1. Classification of the Elements

<table>
<thead>
<tr>
<th>Elements</th>
<th>Electron Configuration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Noble gases</td>
<td>$ns^2np^6$</td>
</tr>
<tr>
<td></td>
<td>$n = 1 \ldots 6$</td>
</tr>
<tr>
<td>Main groups</td>
<td>$ns^xnp^y$</td>
</tr>
<tr>
<td></td>
<td>$n = 2 \ldots 7$</td>
</tr>
<tr>
<td></td>
<td>$x = 1, 2$</td>
</tr>
<tr>
<td></td>
<td>$y = 0 \ldots 5$</td>
</tr>
<tr>
<td>$\Rightarrow$</td>
<td>$s$- and $p$-block</td>
</tr>
<tr>
<td>Subgroups</td>
<td>$[Ar]4s^23d^x$</td>
</tr>
<tr>
<td>(transition metals)</td>
<td>$[Kr]5s^24d^x$</td>
</tr>
<tr>
<td></td>
<td>$x = 1 \ldots 10$</td>
</tr>
<tr>
<td>$\Rightarrow$</td>
<td>$d$-block</td>
</tr>
<tr>
<td></td>
<td>$[Xe]6s^24f^05d^1$</td>
</tr>
<tr>
<td></td>
<td>La</td>
</tr>
<tr>
<td></td>
<td>$[Xe]6s^24f^{14}5d^x$</td>
</tr>
<tr>
<td></td>
<td>Hf - Hg</td>
</tr>
<tr>
<td>Lanthanides</td>
<td>$[Xe]6s^24f^x5d^1$</td>
</tr>
<tr>
<td></td>
<td>$x = 1 \ldots 14$</td>
</tr>
<tr>
<td>Actinides</td>
<td>$[Rn]7s^25f^x6d^1$</td>
</tr>
<tr>
<td></td>
<td>$x = 1 \ldots 14$</td>
</tr>
<tr>
<td>$\Rightarrow$</td>
<td>$f$-block</td>
</tr>
</tbody>
</table>
1. Classification of the Elements

**Electron Configuration of the 3d-Transition Metals**

<table>
<thead>
<tr>
<th></th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>4s</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>3d</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>5</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

**Electron Configuration of the 4d-Transition Metals**

<table>
<thead>
<tr>
<th></th>
<th>Y</th>
<th>Zr</th>
<th>Nb</th>
<th>Mo</th>
<th>Tc</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Ag</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td>5s</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>4d</td>
<td>1</td>
<td>2</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

**Electron Configuration of the 5d-Transition Metals**

<table>
<thead>
<tr>
<th></th>
<th>La</th>
<th>Hf</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
<th>Au</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td>6s</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>5d</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>9</td>
<td>10</td>
<td>10</td>
</tr>
</tbody>
</table>

⇒ More stable configuration due to lower energetic states of the d-orbitals
## 1. Classification of the Elements

### Electron Configuration of the Lanthanides and Their Cations

#### Metals

<table>
<thead>
<tr>
<th>Metals</th>
<th>[Xe]</th>
<th>La</th>
<th>Ce</th>
<th>Pr</th>
<th>Nd</th>
<th>Pm</th>
<th>Sm</th>
<th>Eu</th>
<th>Gd</th>
<th>Tb</th>
<th>Dy</th>
<th>Ho</th>
<th>Er</th>
<th>Tm</th>
<th>Yb</th>
<th>Lu</th>
</tr>
</thead>
<tbody>
<tr>
<td>6s</td>
<td></td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
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<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>5d</td>
<td></td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
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<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>4f</td>
<td></td>
<td>0</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>5</td>
<td>6</td>
<td>7</td>
<td>7</td>
<td>9</td>
<td>10</td>
<td>11</td>
<td>12</td>
<td>13</td>
<td>14</td>
<td>14</td>
</tr>
</tbody>
</table>

#### Cations

| Cations | [Xe] | La\(^{3+}\) | Ce\(^{3+}\) | Pr\(^{3+}\) | Nd\(^{3+}\) | Pm\(^{3+}\) | Sm\(^{3+}\) | Eu\(^{3+}\) | Gd\(^{3+}\) | Tb\(^{3+}\) | Dy\(^{3+}\) | Ho\(^{3+}\) | Er\(^{3+}\) | Tm\(^{3+}\) | Yb\(^{3+}\) | Lu\(^{3+}\) | Ce\(^{4+}\) | Pr\(^{4+}\) | Nd\(^{4+}\) | Sm\(^{2+}\) | Eu\(^{2+}\) | Dy\(^{4+}\) | Tb\(^{4+}\) |
|---------|------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|------------|----|----|----|----|----|----|----|----|
| 4f      |      | 0          | 1          | 2          | 3          | 4          | 5          | 6          | 7          | 8          | 9          | 10         | 11         | 12         | 13         | 14         | 14         |

#### Examples

- **Gd\(^{3+}\)/Eu\(^{2+}\)/Tb\(^{4+}\)**

<table>
<thead>
<tr>
<th>Examples</th>
<th>(m_1)</th>
<th>-3</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>-2</th>
<th>-1</th>
<th>0</th>
<th>1</th>
<th>2</th>
<th>0</th>
<th>-1</th>
<th>0</th>
<th>1</th>
</tr>
</thead>
</table>

| 4f | ![Diagram](https://example.com/diagram.png) | 5d | ![Diagram](https://example.com/diagram.png) | 6s | ![Diagram](https://example.com/diagram.png) | 6p | ![Diagram](https://example.com/diagram.png) |

**Total spin** \(S = \Sigma s = 7/2\)

\[2S + 1 = 8\]

→ highly paramagnetic ions
2. d-Orbitals

The Five d-Orbitals Can Be Divided into Two Groups: Three Are Positioned Between the Axes of the Cartesian Coordinate System and Two Actually on Them

The d-orbitals are accessible for the formation of chemical bonds
Octet rule → 18-electrons rule
3. Coordinative Bonding

**Ionic Bonding**
Formally speaking, all bonding electrons are transferred to the more electronegative bonding partner

\[ 2 \text{ Na} + \text{Cl}_2 \rightarrow 2 \text{ Na}^+ + 2 \text{ Cl}^- \]

**Covalent Bonding**
2-centres: The bonding electrons are contributed by two bonding partners and are distributed evenly between them
3-centres: The bonding electrons originate from two bonding partners but are distributed between three of them

**Coordinative (Dative) Bonding**
The bonding electrons are donated by a single bonding partner only

\[ Z + |L \rightarrow Z-L \]
The Coordinative (Dative) Bond Is the Product of a Lewis Acid-Base Reaction

\[ \text{BF}_3 + \text{NMe}_3 \rightarrow [\text{Me}_3\text{N-BF}_3] \]

Lewis-acid (acceptor) \hspace{2cm} Lewis-base (donor)

\[ \text{BF}_3 + \text{F}^- \rightarrow [\text{BF}_4]^- \]
4. Complexes

Definition of Complexes

Complexes or coordinative compounds are molecules or ions $\text{CL}_n$, wherein a either uncharged or charged central atom $C$ is surrounded by a number - according to its coordination number - of either charged or uncharged mono- or polyatomic groups $L$.

*lat. complexus = embrace, lat. coordinare = associate*

\[
\begin{array}{c}
L \\
\uparrow \\
C \\
\downarrow \\
L \\
\end{array}
\]

$C = \text{central atom = complex centre, coordination centre}$

$L = \text{ligands, ligand shell, coordination sphere}$

All ligands of the same kind \hspace{1cm} \text{homoleptic complexes} \hspace{1cm} [\text{Ni(CN)}_4]^{2-}$

Different ligands \hspace{1cm} \text{heteroleptic complexes} \hspace{1cm} [\text{MoCl}_4(\text{O})_2]^{2-}$
4. Complexes

Studies of Alfred Werner (Nobel Prize 1913) on Cobalt Compounds

a) CoCl$_3$6NH$_3$ yellow Luteo
b) CoCl$_3$5NH$_3$ red Purpureo
c) CoCl$_3$4NH$_3$ green Praseo
d) CoCl$_3$4NH$_3$ violet Violeo

Gravimmetrical determination of chloride with AgNO$_3$ gives

a) 3 AgCl [Co(NH$_3$)$_6$]$^{3+}$ + 3 Cl$^-$
b) 2 AgCl [Co(NH$_3$)$_5$Cl]$^{2+}$ + 2 Cl$^-$
c, d) 1 AgCl [Co(NH$_3$)$_4$Cl$_2$]$^+$ + 1 Cl$^-$ 2 isomers (cis and trans)

Werner’s deductions:
• Co$^{3+}$ is always 6-coordinate
• Ligands are arranged in octahedra
### 4. Complexes

**Studies upon the Electrical Conductivity $L$ During the Formation of Complexes**

<table>
<thead>
<tr>
<th>Complex</th>
<th>$L$ [S·cm$^2$/mol]</th>
<th>Number of ions per formula unit</th>
<th>Number of Cl$^-$-ions per formula unit</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$</td>
<td>523</td>
<td>5</td>
<td>4</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{NH}_3)_5\text{Cl}]\text{Cl}_3$</td>
<td>404</td>
<td>4</td>
<td>3</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}_2$</td>
<td>228</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{NH}_3)_3\text{Cl}_3]\text{Cl}$</td>
<td>97</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>$[\text{Pt}(\text{NH}_3)_2\text{Cl}_4]$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>$\text{K}[\text{Pt}(\text{NH}_3)\text{Cl}_5]$</td>
<td>108</td>
<td>2</td>
<td>0</td>
</tr>
<tr>
<td>$\text{K}_2[\text{PtCl}_6]$</td>
<td>256</td>
<td>3</td>
<td>0</td>
</tr>
</tbody>
</table>

- The electrical conductivity $L$ of the aqueous solution of the complexes is defined by the amount of dissolved cations and anions per formula unit.
- Neutral complexes do not contribute to the electrical conductivity of a solution.
Construction of a Complexes’ Formula

Rule 1: The cation is always placed in front of the anion and complexes are enclosed between squared brackets, e.g. $K_4[Fe(CN)_6]$.

Rule 2: The central atom is positioned at first position, e.g. $[Fe(CN)_6]^{4-}$, $[PF_6]^{-}$.

Rule 3: Anionic ligands come first before neutral ligands.

Rule 4: Alphabetical ordering within a class of ligands.

Rule 5: Molecular ligands as well as abbreviations are written in brackets.

Rule 6: Oxidation number as superscript behind the central atom, e.g. $[Fe^{II}(CN)_6]^{4-}$, $[Co^{III}(NO_2)_3(NH_3)_3]$, $[Co^{II}Cl_2(en)_2]$.
5. Nomenclature of Coordinative Compounds

Deduction of the Name

Rule 1: Ligands in alphabetical order prior to the name of the central atom (last!) with di, tri, … as prefix for multiple ligands

\[ \text{Co(NH}_3\text{)}_6\text{]}^{3+} \\
\text{Hexaamminecobalt(III)}

Rule 2: Statement of:

a) oxidation number of central atom as Roman cipher in parentheses (e.g. I, II) or 
b) charge of coordinating unit as Arabic cipher + charge (e.g. 3+)

behind the corresponding unit

\[ \text{PtCl}_4\text{]}^{2-} \quad \text{[Ni(CN)}_5\text{]}^{3-} \\
\text{Tetrachloroplatinate(II)} \quad \text{Pentacyanonickelate(3-)}

Anionic complexes end on ate!

Attention! 

Cu: Cuprate  Fe: Ferrate  Pb: Plumbate
Au: Aurate  Sn: Stannate  Ag: Argentate
5. Nomenclature of Coordinative Compounds

Deduction of the Name

Rule 3: **Anionic ligands** which end in “-ide” are replaced with an ending “-o” (bromide→bromo), anions ending with “-ite” and ”-ate” are replaced with endings “-ito” and “-ato”, respectively. Most neutral and formally **cationic ligands** carry their normal name.

There are a few exceptions to the naming of neutral ligands

<table>
<thead>
<tr>
<th>Ligand</th>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ammonia</td>
<td>NH$_3$</td>
<td>ammine</td>
</tr>
<tr>
<td>Carbon monoxide</td>
<td>CO</td>
<td>carbonyl</td>
</tr>
<tr>
<td>Water</td>
<td>H$_2$O</td>
<td>aqua (aquo)</td>
</tr>
<tr>
<td>Nitrogen monoxide</td>
<td>NO</td>
<td>nitrosyl</td>
</tr>
<tr>
<td>Oxygen</td>
<td>O$_2$</td>
<td>oxygenyl</td>
</tr>
</tbody>
</table>
6. Ligands

Regularly Used Ligands

Dentallity of ligands = Number of atoms that bind to the central metal atom
6. Ligands

Monodentate Ligands

THF  
Tetrahydrofuran

Pyridine

NH$_3$  
Ammine

P$_3$  
Trimethylphosphane

dmso  
Dimethylsulphoxide

P$_3$(C$_6$H$_5$)$_3$  
Triphenylphosphane
6. Ligands

Bidentate Ligands

- bpy, 2,2’-Bipyridine
- phen, 1,10-Phenanthroline
- acac, Acetylacetonate
- hfacac, Hexafluoroacetylacetonate
- dppe, Diphenylphosphinoethane
- dmpe, Dimethylphosphinoethane
- en, Ethylene diamine
- tmeda, Tetramethylene diamine
Chelating Ligands

Bidentate ligands are also called chelating ligands (Greek: 
*chele* = claw). Literally, the ligand grabs the metal “in its claws”. If thereby (chelating) rings with five or six members are created, the formation of such complexes is entropically favoured in comparison to the formation of a complex with only monodentate ligands and thus considerably more stable.

