The textbook for this course is:
The figures used in these notes are reproduced from that text, except where otherwise noted.

Recap - Oxidation Numbers
- The concept of oxidation number is artificial. In assigning oxidation number to an element in a compound it is assumed that all compounds are ionic.

**USE OF OXIDATION NUMBERS**
- Naming compounds
- Properties of compounds
- Identifying redox reactions

- Oxidation involves an increase in oxidation number
- Reduction involves a decrease in oxidation number

Oxidation Numbers (States)
- O.N. is a measure of how oxidised a species is.
- O.N. is the charge the atom would have if electrons were not shared but were transferred completely.
  - Elements: Oxidation number is zero (0)
    - Ar, N₂, Fe
  - Monatomic ions: Oxidation number is charge
    - Na⁺(I), Ca²⁺(II), Cl⁻(-I), O²⁻(-II)
  - Molecules and polyatomic ions: Shared electrons are assigned to the more electronegative atom

Electronegativity
- **Definition:** Attraction of atom for shared electrons in a bond
- Related to ionization energy:
  - Energy required to remove electron from atom
- Ionization energy depends inversely on atomic size
- Atomic size: increases down group (e’s in outer shells) decreases across period (e’s in same shell)
- Electronegativity: arbitrary units 0.7 to 4.0
  - smallest at lower left Periodic Table - Cs cesium
  - greatest at upper right - F fluorine
**Electronegativity**

Atomic size (spheres) and electronegativity (bars)

---

**Electronegativity (0-4)**

---

**Oxidation Numbers**

- Molecules and polyatomic ions: Shared electrons are assigned to more electronegative atom

- Examples:
  - HF: F\(^{-1}\) H\(^{+1}\)
  - CF\(_4\): F\(^{-1}\) C\(^{+IV}\)
  - CO\(_2\): O\(^{-II}\) C\(^{-IV}\)
  - CH\(_4\): H\(^{+I}\) C\(^{-IV}\)
  - NO\(_3\)^-: -1 charge on anion
    
    \[ = 3 \times O^{-II} + N^{V} \]

---

**Rules: Oxidation numbers (states)**

- The O.N. of an atom in its elemental form is 0;
- The O.N. of a monoatomic ion is its charge;
- The O.N. of F is always -1 (except in F\(_2\));
- The O.N. of Group 1 elements is always +1;
- The O.N. of Group 2 elements is always +2;
- The O.N. of O is usually -2, except in peroxides where it is -1;
- The O.N. of halogens is usually -1;
- The O.N. of H is +1 with non-metals and -1 with metals.

The oxidation numbers for all atoms must add up to the total charge on the molecule/ion.
Oxidation Number Questions

What is the oxidation number of Cr in the following?

\[ \text{CrO}_3 \]

\[ x + 3(-2) = 0, \quad x = +6, \quad \text{Cr(VI)} \]

\[ \text{Cr}_2\text{O}_3 \]

\[ 2(x) + 3(-2) = 0, \quad x = +3, \quad \text{Cr(III)} \]

\[ [\text{Cr}_2\text{O}_7]^{2-} \]

\[ 2(x) + 7(-2) = -2, \quad x = +6, \quad \text{Cr(VI)} \]

Why is the oxidation number important?
Naming compounds, properties of the compound, identifying redox reactions.

Transition Metals

Transition elements - \textit{d} orbitals being filled
Concentrate on First Row (Period 4) - 3\textit{d} orbitals being filled

Filling of Atomic Orbitals

Order for filling with electrons:

In general, the \((n-1)d\) orbitals are filled between the \(ns\) and \(np\) orbitals.
**Transition Metals**

- Large numbers of valence electrons
  
  ⇒ Commonly have multiple oxidation states.

![Transition Metals - Ion Formation](Slide 22-14)

**Transition Metals - Ion Formation**

Consider the Period 4 Transition Metals: as the d orbitals fill, the 3d orbital becomes more stable than the 4s.

∴ the 4s electrons are lost before the 3d electrons to form the Period 4 transition metal ions.

\[
\text{Fe} = \quad [\text{Ar}] \quad \uparrow \downarrow \quad \uparrow \uparrow \uparrow \uparrow \uparrow \\
\text{Fe}^{2+} = \quad [\text{Ar}] \quad \uparrow \downarrow \quad \uparrow \uparrow \uparrow \uparrow \\
\text{Fe}^{3+} + e^- = \quad [\text{Ar}] \quad \uparrow \downarrow \quad \uparrow \uparrow \uparrow \uparrow \\
\]

The 4s orbital and the 3d orbitals have very similar energies ⇒ variable oxidation states.
One of the most characteristic chemical properties of these elements is the occurrence of multiple oxidation states.

