - e.g. $\text{[Ag(NH}_3\text{)}_2\text{]}(\text{NO}_3\text{)}$  diamminesilver(I) nitrate
- Anionic ligands end in "-o"; e.g. chloro, hydroxo, harpo
- Neutral ligands named as molecule, except $\text{H}_2\text{O}$ (aqua), $\text{NH}_3$ (ammine), CO (carbonyl) and NO (nitrosoy)

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**Examples:**

- $\text{[Co(H}_2\text{O)}_6\text{]}\text{CO}_3\text{}$  hexaaquacobalt(II) carbonate
- $\text{[Cu(NH}_3\text{)}_3\text{]}\text{SO}_4\text{}$  tetraamminecopper(II) sulfate
- $\text{(NH}_4\text{)}_3\text{[FeF}_6\text{]}$  ammonium hexafluoroferrate(III)
- $\text{K}_4\text{[Mn(CN)}_6\text{]}$  potassium hexacyanomanganate(II)
- $\text{[Co(en)}_2\text{Cl}_3\text{]}\text{NO}_3\text{}$  dichlorobis(ethylenediamine)cobalt (III) nitrate

---

**Nomenclature (pp.1016-1017 Silberberg)**

- Ligands named in alphabetical order
  - e.g. $\text{[Co(NH}_3\text{)}_5\text{Cl}(\text{SO}_4\text{)}$  pentaamminechlorocobalt(III) sulfate
- Anionic complexes end in "-ate"
  - e.g. $\text{K}_3\text{[CrCl}_6\text{]}$  potassium hexachlorochromate(III)
- Some metals in anionic complexes use Latinate names:
  - Fe (ferrate), Cu (cuprate), Ag (argentate), Pb (plumbate, Au (aureate), Sn (stannate)
- Complex ligands require Latin prefixes bis, tris, ...
  - e.g. bis(ethylenediamine) for $(\text{en)}_2$
Name:

- $K_2[CoCl_4]$  
- $[Cu(NH_3)_2Cl_2]$  
- $[Ag(NH_3)_2]^+$  
- $[Fe(H_2O)_3]Cl_3$

Not on exam...

- Incoming ligands avoid electrons
- Ligand: d-orbital repulsion
- Half-filled orbitals repel more than filled orbitals
- Big, electron rich ligands repelled more than little ones...

**d Orbitals in an Octahedral Field of Ligands**

- Fig. 23.17

**Splitting of d-Orbital Energies by an Octahedral Field of Ligands**

- Fig. 23.18
Hybrid Orbitals and Bonding in the Octahedral $[\text{Cr(NH}_3)_6]^{3+}$ Ion

- unpaired electrons in $d_{xy}$, $d_{xz}$, $d_{yz}$ orbitals → ligands approach along $d_{z^2}$, $d_{x^2-y^2}$ axes...

Fig. 23.13

Hybrid Orbitals and Bonding in the Square Planar $[\text{Ni(CN)}_4]^{2-}$ Ion

- unpaired electrons on $d_{z^2}$, $d_{x^2-y^2}$ axes
- ligands approach along $x$-$y$ plane
- $d_{z^2}$ becomes less favourable;
- $d_{z^2}$ becomes more - electrons pair up in $d_{z^2}$ orbital...

But what do you really need to know?

- $K_{\text{stab}}$ calculations
- The types of isomerism
- Coordination number and geometry, and what metal usually has what coordination number
- How to name coordination compounds
- How inorganic chemists can weasel their way into Biochemistry departments