⇒ Chelating effect (entropic effect)

![Diagram of chelate rings with different angles](image)

- **60°** ring tension
- **90°** optimal ring size (optimal stability)
- **108°** declining chelating effect
- **120°** declining chelating effect
6. Liganden

Chelating Ligands

The formation of complexes with chelating ligands results in more stable complexes compared to the formation with monodentate ligands

\[\text{[Ni(H}_2\text{O)}_6\text{]}^{2+} + 6 \text{NH}_3 \rightleftharpoons \text{[Ni(NH}_3\text{)}_6\text{]}^{2+} + 6 \text{H}_2\text{O} \quad K_K = 2.0 \cdot 10^9\]

\[\text{[Ni(H}_2\text{O)}_6\text{]}^{2+} + 3 \text{en} \rightleftharpoons \text{[Ni(en)}_3\text{]}^{2+} + 6 \text{H}_2\text{O} \quad K_K = 3.8 \cdot 10^{17}\]

Formation of [Ni(NH\textsubscript{3})\textsubscript{6}]\textsuperscript{2+}-complexes \Rightarrow number of particles remains the same
Formation of [Ni(en)]\textsuperscript{3+}-complexes \Rightarrow number of particles increases \Rightarrow \Delta S^0 > 0

Formation of a complex with a chelating ligand leads to an increase in entropy!

\[\Delta H \text{ is about equal for both cases}\]

\[\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad \text{and} \quad \Delta G^\circ = -RT\ln K_K \quad \text{with} \quad K_K = \text{complex formation constant}\]

\[
(\Delta \Delta G^\circ = 0 - T\Delta \Delta S^\circ )
\]

Formation of [Ni(en)]\textsuperscript{3+} \Rightarrow more negative \( \Delta G^\circ \) \Rightarrow higher \( K_K \)
6. Ligands

Tridentate Ligands

- tacn  
  Triazacyclononan

- terpy  
  2,2',2''-Terpyridin

- Tp  
  Trispyrazolylborate

- Diimin-Pyridin
6. Ligands

Tetradentate Ligands

- **por**
  - Porphyrine

- **salen**
  - Bis(salicylidene)ethylenediamine

- **tren**
  - Triethylenetetramine
6. Ligands

Hexadentate Ligands

EDTA
Ethlenediaminetetraacetate

is an extraordinary good complexing agent

Oral EDTA-Chelation Therapy
This site provides research, articles, and products related to Oral EDTA Chelation therapy; an alternative to conventional treatments for cleansing your arteries and veins of plaque.

What is EDTA Chelation?
EDTA chelation is a therapy by which repeated administrations of a weak synthetic amino acid (EDTA, ethlenediamine tetra-acetic acid) gradually reduce atherosclerotic plaque and other mineral deposits throughout the cardiovascular system by literally dissolving them away.

EDTA, ethlenediamine tetra-acetic acid, chelation has frequently been compared to a "Roto-Rooter®; in the cardiovascular system, because it removes plaque and returns the arterial system to a smooth, healthy, pre-atherosclerotic state. A better metaphor might be "Liquid-Plumr®," because, where Roto-Rooter violently scrapes deposits off the interior surfaces of your plumbing with a rapidly rotating blade, Liquid-Plumr simply dissolves them away.
7. Stability of Complexes

Definition of Complex Stability

Complex equilibria in solution (cleavage of ligands)

\[ [ML_n] \rightleftharpoons [ML_{n-1}] + L \quad K_D \quad \text{with } K_D = \text{dissociation constant, } n = \text{coordination number} \]

Normally, the formation of a complex proceeds step by step

\[ M + L \rightleftharpoons [ML] \quad K_1 \]

\[ [ML] + L \rightleftharpoons [ML_2] \quad K_2 \]

\[ [ML_2] + L \rightleftharpoons [ML_3] \quad K_3 \]

and so on

\[ [ML_{n-1}] + L \rightleftharpoons [ML_n] \quad K_n \]

Total constant of formation \( K_B = \beta_n \)

\[ K_B = \beta_n = \prod_{i=1}^{n} K_i = \frac{c(ML_n)}{c(M) \cdot c(L)^n} \]
Complex Stability Using $[\text{Cd(CN)}_4]^{2-}$ as an Example

Stepwise formation of the complex from Cd$^{2+}$ and CN$^{-}$

$\text{Cd}^{2+} + \text{CN}^{-} \rightleftharpoons [\text{Cd(CN)}]^+$ \hspace{1cm} K_1 = 10^{5.5}$

$[\text{Cd(CN)}]^+ + \text{CN}^{-} \rightleftharpoons [\text{Cd(CN)}_2]^0$ \hspace{1cm} K_2 = 10^{5.2}$

$[\text{Cd(CN)}_2]^0 + \text{CN}^{-} \rightleftharpoons [\text{Cd(CN)}_3]^-$ \hspace{1cm} K_3 = 10^{4.6}$

$[\text{Cd(CN)}_3]^-$ + $\text{CN}^{-} \rightleftharpoons [\text{Cd(CN)}_4]^{2-}$ \hspace{1cm} K_4 = 10^{3.5}$

$\text{Cd}^{2+} + 4 \text{CN}^{-} \rightleftharpoons [\text{Cd(CN)}_4]^{2-}$ \hspace{1cm} K_B (ß_4) = 10^{18.8}$

$\Rightarrow$ Often, the more ligands already bound to the metal centre, the lower the complex formation constant $K_n$ gets!

Explanations for this behaviour

- Sterical hindrance
- Coulomb-effect hinders the addition of more charged ligands, such as CN$^{-}$
- Decrease in entropy, because the systems becomes more ordered, i.e. $\Delta S_r^0 < 0$
7. Stability of Complexes

Thermodynamic and Kinetic Complex Stability

**Thermodynamic Stability** is expressed by the complex formation constant $K_B$ and $\beta$, respectively. The higher this constant, the more stable the complex (unstable – stable).

Free reaction enthalpy $\Delta G_r^0 = -RT \ln K_B$

Example:

\[
[Ni(H_2O)_6]^{2+} + 4 \text{CN}^- \rightleftharpoons k_1 \text{Ni(CN)}_4^{2-} + 6 \text{H}_2\text{O} \quad K_B \approx 10^{29}
\]

The equilibrium is shifted almost completely on the right side, meaning the complex is thermodynamically stable. But still, the ligand exchange proceeds very fast, which means that the kinetic stability is poor (labile – inert).

Free activation enthalpy $\Delta G_r^\neq$

\[
[Ni(CN)_4]^{2-} + 4 ^{14}\text{CN}^- \rightleftharpoons k_1 \text{Ni}^{14}(CN)_4^{2-} + 4 \text{CN}^- \quad \tau_{1/2} = 30 \text{ s (fast)}
\]
7. Stability of Complexes

The Kinetic Complex Stability or the Reactivity of a Complex Is Determined by the Structure of the Complex and the Possible Reaction Pathway

Octahedral complexes

\[
[\text{CrCl}_2(\text{H}_2\text{O})_4]^+ + 2 \text{H}_2\text{O} \xrightleftharpoons[\text{k}_1]{\text{k}_1^{-1}} [\text{Cr(\text{H}_2\text{O})}_6]^{3+} + 2 \text{Cl}^-
\]

⇒ Very slow ligand exchange, although the hexaaquachrom(III) complex is more stable

Square-planar complexes

\[
\begin{align*}
\text{Ni} & \quad \text{CN} \\
\text{CN} & \quad \text{Ni} \\
\text{CN} & \quad \text{CN}
\end{align*}
\]

\[
2^- + ^{14}\text{CN}^- \xrightleftharpoons[\text{k}_1]{\text{k}_1^{-1}} \begin{align*}
\text{Ni} & \quad ^{14}\text{CN} \\
\text{CN} & \quad \text{Ni} \\
\text{CN} & \quad \text{CN}
\end{align*} 3^- \xrightleftharpoons[\text{k}_1]{\text{k}_1^{-1}} \begin{align*}
\text{Ni} & \quad ^{14}\text{CN} \\
\text{CN} & \quad \text{Ni} \\
\text{CN} & \quad \text{CN}
\end{align*} 2^- + \text{CN}^-
\]

⇒ Very fast ligand exchange, although there is no thermodynamic reason for it
7. Stability of Complexes

Dependence of Stability Constants of Metal Complexes

1. Central Atom
\[ \text{Ba}^{2+} < \text{Sr}^{2+} < \text{Ca}^{2+} < \text{Mg}^{2+} < \text{Mn}^{2+} < \text{Fe}^{2+} < \text{Co}^{2+} < \text{Ni}^{2+} < \text{Cu}^{2+} \]

⇒ Correlates with decreasing ionic radius of the cation or increasing ionic charge density, respectively

2. Ligands
   - Chelating effect, macro cyclic effect
   - Polarizability (hard - soft)

Hard and Soft Acids and Bases HSAB Concept (R.G. Pearson 1963)
- Metal atoms = acids (electron acceptors)
- Ligands = bases (electron donators)
- High stability: soft metal atoms – soft ligands
  hard metal atoms - hard ligands
- Low stability: soft metal atoms - hard ligands
  hard metal atoms – soft ligands
7. Stability of Complexes

HSAB Concept: Classification of Metal Atoms (Acids) and Ligands (Bases)

<table>
<thead>
<tr>
<th></th>
<th>Bases</th>
<th>Acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hard</td>
<td>NH₃, R-NH₂, N₂H₄, H₂O, OH⁻, O²⁻, R-OH, RO⁻, R₂O, CO₃²⁻, R-COO⁻, NO₃⁻, PO₄³⁻, SO₄²⁻, ClO₄⁻, F⁻, Cl⁻</td>
<td>H⁺, Li⁺, Na⁺, K⁺, Ba²⁺, Mg²⁺, Ca²⁺, Sr²⁺, Ti⁴⁺, Zr⁴⁺, VO³⁺, Cr³⁺, Cr⁶⁺, Mn²⁺, Mn⁴⁺, Mn⁷⁺, Fe³⁺, Co³⁺, Al³⁺, Ga³⁺, In³⁺</td>
</tr>
<tr>
<td></td>
<td><strong>Electron shell is hard to deform</strong></td>
<td><strong>Strongly polarizing</strong></td>
</tr>
<tr>
<td>In between</td>
<td>N³⁻, N₂, Ph-NH₂, NO₂⁻, Br⁻, C₅H₅N, SO₃²⁻</td>
<td>Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺, Rh³⁺, Ir³⁺, Ru³⁺, Sn²⁺, Pb²⁺</td>
</tr>
<tr>
<td>Soft</td>
<td>H⁻, R⁻, CN⁻, CO, SCN⁻, R₃P, R₂S, RS⁻, S₂O₃⁻, I⁻</td>
<td>Pd²⁺, Pt²⁺, Cu⁺, Ag⁺, Hg⁺, Hg²⁺, Tl⁺, Me⁰</td>
</tr>
<tr>
<td></td>
<td><strong>Electron shell is readily deformed</strong></td>
<td><strong>Weakly polarizing</strong></td>
</tr>
</tbody>
</table>
8. Structures and Isomers

Differentiation: Compounds vs. Isomers

- Same atoms? Yes → Isomers
  - Atoms linked to the same partners? Yes → Stereoisomers
    - Complex identical to its mirror image? Yes → Geometrical isomers
    - Complex identical to its mirror image? No → Optical isomers
  - Atoms linked to the same partners? No → Structural isomers
    - Ionization isomers
    - Hydrate isomers
    - Coordination isomers
    - Linkage isomers

- Same atoms? No → Different compositions
8. Structures and Isomers

Isomers Are Compounds with the Same Molecular Formula but Different Spatial Arrangement of the Atoms

1. Structure or Constitutional Isomers
Connectivity of the atoms differs

![Butane and 2-Methylpropane (isobutane) Structures](image)

2. Stereoisomers
Identical connectivity but different spatial arrangement of the atoms
8. Structures and Isomers

1. Constitutional Isomerism

a) Ionisation isomerism
   - Exists in complex salts where ligands and counter ions can interchange positions
   - Example:
     \[
     [\text{Co(NH}_3\text{)}_5\text{(SO}_4\text{)}]\text{Br} \quad \text{red compound}
     \]
     \[
     [\text{Co(NH}_3\text{)}_5\text{Br}]\text{SO}_4 \quad \text{violet compound}
     \]

b) Hydration isomerism
   - Special case of ionisation isomerism whereby H\text{2}O can either be a ligand or incorporated as water of crystallization
   - Example:
     \[
     [\text{Cr(H}_2\text{O)}_6]\text{Cl}_3
     \]
     \[
     [\text{CrCl(H}_2\text{O)}_5]\text{Cl}_2\cdot\text{H}_2\text{O}
     \]
     \[
     [\text{CrCl}_2(\text{H}_2\text{O)}_4]\text{Cl}_2\cdot\text{H}_2\text{O}
     \]
8. Structures and Isomers

1. Constitutional Isomerism

c) Coordination isomerism

- In salts where cations and anions consist of complexes, ligands can be interchanged between the cations and the anions
- Example:
  \[ \text{[Co(NH}_3\text{)_6]} \text{[Cr(CN)}_6\text{]} \]
  \[ \text{[Cr(NH}_3\text{)_6]} \text{[Co(CN)}_6\text{]} \]

d) Bond or salt isomerism

- Asymmetrical ligands that possess various linking positions, can be coordinated in multiple ways
- Examples:
  - Bonding via C-atom: cyano, via N-atom: isocyano
  - Bonding via S-atom: thiocyanato, via N-atom: isothiocyanato
2. Stereoisomerism

a) cis-trans isomerism

- Occurs in square-planar or octahedral complexes which comprise of two different ligands L and L', so that the bonding angle L-Z-L can be 90° (cis) or 180° (trans)
- Square-planar complexes

\[
\begin{align*}
\text{cis} & : \quad \text{Cl} \quad \text{Ni} \quad \text{NH}_3 \quad \text{Cl} \quad \text{NH}_3 \quad \text{Cl} \\
\text{trans} & : \quad \text{Cl} \quad \text{Ni} \quad \text{NH}_3 \quad \text{Cl} \quad \text{NH}_3 \quad \text{Cl}
\end{align*}
\]