**Hexavalent Chromium**
- Cr(VI) is classified as "Carcinogenic to Humans"
- Cr(VI) compounds are soluble in water & may have a harmful effect on the environment.
- Cr(VI) is readily reduced by Fe²⁺ and dissolved sulfides.

**Trivalent Chromium**
- Cr(III) is considered an essential nutrient
- Most naturally occurring Cr(III) compounds are insoluble and it is generally believed that Cr(III) does not constitute a danger to health
- Cr(III) is rapidly oxidised by excess MnO₂, or slowly by O₂ in alkaline solutions.

**Properties of N-compounds**

**HIGHLY VARIED!**

**Incredibly stable:**  
N₂

**Extremely explosive:**  
trinitrotoluene (TNT)

**Strong acid:**  
HNO₃

**Weak base:**  
NH₃

**Photochemical smog:**  
NO₂

**Biologically important:**  
NO + amino acids

**Nitroglycerine**
Properties of N-compounds

Why such a wide range of properties...?

A: N has an intermediate electronegativity and has an odd number (5) of valence electrons. N has one of the widest ranges of common oxidation states of any element.

Oxidation states of N

<table>
<thead>
<tr>
<th>Oxidation No.</th>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>HNO₃ / NO₃⁻</td>
<td>Strong acid</td>
</tr>
<tr>
<td>IV</td>
<td>NO₂, N₂O₄</td>
<td>Smog</td>
</tr>
<tr>
<td>III</td>
<td>HNO₂ / NO₂⁻</td>
<td>Weak acid / weak base</td>
</tr>
<tr>
<td>II</td>
<td>NO</td>
<td>Smog + biology</td>
</tr>
<tr>
<td>I</td>
<td>N₂O</td>
<td>Greenhouse gas + laughing gas</td>
</tr>
<tr>
<td>0</td>
<td>N₂</td>
<td>Stable</td>
</tr>
<tr>
<td>−I</td>
<td>NH₂OH</td>
<td>Hydrazine, rocket fuel</td>
</tr>
<tr>
<td>−II</td>
<td>N₂H₄</td>
<td></td>
</tr>
<tr>
<td>−III</td>
<td>NH₃ / NH₄⁺</td>
<td>Weak base / weak acid</td>
</tr>
</tbody>
</table>

Oxides of nitrogen

<table>
<thead>
<tr>
<th>Oxidation No.</th>
<th>Compound</th>
<th>Free radicals</th>
</tr>
</thead>
<tbody>
<tr>
<td>+1</td>
<td>Nitrous oxide</td>
<td></td>
</tr>
<tr>
<td>(0,+2)</td>
<td>Nitric oxide</td>
<td></td>
</tr>
<tr>
<td>+2</td>
<td>Nitrogen dioxide</td>
<td></td>
</tr>
<tr>
<td>+4</td>
<td>Nitrate radical</td>
<td></td>
</tr>
<tr>
<td>+5</td>
<td>Nitrate radical</td>
<td></td>
</tr>
</tbody>
</table>

Work out the oxidation numbers of N in each compound...
**Oxides of nitrogen**

- **NO** (Nitric oxide)
- **NO₂** (Nitrogen dioxide)

= NOₓ... a principle component of photochemical smog

- Colourless gas
- Brown gas
- Free radical
- Free radical

**Air pollution**

- The brown haze is largely NO₂

**Assigning oxidation numbers**

- **Examples**
  - I₂
    - ON=0 (elemental form)
  - Zn in ZnCl₂
    - ON=+2 (Cl=-1, sum of ONs =0)
  - Al³⁺
    - ON=+3 (ON of monatomic ion=charge)
  - N in HNO₃
    - ON=+5 (O=-2, H=+1, sum of ONs=0)
  - S in SO₄²⁻
    - ON=+6 (O=-2, sum of ONs=charge on ion)

- **Examples**
  - N in NH₃
    - ON=-3 (H=+1, sum of ONs = 0)
  - N in NH₄⁺
    - ON=-3 (H=+1, sum of ONs =charge on ion)
**Solubility and complexes**
Silberberg  19.4, 23.1, 23.4

The textbook for this course is:
The figures used in these notes are reproduced from that text, except where otherwise noted.

- Q and $K_{sp}$ revision
- Complex ions and coordination compounds
- Chelates
- Geometry of complexes
- Biologically important metal complexes
- $K_{stab}$

**Slide 23-1**

**Q vs $K_{sp}$ revision**

Does a precipitate form if equal volumes of $2 \times 10^{-5}$ M HCl and $2 \times 10^{-5}$ M AgNO$_3$ solutions are mixed?

$[Ag^+] = 0.00002$ M

$K_{sp} = 1.6 \times 10^{-10}$ M$^2$

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

$\therefore$ AgCl(s) does not precipitate.

**Slide 23-2**

**Predicting precipitation**

Superaturated solution $Q > K_{sp}$

Product of ions in solution is greater than solution can "handle"

Some ions precipitate out to reduce the difference between $Q$ and $K_{sp}$

Solution and precipitate at equilibrium $Q = K_{sp}$

**Slide 23-3**

**Hyrolysis of Metal Ions**

When a metal ion enters water, a complex ion forms with water as the ligand.

- Metal ions act as Lewis acids.
- Water is the Lewis base.

$[M(H_2O)_4]^{2+}(aq)$

**Slide 23-4**
Metal ions add ligands one at a time.

The stepwise exchange of NH₃ for H₂O in M(H₂O)₄²⁺.

- M(H₂O)₄²⁺ + NH₃ → M(H₂O)₃(NH₃)²⁺ + H₂O
- M(H₂O)₃(NH₃)²⁺ + NH₃ → M(H₂O)₂(NH₃)₃⁺ + H₂O
- M(H₂O)₂(NH₃)₃⁺ + NH₃ → M(NH₃)₄⁺

Acidity of Aqueous Transition Metal Ions

Eg [Fe^{II}(OH₂)₆]²⁺ + H₂O ⇌ [Fe^{II}(OH₂)₅(OH)]⁺ + H₃O⁺

Metal Ion Hydrolysis

<table>
<thead>
<tr>
<th>Free Ion</th>
<th>Hydrated Ion</th>
<th>Kₐ</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe³⁺</td>
<td>Fe(H₂O)₆³⁺(aq)</td>
<td>6 x 10⁻³</td>
</tr>
<tr>
<td>Cr³⁺</td>
<td>Cr(H₂O)₆³⁺(aq)</td>
<td>1 x 10⁻⁴</td>
</tr>
<tr>
<td>Al³⁺</td>
<td>Al(H₂O)₆³⁺(aq)</td>
<td>1 x 10⁻⁴</td>
</tr>
<tr>
<td>Be²⁺</td>
<td>Be(H₂O)₄²⁺(aq)</td>
<td>4 x 10⁻⁴</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>Cu(H₂O)₆²⁺(aq)</td>
<td>3 x 10⁻⁸</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>Fe(H₂O)₆²⁺(aq)</td>
<td>4 x 10⁻⁹</td>
</tr>
<tr>
<td>Pb⁴⁺</td>
<td>Pb(H₂O)₆²⁺(aq)</td>
<td>3 x 10⁻⁹</td>
</tr>
<tr>
<td>Zn²⁺</td>
<td>Zn(H₂O)₆²⁺(aq)</td>
<td>1 x 10⁻⁹</td>
</tr>
<tr>
<td>Co²⁺</td>
<td>Co(H₂O)₆²⁺(aq)</td>
<td>2 x 10⁻¹⁰</td>
</tr>
<tr>
<td>Ni²⁺</td>
<td>Ni(H₂O)₆²⁺(aq)</td>
<td>1 x 10⁻¹⁰</td>
</tr>
</tbody>
</table>

Complex Ions

Reaction of a metal ion (Lewis acid) with anions or molecules (Lewis base) forms a complex ion

e.g. Ag⁺(aq) + 2 NH₃ ⇌ Ag(NH₃)₂⁺(aq)

- A complex ion is a chemical species whose components are capable of separate existence:
  - e.g. Ag(NH₃)₂⁺ distinct from Ag⁺ and NH₃, (not CO₃²⁻ because O²⁻ and C⁴⁺ do not exist independently)
The Coordination Bond

- A **ligand** donates an electron pair towards the metal ion to form a **coordinate covalent (also “Dative”) bond**.
- The lone pair is attracted towards the metal ion.
- Ligands must have at least one lone pair.
- More than one ligand can bind to a metal ion.