- Octahedral complexes

\[
\begin{align*}
\text{cis} & : \quad \text{Co} \quad \text{Cl} \quad \text{Cl} \quad \text{NH}_3 \quad \text{NH}_3 \quad \text{Cl} \\
\text{trans} & : \quad \text{Co} \quad \text{Cl} \quad \text{Cl} \quad \text{NH}_3 \quad \text{NH}_3 \quad \text{Cl}
\end{align*}
\]
Excursion: cis-Platinum

The Metal Complex cis-Platinum Is Cancerostatic

cis-diamminedichloroplatinum(II) (Peyrone’s salt)

\[
\begin{align*}
\text{Cl} & \quad \text{Pt} & \quad \text{NH}_3 \\
\text{Cl} & \quad \text{NH}_3 & \quad \text{Pt} & \quad \text{NH}_3 \\
& & \text{Cl} & \quad \text{Cl}
\end{align*}
\]

orange yellow \hspace{1cm} bright yellow

\[0.252 \text{ g/100 ml } H_2O\] \hspace{1cm} \[0.037 \text{ g/100 ml } H_2O\]

The square-planar cis-platinum disrupts the DNA structure of cancerous cells which leads to apoptosis of those cells

⇒ Chemotherapeutic for bronchial carcinoma and tumors within the genitourinary system

⇒ 95% success rate
8. Structures and Isomers

2. Stereoisomerism

b) fac-mer Isomerism

- If a octahedral complex consists of three identical ligands, two of them can be arranged in two different ways

\[
\begin{align*}
\text{fac(ial)} & : \quad \begin{array}{c}
\text{Cl} \\
\text{Co} \\
\text{Cl} \\
\text{Cl}
\end{array} \\
\text{mer(idional)} & : \quad \begin{array}{c}
\text{Cl} \\
\text{Co} \\
\text{Cl} \\
\text{Cl}
\end{array}
\end{align*}
\]

- cyclic tridentate ligands force a facial arrangement

\[\begin{array}{c}
\text{Co} \\
\text{Cl} \\
\text{Cl}
\end{array}\]

\[\begin{array}{c}
\text{N} \\
\text{Co} \\
\text{Cl}
\end{array}\]

\[\begin{array}{c}
\text{Cl} \\
\text{Co} \\
\text{Cl}
\end{array}\]

\[\begin{array}{c}
\text{Cl} \\
\text{N} \\
\text{N}
\end{array}\]

c) Optical isomerism

- Molecules or complexes which image and mirror image can not be superimposed, are called chiral
- The two isomers of chiral molecules are called enantiomers
2. Stereoisomerism

c) Optical isomerism explained, using the example of octahedral cobalt complexes

If a molecule exhibits inversion or mirror symmetry, it can not be chiral!
8. Structures and Isomers

**Structures in Main Group Chemistry**

Predictions by Valence Shell Electron Pair Repulsion (VSEPR) model!

<table>
<thead>
<tr>
<th>Coordination number</th>
<th>Polyhedron</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear arrangement</td>
</tr>
<tr>
<td>3</td>
<td>equilateral triangle</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedron</td>
</tr>
<tr>
<td>5</td>
<td>trigonal bipyramidal</td>
</tr>
<tr>
<td>6</td>
<td>octahedron</td>
</tr>
<tr>
<td>7</td>
<td>pentagonal bipyramidal</td>
</tr>
<tr>
<td>8</td>
<td>dodecahedron</td>
</tr>
<tr>
<td>9</td>
<td>triply capped prism</td>
</tr>
</tbody>
</table>

Free electron pairs show greater spatial demand than binding electron pairs.
8. Structures and Isomers

Method of Kepert et al.

⇒ The inter-ligand interaction is repulsive
⇒ The ligands are arranged on a sphere in such a way that repulsion between them is minimised

8. Structures and Isomers

Geometry of Complexes

Coordination number (CN)
- Number of bound ligand to the metal center
- Between 2 and 12
- Dependent on
  - Size of the central atom
  - Sterical interaction between ligands
  - Electronic interaction between ligands and metal center

Coordination polyhedra
- Geometrical structure formed by the ligands around the metal center
- Symmetry is determined by sterical and electronical demands
8. Structures and Isomers

Geometry of Complexes

Coordination number 2
- Only with bulky ligands or elements from group 11 (IB) and 12 (IIB)
- Preferably for metals with d$^{10}$-configuration
- Structure: linear or almost linear
- Examples: 
  - $[\text{Ag(NH}_3\text{)}_2]^+$
    - H$_3$N-Ag-NH$_3$
  - $[\text{CuCl}_2]^-$
    - Cl-Cu-Cl
  - $[\text{Hg(CN)}_2]^-$
    - N≡C-Hg-C≡N
  - $[\text{Au(CN)}_2]^-$
    - N≡C-Au-C≡N
8. Structures and Isomers

Geometry of Complexes

Coordination number 4 (common)

1. Tetrahedral coordination preferably for metals with $d^7$- or $d^{10}$-configuration
   Examples: $[\text{Al(OH)}_4]^-$, $[\text{Cd(CN)}_4]^2-$, $[\text{BF}_4]^-$

2. Square-planar coordination preferably for metals with $d^8$-configuration
   Example: $[\text{PtCl}_4]^2-$, $[\text{Ni(dimethylglyoxim)}_2]$, $[\text{AuF}_4]^-$
8. Structures and Isomers

Geometry of Complexes

Coordination number 5 (rare)

1. Trigonal-bipyramidal coordination, 
equatorial and axial (apical) positions
   Examples: Fe(CO)$_5$, [SnCl$_5$]$^-$

2. Square-pyramidal coordination
   preferably for highly asymmetrical
   ligand sphere, e.g. oxo-ligands
   Examples: [VO(acetylacetonate)$_2$]
Geometry of Complexes

Coordination number 6 (most common)

1. Octahedral coordination, 
   equatorial and axial (apical) positions
   Examples: $[\text{Cr(NH}_3)_6]^{3+}$, $[\text{Al(OH}_2)_6]^{3+}$, $[\text{Fe(CN)}_6]^{3-}$

2. Trigonal-prismatic coordination, 
   can be caused by sterical demand of 
   the ligand sphere 
   Examples: $[\text{Re(S}_2\text{C}_2\text{Ph)}_3]$, $[\text{W(CH}_3)_6]$
8. Structures and Isomers

Geometry of Complexes

Coordination number 7

1. Pentagonal-bipyramidal coordination
   - equatorial and axial (apical) positions
   - Examples: IF₇, [UO₂F₅]³⁻, [HfF₇]³⁻

2. Capped trigonal-prismatic coordination
   - Examples: [TaF₇]³⁻

3. Capped octahedral coordination
   - Examples: [IF₆]⁻, [NbOF₆]³⁻
8. Structures and Isomers

Geometry of Complexes

Coordination number 8
1. Cubic coordination (rare)
   Examples: \([\text{UF}_8]^3^-\)

2. Hexagonal-bipyramidal coordination
   Examples: \([\text{UO}_2(\text{acetylacetonate})_3]^-\)

3. Squared-antiprismatic coordination
   Examples: \([\text{TaF}_8]^3-\), \([\text{ReF}_8]^3-\)

4. Dodecahedral coordination
   Examples: \([\text{Mo(CN)}_8]^4-\), \([\text{W(CN)}_8]^4-\)

The difference in energy between the configurations becomes smaller with increasing coordination number
⇒ Fluctuations between different configurations
## 8. Structures and Isomers

### Geometry of Complexes

<table>
<thead>
<tr>
<th>CN</th>
<th>Structure type</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>linear</td>
<td>[Ag(CN)$_2$]$^-$</td>
</tr>
<tr>
<td>3</td>
<td>trigonal-planar, trig.-aplanar (trig.-pyramidal)</td>
<td>[HgI$_3$];</td>
</tr>
<tr>
<td>4</td>
<td>tetrahedral, square-planar</td>
<td>[NiCl$_4$]$^{2-}$, [PtCl$_4$]$^{2-}$</td>
</tr>
<tr>
<td>5</td>
<td>trigonal-bipyramidal, square-pyramidal</td>
<td>[Fe(CO)$_5$]$^0$</td>
</tr>
<tr>
<td>6</td>
<td>octahedral, trigonal-prismatic</td>
<td>[Fe(OH$_2$)$_6$]$^{2+}$</td>
</tr>
<tr>
<td>7</td>
<td>pentagonal-bipyramidal, capped trigonal-prismatic, capped octahedral</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>cubic, hexagonal-bipyramidal, dodecahedral, squared-antiprismatic</td>
<td></td>
</tr>
<tr>
<td>9</td>
<td>triply capped prismatic</td>
<td>[Ln(H$_2$O)$_9$]$^{3+}$, [ReH$_9$]$^{2-}$</td>
</tr>
<tr>
<td>10</td>
<td>doubly trigonal-bipyramidal</td>
<td>(PPh$_3$Et)$_2$[Ce(NO$_2$)$_5$]</td>
</tr>
<tr>
<td>12</td>
<td>icosahedral</td>
<td>(NH$_4$)$_2$[Ce(NO$_2$)$_6$]</td>
</tr>
</tbody>
</table>
8. Structures and Isomers

Geometry of Complexes

Realisation of low coordination numbers
- Metals in low oxidation states (π-backbonding) or small metal cations in high oxidation states
- Soft donor atoms (N, C, P, S)
- Large ligands
- Counter ions with low basicity, e.g. CF₃SO₃⁻, BF₄⁻, PF₆⁻

Realisation of high coordination numbers
- Metals in intermediate oxidation states
- Hard donor atoms (F, O, N, ...)
- Small ligands
- Large non-acidic cations, e.g. [As(Ph₄)]⁺
9. Concepts of Bonding

Chemical Bonding in Complexes Can Be Described by Three Different Theories

• Valence Bond (VB) theory
• Crystal Field or Ligand Field theory
• Molecular Orbital (MO) theory

Valence (VB) Bond theory (Heitler and London 1927)

Explanation of
• geometry (most of the time)
• magnetic properties
• but not colour of transition metal complexes!

In detail, the VB-model demands the following:
Covalent bonds are formed by the overlap of empty metal orbitals (acids) with occupied donor orbitals (bases), i.e. the ligands must possess one free pair of electrons.
9. Concepts of Bonding

Number of Valence Electrons

18-Valence Electrons (VE) rule

- The 18-VE-rule (Nevil Sidgwick 1927) states that transition metal complexes are thermodynamically stable, if the metal atom disposes of 18 VE, and with that accomplishes the electronic configuration of the corresponding noble gas that follows in the periodic table

- Most, but not all, complexes follow the 18-VE-rule!

- The lower the oxidation state/atomic number of the metal atom, and the higher the $\pi$-acceptability of the ligands, the more likely it is that the 18-VE-rule is satisfied

$$\Rightarrow$$ metal organic compounds (organometallic compounds)

The number of electrons of the metal atom is calculated by the addition of its number of valence electrons, for the respective oxidation number, and the number of bonding electrons donated by the ligands!
## 9. Concepts of Bonding

### The 18-VE-Rule

**Typical examples**

<table>
<thead>
<tr>
<th>Complex</th>
<th>Anion</th>
<th>Cation</th>
<th>VE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Co(NO}_2\text{)}_6]^{3-}$</td>
<td>$\text{NO}_2^{-}$</td>
<td>$\text{Co}^{3+}$</td>
<td>6 VE</td>
</tr>
<tr>
<td>$[\text{PtCl}_6]^{2-}$</td>
<td>$\text{Cl}^{-}$</td>
<td>$\text{Pt}^{4+}$</td>
<td>6 VE</td>
</tr>
<tr>
<td>$[\text{Ag(NH}_3\text{)}_4]^+$</td>
<td>$\text{NH}_3$</td>
<td>$\text{Ag}^{+}$</td>
<td>10 VE</td>
</tr>
</tbody>
</table>

### Examples that violate the rule

<table>
<thead>
<tr>
<th>Complex</th>
<th>Anion</th>
<th>Cation</th>
<th>VE</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Cr(NH}_3\text{)}_6]^{3+}$</td>
<td>$\text{NH}_3$</td>
<td>$\text{Cr}^{3+}$</td>
<td>3 VE</td>
</tr>
<tr>
<td>$[\text{Ni(NH}_3\text{)}_6]^{2+}$</td>
<td>$\text{NH}_3$</td>
<td>$\text{Ni}^{2+}$</td>
<td>8 VE</td>
</tr>
<tr>
<td>$[\text{CoCl}_4]^{2-}$</td>
<td>$\text{Cl}^{-}$</td>
<td>$\text{Co}^{2+}$</td>
<td>7 VE</td>
</tr>
</tbody>
</table>
9. Concepts of Bonding

The 18-VE-Rule

Metal organic compounds obey the 18-VE-rule in most cases!

\[
\begin{align*}
\text{Cr} & \quad 6 \text{ VE} & \quad \text{Fe} & \quad 8 \text{ VE} & \quad \text{Ni} & \quad 10 \text{ VE} \\
6 \text{ CO} & \quad 12 \text{ VE} & \quad 5 \text{ CO} & \quad 10 \text{ VE} & \quad 4 \text{ CO} & \quad 8 \text{ VE}
\end{align*}
\]

18 VE

18 VE

18 VE

If the metal possess a odd number of electrons, dimers are formed readily or the complex can be reduced easily

\[
\begin{align*}
\text{[Mn}^{-1}\text{(CO)}_5\text{]}^{-} & \quad \xrightarrow{\text{reduction}} & \quad \text{[Mn}^0\text{(CO)}_5\text{]} & \quad \xrightarrow{\text{dimerisation}} & \quad \text{[Mn}_2^0\text{(CO)}_{10}\text{]} \\
\text{[Co}^{-1}\text{(CO)}_4\text{]}^{-} & \quad \xrightarrow{\text{Not existing!}} & \quad \text{[Co}^0\text{(CO)}_4\text{]} & \quad \xrightarrow{\text{}} & \quad \text{[Co}_2^0\text{(CO)}_8\text{]} \\
\end{align*}
\]
9. Concepts of Bonding

The 18-VE-Rule

The carbonyl ligand (CO) is, as many others (CN⁻, NH₃, OH⁻, H₂O, olefins, ...), too, a typical 2-electron donator.