Complex Ions

- Metals are usually transition metals or Al$^{3+}$ (also Mg$^{2+}$ in chlorophyll).
- Ligands have at least one atom with a lone pair: e.g. H$_2$O, NH$_3$, Cl$^-$, CN$^-$.

Coordination Compounds

Coordination compounds consist of:
- **Complex ion** (metal ion with attached ligands)
- **Counter ions** (additional anions/cations needed to give no net overall charge)

Eg. [Co(NH$_3$)$_6$]Cl$_3$ (s) $\rightleftharpoons$ [Co(NH$_3$)$_6$]$^{3+}$ (aq) + 3 Cl$^-$ (aq)

The square brackets indicate the complex ion and the three Cl$^-$ ions are the counter ions. There are 6 NH$_3$ ligands. When dissolved in water, the complex exists as the cation and the 3 Cl$^-$ ions are separate.

Coordination Number

- The number of ligand atoms attached to the metal is called the coordination number.
  - Varies from 2 to 8 and depends on the size, charge and electron configuration of the metal ion.

Typical coordination numbers for some metal ions.

<table>
<thead>
<tr>
<th>$\text{Metal}$</th>
<th>Coord no.</th>
<th>$\text{Metal}$</th>
<th>Coord no.</th>
<th>$\text{Metal}$</th>
<th>Coord no.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu$^+$</td>
<td>2,4</td>
<td>Mn$^{2+}$</td>
<td>4,6</td>
<td>Sc$^{3+}$</td>
<td>6</td>
</tr>
<tr>
<td>Ag$^+$</td>
<td>2</td>
<td>Fe$^{2+}$</td>
<td>6</td>
<td>Cr$^{3+}$</td>
<td>6</td>
</tr>
<tr>
<td>Au$^+$</td>
<td>2,4</td>
<td>Co$^{2+}$</td>
<td>4,6</td>
<td>Co$^{3+}$</td>
<td>6</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>4,6</td>
<td>Ni$^{2+}$</td>
<td>4,6</td>
<td>Au$^{3+}$</td>
<td>4</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>4,6</td>
<td>Zn$^{2+}$</td>
<td>4,6</td>
<td>Me$^{2+}$</td>
<td>4</td>
</tr>
</tbody>
</table>
**Coordination Number and Geometry**

- The number of ligand atoms 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</td>
</tr>
<tr>
<td>4</td>
<td>PLANAR</td>
<td>electronic cause</td>
</tr>
<tr>
<td>4</td>
<td>TETRAHEDRAL</td>
<td>common</td>
</tr>
<tr>
<td>6</td>
<td>OCTAHEDRAL</td>
<td>common</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** (GREEK: claw)
  - **Monodentate** ligands (denta - tooth) can form 1 bond
    - e.g. $\text{H}_2\text{O}$, $\text{NH}_3$, $\text{Cl}^-$
  - **Bidentate** ligands can form 2 bonds
    - e.g. ethylenediamine (en)
  - **Polydentate** ligands - can form more than 2 bonds
    - some as many as 6

  - e.g. EDTA - ethylenediamminetetraacetate (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.

**Examples of ligands**

Table 23.7: Some Common Ligands in Coordination Compounds

<table>
<thead>
<tr>
<th>Ligand Type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monodentate</td>
<td>$\text{H}_2\text{O}$, water $\text{NH}_3$, ammonia $\text{Cl}^-$, fluoride ion</td>
</tr>
<tr>
<td>Bidentate</td>
<td>$\text{H}_2\text{N}$, ethylenediamine (en) $\text{CO}_3^{2-}$, carbonate ion</td>
</tr>
<tr>
<td>Polydentate</td>
<td>$\text{H}_2\text{N}$, ethylenediamine $\text{PO}_4^{3-}$, phosphate ion $\text{C}_6\text{H}_5\text{O}_7^{2-}$, ethylenediaminetetraacetate (EDTA)</td>
</tr>
</tbody>
</table>

**Examples of ligands in complex ions**

- $[\text{Fe(H}_2\text{O)}_6]^{3+}$
- $[\text{Fe(en)}_3]^{3+}$
- $[\text{Fe(EDTA)}]$
Some chelate ligands

**Bidentate**

ethylenediamine (en)

\[
\begin{align*}
\text{M}^{x+} & : \quad \text{H}_2\text{N} & \text{NH}_2 \\
\text{H}_2\text{N} & : \quad \text{H}_2\text{C} & \text{CH}_2 \\
\end{align*}
\]

\[\text{[Co(en)_3]}^{3+}\]

- Can encapsulate a single metal ion.

EDTA is used to treat severe lead poisoning.

Some chelate ligands

**Hexadentate**

ethylenediaminetetraacetate tetraanion (EDTA\(^4-\))

\[
\begin{align*}
\text{O} & : \quad \text{O} & \text{O} & \text{O} & \text{O} \\
\end{align*}
\]

1597 Libavius publishes first scientific observation of a coordination compound - the blue colour (due to [Cu(NH₃)₂]⁺) formed when lime water containing ammonium chloride comes into contact with brass.

\[\text{[Cu(EDTA)]}^{2-}\]
**Biochemically Important Complexes**

**Heme**
- Carries oxygen in blood
- Gives blood its red colour

**Biologically Important Complexes**

**Chlorophyll**

**Vitamin B₁₂**

Dorothy Crowfoot Hodgkin
The Nobel Prize in Chemistry 1964

**Biologically Important Complexes**

**Carbonic anhydrase**

\[ \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \rightarrow \text{H}_3\text{O}^+\text{(aq)} + \text{HCO}_3^-\text{(aq)} \]
Equilibria involving complexes

Metal ions add ligands one at a time
The metal ions in solution are in equilibrium.

\[ \text{M(H}_2\text{O)}_4^{2+} \rightarrow \text{M(H}_2\text{O)}_3(\text{NH}_3)^2+ \rightarrow \text{M(NH}_3)_4^{2+} \]

\[ \text{NH}_3 \rightarrow 3\text{NH}_3 \]

The stepwise exchange of \text{NH}_3 for \text{H}_2\text{O} in \text{M(H}_2\text{O)}_4^{2+}.

Equilibrium Constant \( K_{\text{stab}} \)

An equilibrium constant can be assigned to the equilibrium process, known as the stability constant, \( K_{\text{stab}} \).

Overall:

\[ [\text{M(OH}_2)_4]^{2+}_{(aq)} + 4 \text{NH}_3(aq) \leftrightarrow [\text{M(NH}_3)_4]^{2+}_{(aq)} + 4 \text{H}_2\text{O} \]

\[ K_{\text{stab}} = \frac{[\text{M(NH}_3)_4]^{2+}}{[\text{M(OH}_2)_4]^{2+}} \times [\text{NH}_3]^4 \]

\( K_{\text{stab}} \) = stability constant or formation constant. The larger \( K_{\text{stab}} \), the more stable the complex.

\( K_{\text{stab}} \) = metal ion + ligand \( \rightarrow \) complex

\[ \text{Ag}^{+}_{(aq)} + \text{NH}_3(aq) \leftrightarrow \text{Ag(NH}_3)^+_{(aq)} \quad K_1 = 2.1 \times 10^3 \]

\[ \text{Ag(NH}_3)^+_{(aq)} + \text{NH}_3(aq) \leftrightarrow \text{Ag(NH}_3)_2^{+}\text{aq}} \quad K_2 = 8.2 \times 10^3 \]

\[ K_{\text{stab}} = K_1 \times K_2 = \frac{[\text{Ag(NH}_3)_2^+]_{(aq)}}{[\text{Ag}^+]_{(aq)} \times [\text{NH}_3]^2} \]

Metal ion \( aq \) + \( n \) ligand \( aq \) \( \leftrightarrow \) complex \( aq \)
**Stepwise Complex Formation**

Overall:
\[
[Ni(H_2O)_6]^{2+} + 3en \rightleftharpoons [Ni(en)_3]^{2+} + 6H_2O
\]

\[
K_{stab} = \frac{[[Ni(en)_3]^{2+}]}{[[Ni(H_2O)_6]^{2+}][en]^3} = 10^{18.28}
\]

Green

\[
[Ni(H_2O)_6]^{2+} + en \rightleftharpoons [Ni(en)(H_2O)_4]^{2+} + 2H_2O
\]

\[K_1\]

blue-green

light blue

\[
[Ni(en)(H_2O)_4]^{2+} + en \rightleftharpoons [Ni(en)_2(H_2O)_2]^{2+} + 2H_2O
\]

\[K_2\]

purple

\[
[Ni(en)_2(H_2O)_2]^{2+} + en \rightleftharpoons [Ni(en)_3]^{2+} + 2H_2O
\]

\[K_3\]

\[
K_{stab} = K_1 \times K_2 \times K_3 = 10^{18.28}
\]

**Example:** A solution is prepared by dissolving AgNO_3 (0.01 mol) in a 1.00 M water solution of KCN (500 mL) and adding enough water to make 1.00 L of solution. Calculate the equilibrium [Ag^+] given \( K_{stab} [Ag(CN)_2]^- = 10^{20} \text{ M}^{-2} \).