But a ligand can also donate more electrons:

- Butadiene: 4 electrons
- Cyclopentadienyl radical: 5 electrons
- Benzene (benzol): 6 electrons

<table>
<thead>
<tr>
<th>ligand</th>
<th>number of electrons</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(C₅H₅)₂]</td>
<td>Fe</td>
</tr>
<tr>
<td>[Mn(CO)₅C₂H₄]⁺</td>
<td>Mn⁺</td>
</tr>
<tr>
<td>[Cr(C₆H₆)₂]</td>
<td>Cr</td>
</tr>
<tr>
<td>Fe</td>
<td>8</td>
</tr>
<tr>
<td>Mn⁺</td>
<td>6</td>
</tr>
<tr>
<td>Cr</td>
<td>6</td>
</tr>
<tr>
<td>2 C₅H₅·</td>
<td>10</td>
</tr>
<tr>
<td>5 CO</td>
<td>10</td>
</tr>
<tr>
<td>2 C₆H₆</td>
<td>12</td>
</tr>
<tr>
<td>18 VE</td>
<td>18 VE</td>
</tr>
<tr>
<td>18 VE</td>
<td>18 VE</td>
</tr>
</tbody>
</table>
9. Concepts of Bonding

Valence Bond (VB) Theory („revisited“)

Assumptions
1. Interaction of atoms if they approach each other
2. Localised bonds due to overlap of suitable atom orbitals
3. Formation of molecule orbitals (mathematics: Linear Combination of Atomic Orbitals LCAOs)
4. Occupation of MOs by an electron pair, whereby the spin of both electrons must be antiparallel to each other (→ Pauli principle)
5. Enhancement of electron density between nuclei causes attraction to the positively charged cores and the negative electron cloud
6. Bonding occurs if the overlapping atom orbitals exhibit suitable symmetry (→ +/+ or -/-)
7. Structure of formed molecules is governed by the geometry of the formed molecule orbitals

Experimentally determined molecule geometry is not always in line with the presence of pure s-, p- and d-atom orbitals ⇒ Hybridisation (model)
9. Concepts of Bonding

Valence Bond (VB) Theory

L. Pauling + J.C. Slater further developed the theory

⇒ The spatial arrangement of the ligands is explained by the hybridisation of the orbitals, located at the central atom:

<table>
<thead>
<tr>
<th>Hybridisation</th>
<th>preferred coordination geometry</th>
<th>LCAOs for sp³-Hybridisation</th>
</tr>
</thead>
<tbody>
<tr>
<td>sp³d</td>
<td>trigonal-bipyramidal</td>
<td>( \psi_1 = \frac{1}{2} (\psi_s + \psi_{p_x} + \psi_{p_y} + \psi_{p_z}) )</td>
</tr>
<tr>
<td>sp³d²</td>
<td>octahedral</td>
<td>( \psi_2 = \frac{1}{2} (\psi_s + \psi_{p_x} - \psi_{p_y} - \psi_{p_z}) )</td>
</tr>
<tr>
<td>sp³d³</td>
<td>pentagonal-bipyramidal</td>
<td>( \psi_3 = \frac{1}{2} (\psi_s - \psi_{p_x} + \psi_{p_y} - \psi_{p_z}) )</td>
</tr>
<tr>
<td>sp³d⁴</td>
<td>cubic</td>
<td>( \psi_4 = \frac{1}{2} (\psi_s - \psi_{p_x} - \psi_{p_y} + \psi_{p_z}) )</td>
</tr>
</tbody>
</table>

- Hybridisation is a mathematical tool and not the description of a physical reality!
- Solely atom orbitals with similar energy form hybrid orbitals
9. Concepts of Bonding

Valence Bond (VB) Theory

M + |L → M←L  dative(coordinative) metal-ligand bonding

Formally, the formation of a complex can be described by the following steps

Course of action

1. Electronic configuration of the metal atom?

2. Formation of the corresponding metal cation by ionisation

3. Hybridisation of free metal orbitals

4. Formation of covalent σ-bonds by the overlap of empty metal hybrid orbitals with occupied ligand orbitals (free electron pairs)

Example: tetrachloroplatinate(II) [PtCl$_4$]$^{2-}$

sp$^2$d-hybrid, square-planar, diamagnetic
9. Concepts of Bonding

Valence Bond (VB) Theory

Further example: Tetrachloronickelate(II) [NiCl$_4$]$^{2-}$

(sp$^{3}$)-hybrid, tetrahedral, paramagnetic (two unpaired electrons: $\mu_{\text{calc.}} = 2.83 \mu_\text{B}$)
9. Concepts of Bonding

Valence Bond (VB) Theory

High and low spin complexes

High spin $[\text{Co}^{\text{III}}\text{F}_6]^{3-}$

<table>
<thead>
<tr>
<th>3d</th>
<th>4s</th>
<th>4p</th>
<th>4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑↓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>↑↓</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>↑↓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Low spin $[\text{Co}^{\text{III}}(\text{NH}_3)_6]^{3+}$

<table>
<thead>
<tr>
<th>3d</th>
<th>4s</th>
<th>4p</th>
<th>4d</th>
</tr>
</thead>
<tbody>
<tr>
<td>↑↓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>↑↓</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>↑↓</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$\text{sp}^3\text{d}^2$-hybrid, octahedral, paramagnetic (4 unpaired electrons)

“magnetically normal”

$\text{sp}^3\text{d}^2$-hybrid, octahedral, diamagnetic (no unpaired electrons)

“magnetically anomalous”
9. Concepts of Bonding

Shortcomings of Valence Bond (VB) Theory

No explanation for:
- Temperature dependence of magnetic moment
- Spectroscopic properties of complexes (colour)
- Properties of excited electronic states

Furthermore, VB theory often falls short predicting the structure of square-planar complexes

Example: \([\text{Cu(NH}_3\text{)}_4]^{2+}\) is square-planar, but according to VB theory the complex should exhibit tetrahedral coordination, due to the expected sp\(^3\)-hybridisation

\[
\begin{array}{c}
\text{Cu}^{2+}\text{-ion} \\
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \\
3d \\
\end{array} \\
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4s \\
\end{array} \\
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4p \\
\end{array} \\
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4d \\
\end{array}
\end{array}
\]

\[
\begin{array}{c}
\text{[Cu}^{\text{II}}(\text{NH}_3)_4]^{2+} \\
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \uparrow \downarrow \\
3d \\
\end{array} \\
\begin{array}{c}
\uparrow \downarrow \\
4s \\
\end{array} \\
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4p \\
\end{array} \\
\begin{array}{c}
\uparrow \downarrow \uparrow \downarrow \\
4d \\
\end{array}
\end{array}
\]
9. Concepts of Bonding

Crystal Field Theory

Assumptions

• The isolated metal atom possesses five degenerate d-orbitals
• The metal atom is situated in a chemical surrounding of electrical point charges
• Between the metal atom and the ligands only electrostatic interactions arise

Stepwise formation of a complex according to crystal field theory

Electrostatic attraction between metal ion and negative point charges

Electrostatic repulsion between d-electrons and negative point charges

Crystal field splitting $\varepsilon_{cfs}$
9. Concepts of Bonding

Crystal Field Theory

Octahedral crystal field (1 d-electron)

The energy gap between the \( t_{2g} \) and \( e_g^* \)-orbitals is called – also for historical reasons – 10 Dq or \( \Delta \) (10 Dq \( \sim 1 - 3 \text{ eV} \sim 5000 - 35000 \text{ cm}^{-1} \) ).
9. Concepts of Bonding

Crystal Field Theory

Octahedral crystal field (1 d-electron)
Example: \([\text{Ti(H}_2\text{O)}_6]^{3+}\) \([\text{Ar}]3d^1\), octahedral, paramagnetic

The complex is violet in colour, thus absorbing from around 500 nm on

\[ \Delta_o = 10Dq \]
\[ \Delta_o = \frac{h \cdot c}{\lambda} \]
\[ = 3.97 \times 10^{-19} \text{ J/photon} \]
\[ = 239 \text{ kJ/mol photons} \]
9. Concepts of Bonding

Crystal Field Theory

Octahedral crystal field (n d-electrons)
Weak crystal field, weak electron-electron interactions, \textit{high spin} configuration

\[
\begin{align*}
\text{d}^2 & \quad \uparrow \uparrow \quad \text{t}_{2g} & \quad \text{d}^6 & \quad \uparrow \uparrow \uparrow \quad \text{e}_g^* \\
\text{d}^3 & \quad \uparrow \uparrow \uparrow \quad \text{t}_{2g} & \quad \text{d}^7 & \quad \uparrow \uparrow \quad \text{e}_g^* \\
\text{d}^4 & \quad \uparrow \uparrow \uparrow \quad \text{t}_{2g} & \quad \text{d}^8 & \quad \uparrow \uparrow \quad \text{e}_g^* \\
\text{d}^5 & \quad \uparrow \uparrow \uparrow \quad \text{t}_{2g} & \quad \text{d}^9 & \quad \uparrow \uparrow \quad \text{e}_g^* 
\end{align*}
\]
9. Concepts of Bonding

Crystal Field Theory

Octahedral crystal field (n d-electrons)
Strong crystal field, weak electron-electron-interactions, high spin vs. low spin

\[ \begin{align*}
d^4 & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
d^5 & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
d^6 & \quad \uparrow \quad \downarrow \quad \uparrow \quad \uparrow \\
d^7 & \quad \uparrow \quad \downarrow \quad \downarrow \quad \uparrow \\
d^4 & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
d^5 & \quad \uparrow \quad \downarrow \quad \downarrow \quad \downarrow \\
d^6 & \quad \uparrow \quad \downarrow \quad \uparrow \quad \uparrow \\
d^7 & \quad \uparrow \quad \downarrow \quad \downarrow \quad \downarrow \\
d^4 & \quad \uparrow \quad \uparrow \quad \uparrow \quad \uparrow \\
d^5 & \quad \uparrow \quad \downarrow \quad \downarrow \quad \downarrow \\
d^6 & \quad \uparrow \quad \downarrow \quad \uparrow \quad \uparrow \\
d^7 & \quad \uparrow \quad \downarrow \quad \downarrow \quad \downarrow \end{align*} \]

1 x spin pair energy
2 x spin pair energy
1 x spin pair energy
2 x spin pair energy
2 x spin pair energy
1 x spin pair energy
## 9. Concepts of Bonding

### Crystal Field Theory

Crystal field stabilisation energy CFSE in octahedral crystal field

\[
CFSE = x(-4Dq_o) + y(+6Dq_o) + SPE
\]

- **CFSE** = spin pair energy
- **SPE** = spin pair energy
- **x** = number of electrons in \( t_{2g} \)
- **y** = number of electrons in \( e_g \)

### Table

<table>
<thead>
<tr>
<th>( d^n )</th>
<th>CFSE \textit{high spin}</th>
<th>CFSE \textit{low spin}</th>
<th>( \Delta CFSE )</th>
<th>Examples</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0 Dq_o</td>
<td>-</td>
<td>-</td>
<td>Sc^{3+}, Y^{3+}, Ln^{3+}, Ti^{4+}</td>
</tr>
<tr>
<td>1</td>
<td>-4 Dq_o</td>
<td>-</td>
<td>-</td>
<td>Ti^{3+}</td>
</tr>
<tr>
<td>2</td>
<td>-8 Dq_o</td>
<td>-</td>
<td>-</td>
<td>V^{3+}</td>
</tr>
<tr>
<td>3</td>
<td>-12Dq_o</td>
<td>-</td>
<td>-</td>
<td>Cr^{3+}, Mo^{3+}, W^{3+}</td>
</tr>
<tr>
<td>4</td>
<td>-6 Dq_o</td>
<td>-16 Dq_o + 1 SPE</td>
<td>-10 Dq_o + 1 SPE</td>
<td>Mn^{2+}</td>
</tr>
<tr>
<td>5</td>
<td>0 Dq_o</td>
<td>-20 Dq_o + 2 SPE</td>
<td>-20 Dq_o + 2 SPE</td>
<td>Mn^{2+}, Fe^{3+}, Ru^{3+}</td>
</tr>
<tr>
<td>6</td>
<td>-4 Dq_o</td>
<td>-24 Dq_o + 2 SPE</td>
<td>-20 Dq_o + 2 SPE</td>
<td>Co^{3+}, Ru^{2+}, Ir^{3+}</td>
</tr>
<tr>
<td>7</td>
<td>-8 Dq_o</td>
<td>-18 Dq_o + 1 SPE</td>
<td>-10 Dq_o + 1 SPE</td>
<td>Co^{2+}</td>
</tr>
<tr>
<td>8</td>
<td>-12 Dq_o</td>
<td>-</td>
<td>-</td>
<td>Ni^{2+}</td>
</tr>
<tr>
<td>9</td>
<td>-6 Dq_o</td>
<td>-</td>
<td>-</td>
<td>Cu^{2+}</td>
</tr>
<tr>
<td>10</td>
<td>0 Dq_o</td>
<td>-</td>
<td>-</td>
<td>Cu^{+}, Zn^{2+}</td>
</tr>
</tbody>
</table>

Spin pairing occurs, if 10 Dq > SPE!
9. Concepts of Bonding

Crystal Field Theory

Crystal field splitting in octahedral crystal field

Consequences:
• High spin complexes are less stable than low spin complexes
• Ions with \( d^3 \) (Cr\(^{3+}\), Mo\(^{3+}\), W\(^{3+}\)) or \( d^6 \) (Co\(^{3+}\), Rh\(^{3+}\), Ir\(^{3+}\)) low spin configuration form highly inert complexes