(Example: A solution is prepared by dissolving AgNO_3 (0.01 mol) in a 1.00 M water solution of KCN (500 mL) and adding enough water to make 1.00 L of solution. Calculate the equilibrium [Ag^+] given \( K_{stab} [Ag(CN)_2]^- = 10^{20} \text{ M}^{-2} \).

EKIAS
(careful with the direction of the equation represented by \( K_{stab} \)!)
Complexes

• Recap
• Solubility and complexes
• Isomers
• Nomenclature

Silberberg 19.4, 23.1, 23.4

Recap

• Unit conversions
• \( K_{sp} \)
• Working out solubility from \( K_{sp} \) and vice versa
• Predicting precipitation: \( Q \) vs \( K_{sp} \)
• Things that affect solubility for the same \( K_{sp} \):
  • common ion effect
  • pH
  • and...

Recap: Last Lecture

• Complexes are...
• Ligands
• Coordination number and geometry
• Biologically important complexes
• \( K_{stab} \)

Recap: Colours of Transition Metals

For a given ligand, the colour depends on the oxidation state of the metal ion.

\[
\begin{align*}
[\text{V(H}_2\text{O)}_6]^{2+} & \quad & [\text{V(H}_2\text{O)}_6]^{3+} \\
[\text{Cr(NH}_3)_6]^{3+} & \quad & [\text{Cr(NH}_3)_5\text{Cl}]^{3+}
\end{align*}
\]

For a given metal ion, the colour depends on the ligand.
Why are we doing complexes together with solubility?

- Example: \( \text{AgBr}_\text{(s)} \rightarrow \text{Ag}^+\text{(aq)} + \text{Br}^-\text{(aq)} \)

- Calculate the solubility of \( \text{AgBr} \) in:
  - a) water
  - b) 0.1M sodium thiosulfate (\( \text{Na}_2\text{S}_2\text{O}_3 \))

\[ \text{AgBr} \ K_{sp} = 5.0 \times 10^{-13}, \quad \text{Ag}(\text{S}_2\text{O}_3)^3^- \ K_{stab} = 4.7 \times 10^{13} \]

Solubility of \( \text{AgBr} \) in water

- a) water
  \[ \text{AgBr}_\text{(s)} \rightarrow \text{Ag}^+\text{(aq)} + \text{Br}^-\text{(aq)} \]
  \[ K_{sp} = [\text{Ag}^+][\text{Br}^-] \]
  \[ = x \times x \]
  (every \( x \) moles of \( \text{AgBr} \) produces \( x \) moles of \( \text{Ag}^+ \) and \( x \) moles of \( \text{Br}^- \))
  \[ K_{sp} = x^2 = 5.0 \times 10^{-13} \]
  \[ x = 7.07 \times 10^{-7} \text{ M} \]
- Solubility = 7.1 \( \times 10^{-7} \) M

Solubility of \( \text{AgBr} \) in “hypo”

- b) 0.1 M \( \text{Na}_2\text{S}_2\text{O}_3 \)

\[ \text{AgBr}_\text{(s)} + 2\text{S}_2\text{O}_3^{2-}_\text{(aq)} \rightarrow \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}_\text{(aq)} + \text{Br}^-\text{(aq)} \]

\[ K_{overall} = K_{sp} \times K_{stab} = 5.0 \times 10^{-13} \times 4.7 \times 10^{13} = 24 \]

Solubility of \( \text{AgBr} \) in “hypo”

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\[ \text{AgBr}_\text{(s)} + 2\text{S}_2\text{O}_3^{2-}_\text{(aq)} \rightarrow \text{Ag}(\text{S}_2\text{O}_3)_2^{3-}_\text{(aq)} + \text{Br}^-\text{(aq)} \]

I

\[ \begin{array}{ccc}
\text{0.1M} & \text{0} & \text{0} \\
\text{-2x} & +x & +x \\
\text{0.1-2x} & x & x
\end{array} \]

Assume: in this case not nec.

\[ K_{overall} = x^2/(0.1-2x)^2 = 24 \]

Substitute:
\[ x/(0.1-2x) = 4.9 \]
\[ x = 0.45 \]

Check: in this case not nec.

Solubility of \( \text{AgBr} \) in hypo is 0.45 M (cf in water 7.1 \( \times 10^{-7} \) M)
Complex Formation and Solubility

- Metal complex formation can influence the apparent solubility of a compound.

  - eg AgCl(s) + 2 NH₃ ⇌ [Ag(NH₃)₂]⁺ + Cl⁻

- This occurs in 2 stages:
  1. AgCl(s) ⇌ Ag⁺ + Cl⁻
  2. Ag⁺ + 2 NH₃ ⇌ [Ag(NH₃)₂]⁺

Complex formation (reaction 2) removes the free Ag⁺ from solution and so drives the dissolution of AgCl (reaction 1) forward.

A ligand increases the solubility of a slightly soluble ionic compound if it forms a complex ion with the cation.

---

Types of Isomerism in Complexes

- **Structural Isomers**: different atom connectivities
  - Coordination sphere isomerism
  - Linkage isomerism

- **Stereoisomers**: same atom connectivities but different arrangement of atoms in space
  - Geometric isomerism
  - Optical isomerism
Isomers

• **Coordination isomerism**
  (which ligands are in coordination sphere and which outside)

Example:

\[
\text{[Pt(NH}_3\text{)}_4\text{Cl}_2\text{]}(\text{NO}_2\text{)}_2
\]

\[
\text{tetraamminedichloroplatinum(IV) nitrite}
\]

\[
\text{[Pt(NH}_3\text{)}_4\text{(NO}_2\text{)}_2\text{]}\text{Cl}_2
\]

\[
\text{tetraamminedinitroplatinum(IV) chloride}
\]

Isomers

• **Linkage isomerism**
  (occurs when a ligand has two alternative donor atoms)

Example: Thiocyanate ion

\[
\text{[S}=\text{C}=\text{N]}^{\text{-}}
\]

\[
\begin{array}{c}
\text{H}_3\text{N} \\
\text{N} \\
\text{H}_3\text{N} \\
\text{NH}_3 \\
\text{NH}_3 \\
\text{NH}_3
\end{array}
\text{and}
\begin{array}{c}
\text{H}_3\text{N} \\
\text{N} \\
\text{H}_3\text{N} \\
\text{NH}_3 \\
\text{NH}_3 \\
\text{S}=\text{C}=\text{N}
\end{array}
\]

Isomers

• **Geometric Isomerism**
  (occurs when a ligand has two alternative donor atoms)

Example 2: NO\text{}_2^-

\[
\text{[Pt(NH}_3\text{)}_2\text{Cl}_2\text{]}
\]

\[
\text{cis- and trans-}
\]

\[
\text{[Co(NH}_3\text{)}_4\text{Cl}_2\text{]}^{\text{+}}
\]

\[
\text{cis- and trans-}
\]

\[
\text{cis-}
\]

\[
\text{trans-}
\]

\[
\text{Square planar}
\]

\[
\text{Octahedral}
\]

\[
\text{cis-}
\]

\[
\text{trans-}
\]

\[
\text{cis-}
\]

\[
\text{trans-}
\]
Isomers

• Optical Isomerism

\[ \text{[NiClBrFI]}^2- \]

Four different substituents about tetrahedral centre.
Non-superimposable on its mirror image.
The two molecules are optical isomers.

Slide 24-17

Isomers

• Optical Isomerism

compare \( \text{cis-[Cr(NH}_3)_4\text{Cl}_2]^+ \) and \( \text{cis-[Cr(en)_2Cl}_2]^+ \)

\[ [\text{M(en)}_3]^{n+} \text{ complexes have optical isomers:} \]

Not superimposable

Mirror plane

Slide 24-18

Optical isomerism in an octahedral complex ion.

\[ \text{cis-[Co(en)_2Cl}_2]^+ \]
\[ \text{trans-[Co(en)_2Cl}_2]^+ \]

rotation of \( \text{i} \) gives \( \text{III} \neq \text{II} \)
rotation of \( \text{i} \) gives \( \text{III} = \text{II} \)

Slide 24-19

Nomenclature

• Name cation, then anion, as separate words
Example
\[ \text{[Pt(NH}_3)_4\text{Cl}_2](\text{NO}_2)_2 \text{ tetraamminedichloroplatinum(IV) nitrite} \]
\[ \text{[Pt(NH}_3)_4(\text{NO}_2)_2]\text{Cl}_2 \text{ tetraamminedinitroplatinum(IV) chloride} \]

• Ligands, then metal, in same word

• Number of ligands as Greek prefixes
\( \text{(di-, tri-, tetra-, penta-, hexa-)} \)