Dimension of crystal field splitting
• Atomic number of metal atom (position in periodic table)
  With increasing atomic number, the core charge increases, resulting in a strengthened electrostatic field strength
  General trend for 10 Dq: \( \begin{array}{c} 3d \xrightarrow{\sim +50\%} 4d \xrightarrow{\sim +25\%} 5d \\ [\text{Co(NH}_3\text{)}_6]^{3+} \quad [\text{Rh(NH}_3\text{)}_6]^{3+} \quad [\text{Ir(NH}_3\text{)}_6]^{3+} \\ 22870 \text{ cm}^{-1} \quad 34100 \text{ cm}^{-1} \quad 41200 \text{ cm}^{-1} \end{array} \)

• Oxidation states of the metal atom (ionic charge density)
  Trend for 10 Dq: \( \text{M}^{2+} < \text{M}^{3+} < \text{M}^{4+} \ldots \)

⇒ Metals of the 4d- and 5d-series in high oxidation states form low spin complexes, only
9. Concepts of Bonding

Crystal Field Theory

Tetrahedral crystal field (1 d-electron)

The energy gap between $t_2$- and e-orbitals, $\Delta_t$, amounts to only $4/9$ of $\Delta_0$, since there are only four instead of six ligands which are furthermore not aligned along the axes of the d-orbitals.
9. Concepts of Bonding

Crystal Field Theory

Tetrahedral crystal field (n d-electrons)
Strong crystal field, weak electron-electron interactions, **high spin** configuration

<table>
<thead>
<tr>
<th>d^1</th>
<th>d^2</th>
<th>d^3</th>
<th>d^4</th>
<th>d^5</th>
<th>d^6</th>
<th>d^7</th>
<th>d^8</th>
<th>d^9</th>
<th>d^10</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="t2_e" alt="d1" /></td>
<td><img src="t2_e" alt="d2" /></td>
<td><img src="t2_e" alt="d3" /></td>
<td><img src="t2_e" alt="d4" /></td>
<td><img src="t2_e" alt="d5" /></td>
<td><img src="t2_e" alt="d6" /></td>
<td><img src="t2_e" alt="d7" /></td>
<td><img src="t2_e" alt="d8" /></td>
<td><img src="t2_e" alt="d9" /></td>
<td><img src="t2_e" alt="d10" /></td>
</tr>
</tbody>
</table>

⇒ **Low spin configurations** would be possible for d^3 – d^6
### 9. Concepts of Bonding

#### Crystal Field Theory

**Crystal field stabilisation energy in tetrahedral vs. octahedral crystal field**

Calculation with $\Delta_t = 4/9 \Delta_o$

<table>
<thead>
<tr>
<th>$d^n$</th>
<th>CFSE(tetrahedral)</th>
<th>CFSE(octahedral)</th>
<th>$\Delta$CFSE(octah. – tetrah.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-2.67 D$q_o$</td>
<td>-4 D$q_o$</td>
<td>-1.33 D$q_o$</td>
</tr>
<tr>
<td>2</td>
<td>-5.33 D$q_o$</td>
<td>-8 D$q_o$</td>
<td>-2.67 D$q_o$</td>
</tr>
<tr>
<td>3</td>
<td>-3.55 D$q_o$</td>
<td>-12 D$q_o$</td>
<td>-8.45 D$q_o$</td>
</tr>
<tr>
<td>4</td>
<td>-1.78 D$q_o$</td>
<td>-6 D$q_o$ (h.s.)</td>
<td>-4.22 D$q_o$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-16 D$q_o$ + 1 SPE (l.s.)</td>
<td>-14.22 D$q_o$ + 1 SPE</td>
</tr>
<tr>
<td>5</td>
<td>0 D$q_o$</td>
<td>0 D$q_o$ (h.s.)</td>
<td>0 D$q_o$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-20 D$q_o$ + 2 SPE (l.s.)</td>
<td>-20 D$q_o$ + 2 SPE</td>
</tr>
<tr>
<td>6</td>
<td>-2.67 D$q_o$</td>
<td>-4 D$q_o$ (h.s.)</td>
<td>-1.33 D$q_o$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-24 D$q_o$ + 2 SPE (l.s.)</td>
<td>-21.33 D$q_o$ + 2 SPE</td>
</tr>
<tr>
<td>7</td>
<td>-5.33 D$q_o$</td>
<td>-8 D$q_o$ (h.s.)</td>
<td>-2.67 D$q_o$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>-18 D$q_o$ + 1 SPE (l.s.)</td>
<td>-12.67 D$q_o$ + 1 SPE</td>
</tr>
<tr>
<td>8</td>
<td>-3.55 D$q_o$</td>
<td>-12 D$q_o$</td>
<td>-8.45 D$q_o$</td>
</tr>
<tr>
<td>9</td>
<td>-1.78 D$q_o$</td>
<td>-6 D$q_o$</td>
<td>-4.22 D$q_o$</td>
</tr>
<tr>
<td>10</td>
<td>0 D$q_o$</td>
<td>0 D$q_o$</td>
<td>0 D$q_o$</td>
</tr>
</tbody>
</table>
9. Concepts of Bonding

Crystal Field Theory

Crystal field splitting in tetrahedral crystal field

**Amounts to only 4/9 of the splitting in a octahedral crystal field!**

- Solely high spin complexes
- Ions with a electronic configuration that gives rise to high CFSE, e.g. \([\text{Ar}]d^3\), \([\text{Ar}]d^5\) (low spin) or \([\text{Ar}]d^6\) (low spin)-configuration, prefer – if possible – octahedral coordination

⇒ ordinary spinel → inverse spinel

Tetrahedral coordination polyhedra are observed for:

- Sterically demanding ligands, such as chloro, bromo and iodo ligands
- Ligands forming multiple bonds to the metal centre, e.g. oxo and nitrido ligands

Remember: There is no electronic configuration, where the electronic stabilisation in a tetrahedron is higher than in a octahedron (site preference) ⇒ octahedral geometry favoured

**Exception:** \(d^5\) (high spin) and \(d^{10}\), since in these cases CFSE for octahedral and tetrahedral geometry equals zero
Spinels Are Compounds of the Following Composition, \( \text{AB}_2\text{O}_4 \)

The oxygen anions almost form a cubic close packing (cubic face centred). In the spinel \( \text{MgAl}_2\text{O}_4 \), 1/8 of all tetrahedral sites are occupied by Mg atoms (A\(^{II}\)), 1/2 of all octahedral sites are taken up by Al atoms (B\(^{III}\)) in such a way, that every O atom is coordinated by one Mg and three Al atoms in a distorted tetrahedral fashion

\[ \text{A}^{II} = \text{Mg, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sn} \]
\[ \text{B}^{III} = \text{Al, Ga, In, Ti, V, Cr, Mn, Fe, Co, Rh, Ni} \]

**Normal spinel structure**

\[ [\text{A}^{II}]_{\text{tet}}\cdot[\text{B}^{III}]_{\text{oct}}\cdot\text{O}_4 \]

Examples: \( \text{MgAl}_2\text{O}_4 \), \( \text{MnMn}_2\text{O}_4 \) (\( \text{Mn}_3\text{O}_4 \)), \( \text{FeAl}_2\text{O}_4 \)

\( \text{CoCo}_2\text{O}_4 \) (\( \text{Co}_3\text{O}_4 \))

**Inverse spinel structure**

\[ [\text{B}^{III}]_{\text{tet}}\cdot[\text{A}^{II}]_{\text{oct}}\cdot[\text{B}^{III}]_{\text{oct}}\cdot\text{O}_4 \]

Examples: \( \text{CoFe}_2\text{O}_4 \), \( \text{FeFe}_2\text{O}_4 \) (\( \text{Fe}_3\text{O}_4 \)), \( \text{NiFe}_2\text{O}_4 \)
9. Concepts of Bonding

Crystal Field Theory

The site preference determines the distribution of the transition metal cations in spinels

\[
\text{Mn}_3\text{O}_4 \quad \text{Mn}^{2+} \quad \text{d}^5 \text{ high spin} \quad \text{no site preference} \\
\text{Mn}^{3+} \quad \text{d}^4 \text{ high spin} \quad \text{site preference} = -4.22 \text{ Dq} \\
\Rightarrow \text{preferably octahedral site } [\text{B}^{\text{III}}]^{\text{oct.}}
\]

\[
\Rightarrow \text{normal spinel } [\text{Mn}^{\text{II}}]^{\text{tetr.}}[\text{Mn}^{\text{III}}]^{\text{oct.}}_2\text{O}_4
\]

\[
\text{Fe}_3\text{O}_4 \quad \text{Fe}^{2+} \quad \text{d}^6 \text{ high spin} \quad \text{site preference} = -1.33 \text{ Dq} \\
\text{Fe}^{3+} \quad \text{d}^5 \text{ high spin} \quad \text{no site preference} \\
\Rightarrow \text{preferably octahedral site } [\text{A}^{\text{II}}]^{\text{oct.}}
\]

\[
\Rightarrow \text{Inverse spinel } [\text{Fe}^{\text{III}}]^{\text{tetr.}}[\text{Fe}^{\text{II}}]^{\text{oct.}}[\text{Fe}^{\text{III}}]^{\text{oct.}}\text{O}_4, \text{ meaning all Fe}^{2+}\text{-ions occupy octahedral sites and force half of the Fe}^{3+}\text{-ions onto tetrahedral sites}
\]
Crystal Field Theory

Tetragonally distorted octahedral crystal field

**Jahn-Teller-Theorem (Hermann Arthur Jahn and Edward Teller 1937)**

“Every non-linear molecule, which possesses a degenerate electronic state, is prone to distortion, lowering the symmetry and thus revoking electronic degeneration“

⇒ Large gain in energy for $d^4$ (high spin), $d^7$ (low spin) and $d^9$-configuration
9. Concepts of Bonding

Crystal Field Theory

Tetragonally distorted crystal field as a result of the Jahn-Teller effect

<table>
<thead>
<tr>
<th>Electronic configuration</th>
<th>nd$^1$</th>
<th>nd$^2$</th>
<th>nd$^3$</th>
<th>nd$^4$</th>
<th>nd$^5$</th>
<th>nd$^6$</th>
<th>nd$^7$</th>
<th>nd$^8$</th>
<th>nd$^9$</th>
<th>nd$^{10}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>High spin J.T.</td>
<td>Weak</td>
<td>Weak</td>
<td>-</td>
<td>Strong</td>
<td>-</td>
<td>Weak</td>
<td>Weak</td>
<td>-</td>
<td>Strong</td>
<td>-</td>
</tr>
<tr>
<td>Low spin J.T.</td>
<td>Weak</td>
<td>Weak</td>
<td>-</td>
<td>Weak</td>
<td>Weak</td>
<td>-</td>
<td>Strong</td>
<td>-</td>
<td>Strong</td>
<td>-</td>
</tr>
</tbody>
</table>
9. Concepts of Bonding

Crystal Field Theory

Crystal field splitting in various crystal field symmetries

- $d_{x^2-y^2}$
- $d_z^2$
- $d_{xy}$
- $d_{xz}$, $d_{yz}$

Energy $[\Delta_0]$:

- Square-planar
- Trigonal-bipyramidal
- Square-pyramidal
- Octahedral
- Pentagonal-bipyramidal
- Square-antiprism
- Cubic = 2x tetrahedral

Inorganic Chemistry II
Prof. Dr. T. Jüstel
9. Concepts of Bonding

Crystal Field Theory – Applications and Implications

1. Magnetic properties ↔ electronic configuration
   paramagnetic Fe(II)-compounds: high spin (magnetically normal)
   (unpaired electrons)
   diamagnetic Fe(II)-compounds: low spin (magnetically anomalous)
   (no unpaired electrons)

2. Optical properties (absorption and luminescence spectra)

3. Ionic radii of transition metal cations

4. Hydration enthalpies of transition metal cations

5. Lattice energy of transition metal salts
Crystal Field Theory

To 1. Magnetic properties

The base unit of the magnetic momentum is called Bohr’s magneton, and equals the magnetic momentum, induced by a single electron on a circular path - with Bohr’s radius (53 pm) - around a proton

Every moving electrical charge induces a magnetic field with the magnetic momentum \( \mu \) (exp.: electrical current in a wire)

\[
\mu_B = \frac{e \cdot \hbar}{2 \cdot m_e}
\]

For elements of the first row of transition metals with \( n \) unpaired electrons, the following approximate correlation can be stated:

\[
\mu_{\text{ber}} = \sqrt{n(n+2)} \cdot \mu_B
\]

“Spin only value“, i.e. only spin angular momentum and no orbital momentum

\[
\mu_{\text{ber}} = 2\sqrt{S(S+1)} \cdot \mu_B
\]

Total spin \( S = \sum s \) with \( s = \frac{1}{2} \) and \( S = n/2 \)
9. Concepts of Bonding

Crystal Field Theory

To 1. Magnetic properties
The calculated spin-only values are in good agreement with experimental data
⇒ For this reason it is possible to deduce the number of unpaired electrons in 3d-complexes directly from magnetic measurements

<table>
<thead>
<tr>
<th>3d-Ion</th>
<th>Electronic configuration</th>
<th>n</th>
<th>$\mu_{\text{calc.}} , [\mu_B]$ high spin</th>
<th>$\mu_{\text{exp.}} , [\mu_B]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti$^{3+}$</td>
<td>[Ar]3d$^1$</td>
<td>1</td>
<td>1.73</td>
<td>1.7 – 1.8</td>
</tr>
<tr>
<td>V$^{3+}$</td>
<td>[Ar]3d$^2$</td>
<td>2</td>
<td>2.83</td>
<td>2.7 – 2.9</td>
</tr>
<tr>
<td>V$^{2+}$, Cr$^{3+}$</td>
<td>[Ar]3d$^3$</td>
<td>3</td>
<td>3.87</td>
<td>3.7 – 3.9</td>
</tr>
<tr>
<td>Cr$^{2+}$, Mn$^{3+}$</td>
<td>[Ar]3d$^4$</td>
<td>4</td>
<td>4.90</td>
<td>4.8 – 4.9</td>
</tr>
<tr>
<td>Mn$^{2+}$, Fe$^{3+}$</td>
<td>[Ar]3d$^5$</td>
<td>5</td>
<td>5.92</td>
<td>5.7 – 6.0</td>
</tr>
<tr>
<td>Fe$^{2+}$, Co$^{3+}$</td>
<td>[Ar]3d$^6$</td>
<td>4</td>
<td>4.90</td>
<td>5.0 – 5.6</td>
</tr>
<tr>
<td>Co$^{2+}$, Ni$^{3+}$</td>
<td>[Ar]3d$^7$</td>
<td>3</td>
<td>3.87</td>
<td>4.3 – 5.2</td>
</tr>
<tr>
<td>Ni$^{2+}$</td>
<td>[Ar]3d$^8$</td>
<td>2</td>
<td>2.83</td>
<td>2.9 – 3.9</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>[Ar]3d$^9$</td>
<td>1</td>
<td>1.73</td>
<td>1.9 – 2.1</td>
</tr>
<tr>
<td>Cu$^+$, Zn$^{2+}$</td>
<td>[Ar]3d$^{10}$</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>
Crystal Field Theory

To 2. Optical properties
Electronic transitions between d-orbitals (d-d-transitions) often lead to absorption bands situated in the visible spectral range.

Example: octahedral Ti$^{3+}$-complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>10 Dq [kJ/mol]</th>
<th>10 Dq [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Ti(H$_2$O)$_6$]$^{3+}$</td>
<td>239</td>
<td>500</td>
</tr>
<tr>
<td>[TiF$_6$]$^{3-}$</td>
<td>203</td>
<td>630</td>
</tr>
<tr>
<td>[TiCl$_6$]$^{3-}$</td>
<td>160</td>
<td>770</td>
</tr>
</tbody>
</table>

CFSE:

- CO > CN$^-$ > NO$_2^-$ > en > NH$_3$ > H$_2$O > OH$^-$ > F$^-$ > NO$_3^-$ > Cl$^-$ > SCN$^-$ > S$^{2-}$ > Br$^-$ > I$^-$
- Spectrochemical series
  - Arranges ligands relative to the strength of the resulting crystal field splitting
  - The sequence can not be explained by crystal field theory (point charges)
Crystal Field Theory

To 2. Optical properties

Example: octahedral Cu$^{2+}$-complexes (d$^9$)

<table>
<thead>
<tr>
<th>Complex</th>
<th>10 Dq</th>
<th>Colour</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Cu(H$_2$O)$_6$]$^{2+}$</td>
<td>800 nm</td>
<td>colourless</td>
</tr>
<tr>
<td>[Cu(NH$_3$)$_2$(H$_2$O)$_4$]$^{2+}$</td>
<td>670 nm</td>
<td>pale blue</td>
</tr>
<tr>
<td>[Cu(NH$_3$)$_4$(H$_2$O)$_2$]$^{2+}$</td>
<td>600 nm</td>
<td>blue</td>
</tr>
</tbody>
</table>

Comparably simple situations – one absorption band – can also be found for octahedral complexes with d$^4$ high spin or d$^6$ high spin configurations at the metal centres. For the electronic configurations d$^2$ – d$^8$, the situation becomes more complex, due to interactions between the electrons (electron-electron-correlation)
### 9. Concepts of Bonding

**Crystal Field Theory**

#### To 2. Optical properties

**Example: Octahedral Co$^{3+}$-complexes (d$^6$ low spin)**

<table>
<thead>
<tr>
<th>#</th>
<th>Complex</th>
<th>10 Dq</th>
<th>Colour</th>
<th>Absorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>[Co(CN)$_6$]$^{3-}$</td>
<td>colourless</td>
<td>UV</td>
<td></td>
</tr>
<tr>
<td>b</td>
<td>[Co(NO$_2$)$_6$]$^{3-}$</td>
<td>pale yellow</td>
<td>violet</td>
<td></td>
</tr>
<tr>
<td>c</td>
<td>[Co(phen)$_3$]$^{3+}$</td>
<td>yellow</td>
<td>blue</td>
<td></td>
</tr>
<tr>
<td>d</td>
<td>[Co(en)$_3$]$^{3+}$</td>
<td>deep yellow</td>
<td>cyan-blue</td>
<td></td>
</tr>
<tr>
<td>e</td>
<td>[Co(NH$_3$)$_6$]$^{3+}$</td>
<td>orange</td>
<td>cyan</td>
<td></td>
</tr>
<tr>
<td>f</td>
<td>[Co(gly)$_3$]$^{3+}$</td>
<td>violet</td>
<td>green</td>
<td></td>
</tr>
<tr>
<td>g</td>
<td>[Co(H$_2$O)$_6$]$^{3+}$</td>
<td>blue</td>
<td>yellow</td>
<td></td>
</tr>
<tr>
<td>h</td>
<td>[Co(ox)$_3$]$^{3-}$</td>
<td>cyan</td>
<td>orange</td>
<td></td>
</tr>
<tr>
<td>i</td>
<td>[Co(CO$_3$)$_3$]$^{3-}$</td>
<td>green</td>
<td>red (+ blue)</td>
<td></td>
</tr>
</tbody>
</table>
9. Concepts of Bonding

Crystal Field Theory

To 3. Ionic radii

A plot of the ionic radii of divalent 3d-ions in the oxides MO (M = metal) in octahedral ligand coordination and high spin state does not show a steady linear decrease (blue graph)!

⇒ Electronic configurations with unoccupied orbitals, which are directed to the ligands (d$_{z^2}$, d$_{x^2-y^2}$), result in small ionic radii

⇒ V$^{2+}$, Ni$^{2+}$
9. Concepts of Bonding

Crystal Field Theory

To 4. Hydration enthalpy
During the reaction:

\[ M^{n+}(g) + 6 \text{H}_2\text{O}(l) \rightarrow [M(\text{H}_2\text{O})_6]^{n+}(\text{aq}) \]

energy is set free by the electrostatic forces between the metal, M, and the ligand, water

Small cations provide high hydration enthalpies

Therefore, the trend for hydration enthalpies corresponds with the one for the ionic radii
9. Concepts of Bonding

Crystal Field Theory

To 5. Lattice energy of transition metal salts

\[ \text{M}^{n+} (g) + \frac{n}{2} \text{O}^2-(g) \rightarrow \text{MO}_{n/2} (s) \]

Through the deviation between measured and calculated values for \( U_g \), the parameter 10 Dq (crystal field splitting) can be calculated

\[ \text{Ni}^{2+} \ [\text{Ar}]d^8 \Rightarrow t_{2g}^6 e_g^2 \]

Crystal field stabilisation energy CFSE = -12 Dq

\[ U_g (\text{exp.}) - U_g (\text{calc.}) = 165 \text{ kJ/mol} = 13600 \text{ cm}^{-1} = 12 \text{ Dq} \]

10 Dq = 11330 cm\(^{-1}\)
9. Concepts of Bonding

Ligand Field Theory

Disadvantages of crystal field theory: There is a number of spectroscopic phenomena that the concept of electrostatic point charges can not explain: Electron Paramagnetic Resonance (EPR) spectra, ordering of spectrochemical series

⇒ It is necessary to account for the covalence of the metal-ligand bond

Effects of covalent interactions

• Delocalisation of electron density from metal d-orbitals towards ligands (nephelauxetic effect)
• Reduction of inter-electronic repulsion at the metal centre
• Shift of electron density towards ligands, possibly leading to weakening of intra-ligand bonds (back-bonding-effect)

⇒ Change of electronic, magnetic, and spectroscopic properties
9. Concepts of Bonding

Ligand Field Theory

Back-bonding to ligands
- Typically for metalcarbonyls and -nitrosyls
- Metal experiences formally low oxidation states, coinciding with high electron density that is reduced by a withdrawal of charge towards the ligands

Example: M(CO)$_6$ “metalcarbonyl“

\[ M-\text{C} \equiv \text{O} \leftrightarrow M=\text{C}=\text{O} \]

a) $\sigma$-donor-bond

b) $\pi$-acceptor-bond

“synergetic effect“
9. Concepts of Bonding

Ligand Field Theory

Explanation for the sequence of ligands within the spectrochemical series

\[ \text{CO} > \text{CN}^- > \text{NO}_2^- > \text{en} > \text{NH}_3 > \text{H}_2\text{O} > \text{OH}^- > \text{F}^- > \text{NO}_3^- > \text{Cl}^- > \text{SCN}^- > \text{S}^2- > \text{Br}^- > \text{I}^- \]

**strong ligands** \hspace{1cm} **weak ligands**

\(\pi\)-back-bonding \hspace{1cm} no \(\pi\)-back-bonding

The spectrochemical series does not correlate with the charge of the ligands, but with the ability of the ligands to delocalise electron density from the metal atom and thus intensifying the positive charge density or effective field strength at the metal atom.

\(\pi\)-acceptor ligands: stabilise metals in low oxidation states \(\Rightarrow\) CO, NO (back-bonding)

\(\pi\)-donor ligands: stabilise metals in high oxidation states \(\Rightarrow\) O\(^2-\), N\(^3-\) (multiple metal-ligand-bonds)
9. Concepts of Bonding

Molecular Orbital (MO) Theory

- Overlap of metal and ligand orbitals leads to the formation of molecular orbitals
- Example: octahedral complex consisting of 6 σ-donor ligands and 3d-metal atom
9. Concepts of Bonding

Molecular Orbital (MO) Theory

Consequences of $\pi$-back-bonding

- Strengthening of metal-ligand bond
- Increase of crystal field splitting by lowering the energy of $t_{2g}$-orbitals
- Weakening of intra-ligand bonds by transfer of electronic density into anti-bonding ligand orbitals
  - Decrease of vibrational frequencies
  - Increased reactivity of the ligands (activation)
  - Catalytic and enzymatic reactions

\[ \begin{align*}
\sigma \text{ bond:} & \\
\pi \text{ backbond:} & \\
\end{align*} \]
9. Concepts of Bonding

Molecular Orbital (MO) Theory

Explanation for the sequence of ligands within the spectrochemical series

CO > CN⁻ > NO₂⁻ > en > NH₃ > H₂O > OH⁻ > F⁻ > NO₃⁻ > Cl⁻ > SCN⁻ > S²⁻ > Br⁻ > I⁻

- **Strong ligands**: unoccupied π*-orbitals
- **Weak ligands**: occupied p-orbitals
- **π-acceptor ligands**: no suitable p-orbitals
- **π-donor ligands**: exclusively σ-donor ligands

<table>
<thead>
<tr>
<th>Type of ligand</th>
<th>Effect upon metal-ligand-bond</th>
<th>Crystal field splitting</th>
</tr>
</thead>
<tbody>
<tr>
<td>π-acceptor</td>
<td>highly stabilising</td>
<td>high</td>
</tr>
<tr>
<td>σ-donor</td>
<td>stabilising</td>
<td>intermediate</td>
</tr>
<tr>
<td>π-donor</td>
<td>destabilising</td>
<td>small</td>
</tr>
</tbody>
</table>
**10. Chemistry of Transition Metals**

**Physical Properties**

Transition metals experience high melting/boiling points, along with high/highest densities

Numerous transition metals are highly relevant as materials or catalysts

10. Chemistry of Transition Metals

Oxidation States

<table>
<thead>
<tr>
<th>3d-Elements</th>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
<th>Cr</th>
<th>Mn</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Cu</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+3</td>
<td>+2, +3, +4</td>
<td>+2, +3, +4, +5</td>
<td>+2, +3, +4, +6</td>
<td>+2, +3</td>
<td>+2, +3</td>
<td>+2</td>
<td>+2</td>
<td>+1, +2</td>
<td>+2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>4d-Elements</th>
<th>Y</th>
<th>Zr</th>
<th>Nb</th>
<th>Mo</th>
<th>Tc*</th>
<th>Ru</th>
<th>Rh</th>
<th>Pd</th>
<th>Ag</th>
<th>Cd</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+3</td>
<td>+4</td>
<td>+5</td>
<td>+4, +6</td>
<td>+7</td>
<td>+2, +3, +4</td>
<td>+3</td>
<td>+2</td>
<td>+1, +2</td>
<td>+2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>5d-Elements</th>
<th>La</th>
<th>Hf</th>
<th>Ta</th>
<th>W</th>
<th>Re</th>
<th>Os</th>
<th>Ir</th>
<th>Pt</th>
<th>Au</th>
<th>Hg</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>+3</td>
<td>+4</td>
<td>+5</td>
<td>+4, +6</td>
<td>+4, +7</td>
<td>+4, +8</td>
<td>+3, +4</td>
<td>+2, +4</td>
<td>+1, +3</td>
<td>+1, +2</td>
</tr>
</tbody>
</table>

- All TM, with a sufficient abundance in the earth’s crust and relatively stable low oxidation states, are accessible for **biological/biochemical** processes, and are thus of great importance as trace elements.
- Highest oxidation states ($\text{Mn}^{\text{VII}}, \text{Os}^{\text{VIII}}$) are only possible with $\pi$-donor ligands ($\text{O}^{2-}, \text{N}^{3-}$) $\Rightarrow [\text{MnO}_4]^{-}, \text{OsO}_4$, $[\text{OsO}_3\text{N}]^{-}$, whereas $\text{MnF}_7$ and $\text{OsF}_8$ are not known!
10. Chemistry of Transition Metals

Oxidation States (Frost-Diagram of 3d-Metals in Acidic Solution)

- Metallic titanium is a potent reductive agent
- Mn^{VI}, Mn^{VII} and Fe^{VI} are strong oxidising agents
- Most stable oxidation states: Ti^{III/IV}, V^{III}, Cr^{III}, Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{0}, Zn^{II}

⇒ Copper is a noble metal
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

⇒ 1. Subgroup or group 11 \((n-1)d^{10}ns^1\) with \(n = 4, 5, 6\)

Properties of the elements:

- Melting points at about 1000° C (readily form alloys and are easy to be refound)
- High electric conductivity (Ag > Cu > Au)
- \(ns^1\)-electron is more tightly bound than in alkaline metals, due to the higher core charge
- Copper and gold are, together with Cs, the only coloured metals ⇒ absorption in visible range of the spectrum
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