Slide 24-20
**Nomenclature**

- Oxidation state in Roman numeral in parentheses after name of metal
  - e.g. \([\text{Ag(NH}_3\text{)}_2]\text{NO}_3\) diamminesilver(I) nitrate

- Anionic ligands end in '-o'; e.g. chloro, hydroxo

- Neutral ligands named as molecule, except \(\text{H}_2\text{O}\) (aqua), \(\text{NH}_3\) (ammine), \(\text{CO}\) (carbonyl) and \(\text{NO}\) (nitrosyl)

**Naming Ligands**

<table>
<thead>
<tr>
<th>Name</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>A. Neutral</td>
<td></td>
</tr>
<tr>
<td>Aqua</td>
<td>(\text{H}_2\text{O})</td>
</tr>
<tr>
<td>Ammine</td>
<td>(\text{NH}_3)</td>
</tr>
<tr>
<td>Carbonyl</td>
<td>(\text{CO})</td>
</tr>
<tr>
<td>Nitrosyl</td>
<td>(\text{NO})</td>
</tr>
</tbody>
</table>

- Anionic ligands end in '-o'; e.g. chloro, hydroxo

- Neutral ligands named as molecule, except \(\text{H}_2\text{O}\) (aqua), \(\text{NH}_3\) (ammine), \(\text{CO}\) (carbonyl) and \(\text{NO}\) (nitrosyl)

**Nomenclature (pp.1020-1021 Silberberg)**

- Ligands named in alphabetical order (Note: prefixes do not affect the order)
  - e.g. \([\text{Co(NH}_3\text{)}_5\text{Cl}]\text{SO}_4\) pentaamminechlorocobalt(III) sulfate

- Anionic complexes end in 'ate'
  - e.g. \(\text{K}_3[\text{CrCl}_6]\) potassium hexachlorochromate(III)

- Some metals in anionic complexes use Latin -ate names:
  - Fe (ferrate), Cu (cuprate), Ag (argentate), Pb (plumbate), Au (aureate), Sn (stannate)

- Complex ligands require Latin prefixes \(\text{bis, tris, tetrakis}\ldots\)
  - e.g. \(\text{bis(ethylenediamine)}\) for \((\text{en})_2\)

**Naming Metal Ions**

(a) If the complex is neutral or positively charged the normal metal name is used.

(b) If the complex is negatively charged, 'ate' is added to the metal name.

- e.g. Co cobaltate, Zn zincate, etc.

**Special cases:**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Name in Anion</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>Ferrate</td>
</tr>
<tr>
<td>Copper</td>
<td>Cuprate</td>
</tr>
<tr>
<td>Lead</td>
<td>Plumbate</td>
</tr>
<tr>
<td>Silver</td>
<td>Argentate</td>
</tr>
<tr>
<td>Gold</td>
<td>Aureate</td>
</tr>
<tr>
<td>Tin</td>
<td>Stannate</td>
</tr>
</tbody>
</table>
Nomenclature - Examples

- \([\text{Co(H}_2\text{O)}_6]\text{CO}_3\) hexaaquacobalt(II) carbonate
- \([\text{Cu(NH}_3)_4]\text{SO}_4\) tetraamminecopper(II) sulfate
- \((\text{NH}_4)_3[\text{FeF}_6]\) ammonium hexafluoroferrate(III)
- \(K_4[\text{Mn(CN)}_6]\) potassium hexacyanomanganate(II)

Recap: Assigning oxidation numbers

Example

- Find ON of Co in: \([\text{Co(NH}_3)_5\text{Cl}]\text{SO}_4\) pentaamminechlorocobalt(III) sulfate
  - \([\text{Co(NH}_3)_5\text{Cl}]^{2+}\) ammine is neutral, chloro is -1
  - \(\text{ON} + (5\times0) + -1 = +2\) (sum of ONs=overall charge)
    - \(\text{ON} = +3\)

Example

- Find ON of Mn in: \(K_4[\text{Mn(CN)}_6]\) potassium hexacyanomanganate(II)
  - \([\text{Mn(CN)}_6]^{2-}\) (CN) is -1 overall
  - \(\text{ON} + (6\times-1) = -4\) (sum of ONs=overall charge)
    - \(\text{ON} = +2\)

Complexes

What you need to know:

- See recap slides
- Won’t be asked to draw formulae of complicated biological complexes
- Be able to use the naming rules to write formulae from names and names from formulae