⇒ Metals of the copper group and their respective alloys “coined” the development of the first advanced civilisations (Au: 5000 BC, Ag: ca. 3500 BC, Copper Age: ca. 5000 BC, Bronze Age: ca. 3000 BC)

Alloys of technical importance

<table>
<thead>
<tr>
<th>Name</th>
<th>Main component</th>
<th>Alloying addition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brass</td>
<td>Cu</td>
<td>Zn</td>
</tr>
<tr>
<td>Bronze</td>
<td>Cu</td>
<td>Sn</td>
</tr>
<tr>
<td>Cupronickel</td>
<td>Cu</td>
<td>Ni</td>
</tr>
<tr>
<td>Nickel silver</td>
<td>Cu</td>
<td>Ni, Zn</td>
</tr>
<tr>
<td>Billion</td>
<td>Cu</td>
<td>Ag</td>
</tr>
<tr>
<td>White gold</td>
<td>Au</td>
<td>Pd, Ni</td>
</tr>
<tr>
<td>Red gold</td>
<td>Au</td>
<td>Cu</td>
</tr>
</tbody>
</table>

(→ presentations)
### 10. Chemistry of Transition Metals

#### Copper Group (Coinage Metals)

<table>
<thead>
<tr>
<th>Occurrence</th>
<th>Compound</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper (aes cyprium, cuprum)</td>
<td>Cu₂S</td>
<td>Copper shine</td>
</tr>
<tr>
<td>Cyprus</td>
<td>CuFeS₂</td>
<td>Chalcopryte</td>
</tr>
<tr>
<td></td>
<td>Cu(OH)₂·CuCO₃</td>
<td>Malachite</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>Dignified</td>
</tr>
<tr>
<td>Silver (argos, argentum)</td>
<td>Ag₂S</td>
<td>Silver glance</td>
</tr>
<tr>
<td>shiny, white</td>
<td>Ag</td>
<td>Sterling</td>
</tr>
<tr>
<td>Gold (aurum)</td>
<td>Au</td>
<td>Dignified</td>
</tr>
<tr>
<td>shiny, blank</td>
<td>(E175)</td>
<td>Gold leaf</td>
</tr>
</tbody>
</table>

#### Fabrication
- Cu and Ag by calcination of sulphide ores, e.g. Cu₂S or Ag₂S
  
  \[ 2 \text{Cu}_2\text{S} + 3 \text{O}_2 \rightarrow 2 \text{Cu}_2\text{O} + 2 \text{SO}_2 \]
  
  \[ 2 \text{Cu}_2\text{O} + \text{Cu}_2\text{S} \rightarrow 6 \text{Cu} + \text{SO}_2 \]
- Au (and partially Ag, too) by cyaniding (→ presentations)
10. Chemistry of Transition Metals

Excursion: Gold mining

Gold bound in rocks  Released Gold

Milling

Minerals (Quartz)

Gold

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Formula</th>
<th>pH-value</th>
<th>Formed Au complex</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thio urea</td>
<td>(NH₂)₂C=S</td>
<td>1-4</td>
<td>[Au(NH₂CSNH₂)₂]⁺</td>
</tr>
<tr>
<td>Bromide</td>
<td>Br⁻</td>
<td>1-7</td>
<td>[AuBr₄]⁻</td>
</tr>
<tr>
<td>Iodide</td>
<td>I⁻</td>
<td>1-5</td>
<td>[AuI₂]⁻</td>
</tr>
<tr>
<td>Thiocyanate</td>
<td>SCN⁻</td>
<td>1-3</td>
<td>[Au(SCN)₄]⁻</td>
</tr>
<tr>
<td>Thiosulphate</td>
<td>S₂O₃²⁻</td>
<td>8-11</td>
<td>[Au(S₂O₃)₂]³⁻</td>
</tr>
<tr>
<td>Chlor compounds</td>
<td>Cl⁻, OCl⁻, Cl₂, ClO₃⁻</td>
<td>1-4</td>
<td>[AuCl₄]⁻</td>
</tr>
</tbody>
</table>
### Copper Group (Coinage Metals)

#### Oxidation States

<table>
<thead>
<tr>
<th>Coinage metal</th>
<th>Oxidation state</th>
<th>$E_{M/M^+}^0$ [V]</th>
<th>1. IE [kJ/mol]</th>
<th>soluble in</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>+1, +2, +3</td>
<td>0.52</td>
<td>745.3</td>
<td>HNO$_3$</td>
</tr>
<tr>
<td>Ag</td>
<td>+1, +2, +3</td>
<td>0.80</td>
<td>730.8</td>
<td>HNO$_3$</td>
</tr>
<tr>
<td>Au</td>
<td>+1, +3</td>
<td>1.68</td>
<td>889.9</td>
<td>HNO$_3$/HCl (1:3)</td>
</tr>
</tbody>
</table>

Cu$^+$ and Au$^+$ tend to disproportionate in aqueous solution

2 Cu$^+$ → Cu$^0$ + Cu$^{2+}$

Hydration enthalpy of Cu$^{2+}$: -2100 kJ/mol, Cu$^+$: -590 kJ/mol

Ag$^+$ is stable

2. Ionisation energy: Ag$^+$ > Au$^+$ > Cu$^+$

3 Au$^+$ → 2 Au$^0$ + Au$^{3+}$

High CFSE for square-planar Au$^{3+}$([Xe]4f$^{14}$5d$^8$)-ions
Copper Group (Coinage Metals)

Stereo chemistry
⇒ Strong influence of oxidation state

+I (d^{10}): Cu^+, Ag^+, Au^+ favour CN 2 ⇒ linear coordination ⇒ [H_3N→Ag ←NH_3]^+
   Tetrahedral coordination of Cu^+ in [Cu(py)_4]^+ and [Cu(CN)_4]^3-
   ⇒ sp^3-hybridisation (CFSE = 0)
   Due to the high energy gap between s- and p-orbitals, Ag^+ and Au^+ generally form no tetrahedral complexes!

+II (d^9): Favoured coordination geometry for Cu^{2+}-complexes is a distorted octahedron
   ⇒ [Cu(NH_3)_4(H_2O)_2]^{2+}, [Cu(H_2O)_6]^{2+} and square-planar ⇒ [CuCl_2(H_2O)_2]^0
   ⇒ Jahn-Teller-Effect

+III (d^8): Au^{3+} is usually coordinated in a square-planar fashion ⇒ [AuCl_4]^−
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Stereochemistry and crystal field splitting

- Spherical field: $d^{10}$ ($\text{Cu}^+, \text{Ag}^+, \text{Au}^+$)
- Octahedral field: $d^9$ ($\text{Cu}^{2+}, \text{Ag}^{2+}$)
- Tetragonally distorted octahedral field by Jahn-Teller-effect
- Square-planar field: $d^8$ ($\text{Au}^{3+}$) ions

Energy level diagram:
- $t_{2g}$: $d_{xy}$, $d_{xz}$, $d_{yz}$
- $e_{g}^*$: $d_{z^2}$, $d_{x^2-y^2}$
- $10 \text{Dq}$

Maximal stabilisation:
- for $d^9$ ($\text{Cu}^{2+}, \text{Ag}^{2+}$) ions
- for $d^{10}$ ($\text{Cu}^+, \text{Ag}^+, \text{Au}^+$) ions
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Cu(II)-compounds
CuSO₄·5 H₂O or [Cu(H₂O)₄]SO₄·H₂O (copper(II)-sulphate-pentahydrate) blue

Synthesis
2 Cu + O₂ + 2 H₂SO₄ → 2 CuSO₄ + 2 H₂O

Dehydration
CuSO₄·5H₂O → CuSO₄·H₂O → CuSO₄ (blue) → CuSO₄ (white)

White (dry) copper sulphate readily takes up H₂O becoming blue in the process
⇒ detection of small amounts of H₂O, e.g. in ethanol

Copper sulphate behaves as an acid, when dissolved in water (cation acid)
CuSO₄·5 H₂O(s) + H₂O → [Cu(H₂O)₆]²⁺(aq) + SO₄²⁻(aq)
[Cu(H₂O)₆]²⁺ + H₂O ⇌ [Cu(OH)(H₂O)₅]⁺ + H₃O⁺
⇒ pH of a 0.1 molar solution ~ 3
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Cu(II)-compounds
Bis(tartrato)cuprate(II)-complex (Fehling’s solution 1850)

\[
2[\text{C}_4\text{H}_4\text{O}_6]^{2-} + \text{Cu}^{2+} + 2\text{OH}^- \xrightarrow{\text{Fehling's solution}} \text{Cu}_2\text{O}_4^{4-} + 2\text{H}_2\text{O}
\]

löslicher tiefblauer Cu(II)-Komplex

In presence of reducing agents and elevated temperatures, reduction to poorly soluble Cu$_2$O takes place, which than precipitates as brick red (in the beginning yellow) powder

Fehling’s test: detection of reducing agents (aldehydes and sugars, such as D-Glucose) \(\Rightarrow\) analysis of urine (diabetes)

\[
\text{R-CH}=\text{O} + 2\text{ Cu}^{2+} + \text{H}_2\text{O} \rightarrow \text{R-COOH} + \text{Cu}_2\text{O} + 2\text{ H}^+
\]
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Cu(I)-compounds
In water readily soluble Cu(I)-compounds disproportionate:
\[ \text{Cu}_2\text{SO}_4(\text{s}) \rightarrow \text{Cu}^{2+}(\text{aq}) + \text{SO}_4^{2-}(\text{aq}) + \text{Cu}(\text{s}) \]  
high hydration enthalpy for Cu\(^{2+}\)

Remember: Ions disproportionate, if the redox potential for the reduction to the next lower oxidation state is more positive than the redox potential for the oxidation to the next higher oxidation state

<table>
<thead>
<tr>
<th>Reduced form</th>
<th>⇄</th>
<th>Oxidised form + e(^-)</th>
<th>Standard potential (E^0) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>⇄</td>
<td>Cu(^+)</td>
<td>+ e(^-) +0.52</td>
</tr>
<tr>
<td>Cu(^+)</td>
<td>⇄</td>
<td>Cu(^{2+})</td>
<td>+ e(^-) +0.15</td>
</tr>
</tbody>
</table>

\[ \text{Cu}^+ + \text{Cu}^+ \rightleftharpoons \text{Cu} + \text{Cu}^{2+} \]  
\[ \Delta E = E^0_{\text{Cu/Cu}^+} - E^0_{\text{Cu}^+/\text{Cu}^{2+}} = +0.52 \text{ V} - 0.15 \text{ V} = +0.37 \text{ V} \]

Poorly soluble Cu(I)-compounds (Cu\(_2\)O, CuI, CuCN, Cu\(_2\)S) are stable in aqueous solution and do not disproportionate
⇒ Impact of solubility upon redox potentials
Superconductors Are Materials which Specific Electrical Resistance Diminish to About Zero, Below a Certain Transition Temperature ($T_c$)

⇒ Virtually lossless electrical power transmission possible  
⇒ Application in superconducting magnetic coils  
⇒ (N)MR-devices, magnetometer, particle accelerator

### History of superconductor research

<table>
<thead>
<tr>
<th>Year</th>
<th>Material</th>
<th>$T_c$ [K]</th>
<th>Year</th>
<th>Material</th>
<th>$T_c$ [K]</th>
<th>Year</th>
<th>Material</th>
<th>$T_c$ [K]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1911</td>
<td>Hg</td>
<td>4.2</td>
<td>1972</td>
<td>Nb$_3$Ge</td>
<td>23.3</td>
<td>1986</td>
<td>La$<em>{1.8}$Ba$</em>{0.2}$CuO$_4$</td>
<td>35</td>
</tr>
<tr>
<td>1986</td>
<td>La$<em>{1.8}$Ba$</em>{0.2}$CuO$_4$</td>
<td>35</td>
<td>1987</td>
<td>YBa$_2$Cu$<em>3$O$</em>{7-x}$</td>
<td>93</td>
<td>1988</td>
<td>Bi$_2$Sr$<em>2$Ca$</em>{n-1}$Cu$_n$O$_x$</td>
<td>125 (&gt; 77 K = $T_b$(N$_2$))</td>
</tr>
<tr>
<td>1988</td>
<td>Bi$_2$Sr$<em>2$Ca$</em>{n-1}$Cu$_n$O$_x$</td>
<td>125 (&gt; 77 K = $T_b$(N$_2$))</td>
<td>1993</td>
<td>HgBa$<em>2$CuO$</em>{4+x}$</td>
<td>155</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

#### High-temperature superconductors ⇒ mixed-valent Cu(II)/Cu(III)-ceramics

Excursion: Superconductor

> $T_b$(N$_2$) = 77 K

⇒ liquid nitrogen as cooling agent
YBa$_2$Cu$_3$O$_{7-x}$ – Electronic properties

**Dependence on Oxygen content**

- **YBa$_2$Cu$_3$O$_{6.5}$** 100% Cu$^{2+}$  [Ar]3d$^9$, paramagnetic, distorted octahedr. (J.T.-Effect)
- **YBa$_2$Cu$_3$O$_{7}$** 66.7% Cu$^{2+}$  [Ar]3d$^9$, paramagnetic, distorted octahedr. (J.T.-Effect)
  33.3% Cu$^{3+}$  [Ar]3d$^8$, diamagnetic, quadratic-planar

**Layer structure enables 2D-conductivity**

\[
\begin{align*}
\text{Cu}^{2+} & \rightleftharpoons \text{Cu}^{3+} & \text{Cu}^{2+} & \rightleftharpoons \text{Cu}^{2+} \\
\text{Cu}^{2+} & \rightleftharpoons \text{Cu}^{3+} & \text{Cu}^{2+} & \rightleftharpoons \text{Cu}^{2+} \\
\end{align*}
\]

\(\oplus\oplus\) Copplng of electrons by virtual phonons to form Cooper-Pairs (Bosons)

\[
\begin{align*}
\text{Cu}^{2+}(\text{distorted octahedral}) & \leftrightarrow \text{Cu}^{3+}(\text{quadratic-planar}) \Rightarrow \text{Oscillations (J.T.-Polarons)}
\end{align*}
\]
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Ag(I)-compounds

- Most Ag(I) salts (Ag₂CO₃, Ag₃PO₄ and AgX with X = Cl, Br, I, SCN, OCN, N₃) are poorly soluble
  ⇒ high covalence, high lattice energies and low hydration enthalpies
- 3 Ag + 4 HNO₃ → NO + 2 H₂O + AgNO₃ (soluble in water) ⇒ application as precursor for other silver salts and as Höllenstein

Ag(I)-halides

<table>
<thead>
<tr>
<th>AgX</th>
<th>Covalence</th>
<th>Solubility</th>
<th>Colour</th>
<th>Sensitivity to light</th>
</tr>
</thead>
<tbody>
<tr>
<td>AgCl</td>
<td></td>
<td></td>
<td>white</td>
<td></td>
</tr>
<tr>
<td>AgBr</td>
<td></td>
<td></td>
<td>yellowish-white</td>
<td></td>
</tr>
<tr>
<td>AgI</td>
<td></td>
<td></td>
<td>yellow</td>
<td>⇒ photosensitive pigments</td>
</tr>
</tbody>
</table>
Excursion: The Photographic Process

B/W as well as Colour Photography Require a Photosensitive Layer that Can Be Brought upon a Substrate as a Thin Layer (Film)

1. Fabrication

AgNO₃(aq) + KX(aq) → AgX↓(s) + KNO₃(aq)

(+) sensitizers

AgBr and AgI are yellow and absorb only in the blue region of the spectrum. The sensitizers absorb in the green, yellow and red region of the spectrum and transfer the energy into the conduction band of AgBr, so that all spectral colours trigger the reaction

ColloidalAgX, means finely distributed AgX (grain), upon transparent substrate (silver bromide gelatine)

⇒ potentially too insensitive to light
⇒ maturation with thiosulphate, S₂O₃²⁻ and NH₃
⇒ Formation of seed crystals, e.g. Ag₂S
⇒ considerable spike in photosensitivity

“seeds on nanometer scale“
Excursion: The Photographic Process

B/W and Colour Photography Are Based on the Photo Induced Reduction of AgBr Crystallites

2. Exposure

\[ n \text{AgBr(s)} \xrightarrow{hv} \text{Ag} + n \text{Br} \] (bound by gelatine)
Silver seeds → latent picture seed (10 – 100 Ag atoms)
latens (lat.) = concealed, hidden

3. Development

\[ 2 \text{AgX} + \text{hydroquinone} + 2 \text{OH}^- \rightarrow \text{Ag} + 2 \text{X}^- + \text{quinone} + 2 \text{H}_2\text{O} \]
Conversion of the latent picture to the actual visible picture by complete reduction of AgBr grains (~ 10^{12} Ag atoms)

4. Fixation

\[ \text{AgX} + 2 \text{S}_2\text{O}_3^{2-} \rightarrow [\text{Ag(S}_2\text{O}_3)_2]^{3-} + \text{X}^- \]
Removal of non-exposed AgX through treatment with fixing salt, Na_2S_2O_3
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Au(I)-compounds

- Halides: $\text{AuX} + \text{X}^- \rightarrow [\text{AuX}_2]^-$ (linear)
- Importance of cyaniding (→ presentations)

$$4 \text{Au} + 2 \text{H}_2\text{O} + \text{O}_2 + 8 \text{KCN} \rightarrow 4 \text{K[Au(CN)]}_2 + 4 \text{KOH}$$

(gold ore) (dicyanoaurate(I)-complex)

$$2 [\text{Au(CN)}_2] + \text{Zn} \rightarrow [\text{Zn(CN)}_4]^{2-} + 2 \text{Au}$$

(dust) (raw gold)

- The colourless $\text{Au}^+$-ion shows disproportionation in solution:

<table>
<thead>
<tr>
<th>Reduced form</th>
<th>$\Leftrightarrow$</th>
<th>Oxidised form</th>
<th>$+ e^-$</th>
<th>Standard potential $E^0$ [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2 \text{Au}$</td>
<td>$\Leftrightarrow$</td>
<td>$2 \text{Au}^+$</td>
<td>$+ 2e^-$</td>
<td>$+1.69$</td>
</tr>
<tr>
<td>$\text{Au}^+$</td>
<td>$\Leftrightarrow$</td>
<td>$\text{Au}^{3+}$</td>
<td>$+ 2e^-$</td>
<td>$+1.40$</td>
</tr>
</tbody>
</table>

$2 \text{Au}^+ + \text{Au}^+ \Leftrightarrow 2 \text{Au} + \text{Au}^{3+}$

$\Delta E = E^0_{\text{Au/Au}^+} - E^0_{\text{Au}^+/\text{Au}^{3+}} = +1.69 \text{ V} - 1.40 \text{ V} = +0.29 \text{ V}$
10. Chemistry of Transition Metals

Copper Group (Coinage Metals)

Au(III)-compounds

\[ \text{Au} + 3 \text{H}_3\text{O}^+ + 4 \text{Cl}^- + \text{HNO}_3 \rightarrow [\text{AuCl}_4]^- + \text{NO} + 5 \text{H}_2\text{O} \]

Evaporation leads to tetrachloro auric acid \( \text{H}[\text{AuCl}_4]3\text{H}_2\text{O} \)

\[ \Rightarrow \text{gold salt: Na}[\text{AuCl}_4]2\text{H}_2\text{O} \]

Gold cluster and colloidal gold

\[ 2 \text{Na}[\text{AuCl}_4]2\text{H}_2\text{O} + 3 \text{SnCl}_2 + 2 \text{H}_2\text{O} \rightarrow 2 \text{NaCl} + 12 \text{HCl} + 3 \text{SnO}_2 + \text{colloidal Au} \]

(Cassius’ gold purple)

\[ \text{Au}^{3+} + 3 \text{e}^- \rightarrow \text{Au} \rightarrow \text{Au}_{13} \rightarrow \text{Au}_{55} \text{ (cluster)} \rightarrow \text{Au}_n \text{ (with } n = 10^3 - 10^9, \text{ colloids 1 – 100 nm)} \]

Colloids can be detected by the Tyndall-effect (light scattering)
10. Chemistry of Transition Metals

Zinc Group

⇒ 2. subgroup or group 12 \((n-1)d^{10}ns^2\) with \(n = 4, 5, 6\)

The elements possess a relatively noble character, due to their full outer electron shell, which becomes particularly apparent for Hg.

Properties of the elements

<table>
<thead>
<tr>
<th>Element</th>
<th>(T_m[^{\circ}\text{C}])</th>
<th>Oxidation state</th>
<th>(r(M^{2+})) [pm]</th>
<th>(E^\circ) (M/M^{2+}) [V]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>419</td>
<td>+II</td>
<td>74</td>
<td>-0.76 (non-precious)</td>
</tr>
<tr>
<td>Cd</td>
<td>321</td>
<td>+II</td>
<td>97</td>
<td>-0.40 (non-precious)</td>
</tr>
<tr>
<td>Hg</td>
<td>-39</td>
<td>+I, +II</td>
<td>110</td>
<td>+0.85 (precious)</td>
</tr>
</tbody>
</table>

⇒ Hg is the only metal liquid at room temperature, exhibiting a vapour pressure of \(2.6 \cdot 10^{-3}\) mbar at that temperature.

Alloy

Brass          \(\text{Zn + Cu}\)
Amalgams       \(\text{Hg + Na and Hg + Zn}\) reducing agent at the lab
                 \(\text{Hg + Ag/Cu/Sn}\) dental filling
10. Chemistry of Transition Metals

**Zinc Group**

**Occurrence**

- **Zink (zinc spar)**
  - $\text{ZnS}$: sphalerite
  - $\text{ZnCO}_3$: zinc spar

- **Cadmium (Greek: kadmeia)**
  - $\text{CdS}$: greenocite
  - $\text{CdCO}_3$: otavite

- **Mercury (Greek: hydrargyrum)**
  - $\text{HgS}$: zinnober
  - $\text{Hg}\left[\text{Sb}_4\text{S}_7\right]$: levingstonite

  *Water silver, mobile, Mercury*

**Mineral name**

- **Zinc spar**
- **CdCO$_3$**
- **Hg[Sb$_4$S$_7$]**

**Preparation by calcination**

- **Zn/Cd:**
  $$2 \text{ZnS} + 3 \text{O}_2 \rightarrow 2 \text{ZnO} + 2 \text{SO}_2$$
  $$\text{ZnO} + \text{CO} \rightarrow \text{Zn} + \text{CO}_2$$

- **Hg:**
  $$\text{HgS} + \text{O}_2 \rightarrow \text{Hg} + \text{SO}_2$$
10. Chemistry of Transition Metals

Zinc Group

Reactions and applications of Zinc

- Soluble in acids and bases (amphoteric character of Zn(OH)\(_2\)) under development of H\(_2\):
  \[ \text{Zn} + 2 \text{H}^+ \rightarrow \text{Zn}^{2+} + \text{H}_2 \uparrow \]
  \[ \text{Zn} + 2 \text{OH}^- + 2 \text{H}_2\text{O} \rightarrow [\text{Zn(OH)}_4]^{2-} + \text{H}_2 \uparrow \]

- Highly pure Zinc (99.999\%) is not attacked any more (H\(_2\)-overvoltage 0.7 V, kinetic inhibition of the discharge of H\(_3\)O\(^+\) ions upon the Zinc surface)

Therefore: \( \text{Zn} + \text{dil. HCl} \rightarrow \text{very weak development of H}_2 \)
But: \( \text{Zn} + \text{Cu}^{2+} + \text{dil. HCl} \rightarrow \text{violent development of H}_2 \)

Explanation: \( \text{Zn} + \text{Cu}^{2+} \rightarrow \text{Cu} + \text{Zn}^{2+} \Rightarrow \) Copper precipitates upon the Zinc \( \Rightarrow \) zinc surface is occupied by Cu \( \Rightarrow \) local elements are formed

Metals more precious than Zinc catalyse the solvation of Zn, which is why corrosion inhibition by galvanization works

Redox pair \hspace{1cm} E\(^0\) [V]

Zn/Zn\(^{2+}\) \hspace{1cm} -0.76
Fe/Fe\(^{2+}\) \hspace{1cm} -0.41
10. Chemistry of Transition Metals

Zinc Group

Zinc(II)-compounds

- Zinc sulphate heptahydrate “zinc vitriol“
  \[ \text{ZnSO}_4 \cdot 7\text{H}_2\text{O} = [\text{Zn(H}_2\text{O)}_6]\cdot\text{H}_2\text{O} \]
- Zinc oxide “zinc white“: pigment with wurtzite-like structure
  \[ \text{ZnO} \rightarrow \text{ZnO:Zn} \text{ (yellow)} \quad \Rightarrow \quad \text{Upon heating, anion defects occur} \]
  \[ \text{ZnO} + \text{Co}_2\text{O}_3 \rightarrow \text{ZnCo}_2\text{O}_4 \text{ (Rinmans’ green)} \quad \Rightarrow \quad \text{normal spinel} \]
- Zink sulphide: dimorphous white pigment \( \Rightarrow \) zinc blende (sphalerite) \( \rightleftharpoons \) wurtzite
  Zinc blende: cubic close packing of anions
  Wurtzite: hexagonal close packing of anions
  Doping results in a variety of phosphors:
  \[
  \begin{align*}
  \text{ZnS:Ag} & \quad 450 \text{ nm} \\
  \text{ZnS:Cu,Al,Au} & \quad 530 \text{ nm} \\
  \text{ZnS:Mn} & \quad 580 \text{ nm}
  \end{align*}
  \]
  \( \Rightarrow \) application in RGB cathode ray tubes and electroluminescence screens
10. Chemistry of Transition Metals

Zinc Group

Reactions and applications of Cadmium

- Cd(OH)₂ in contrary to Zn(OH)₂ is not amphoteric!
  \[ \text{Cd}^{2+} + 2 \text{OH}^- \rightarrow \text{Cd(OH)}_2 \downarrow \text{OH}^- \rightarrow \text{no reaction} \]
  \[ \text{NH}_3 \]
  \[ \text{[Cd(NH}_3\text{)}_6\text{]}^{2+} + 2 \text{OH}^- \]

- Cd²⁺ can be detected next to Cu²⁺ ⇒

\[ \text{Cu}^{2+}/\text{Cd}^{2+} + \text{NH}_3 \]
\[ \rightarrow \text{[Cu(NH}_3\text{)}_4\text{]}^{2+} + \text{[Cd(NH}_3\text{)}_6\text{]}^{2+} \]
\[ + \text{CN}^- \rightarrow \text{(discolouration)} \]
\[ \rightarrow \text{[Cu(CN)}_4\text{]}^{3-} + \frac{1}{2} \text{(CN)}_2 + \text{[Cd(CN)}_4\text{]}^{2-} \]
\[ + \text{S}^{2-} \rightarrow \text{CdS} \downarrow \text{yellow} \]

- Cadmium sulphide, CdS, and Cadmium selenide, CdSe, are used as pigments and quantum dots
10. Chemistry of Transition Metals

**Zinc Group**

**Redox chemistry of mercury**
- Hg forms Hg\(^+\) and, as Hg\(^{2+}\), salts
  - \(2 \text{Hg} \rightleftharpoons \text{Hg}^{2+} + 2 \text{e}^-\), \(E^0 = +0.79\) V
  - \(\text{Hg}^{2+} \rightleftharpoons 2 \text{Hg}^{2+} + 2 \text{e}^-\), \(E^0 = +0.91\) V
  - \(\text{Hg} \rightleftharpoons \text{Hg}^{2+} + 2 \text{e}^-\), \(E^0 = +0.85\) V
- Hg\(^+\)-salts contain dimeric Hg\(^{2+}\) (metal-metal bonds!)
- Hg\(^{2+}\) does not disproportionate, but reagents that drastically reduce the concentration of Hg\(^{2+}\) (precipitation agents (OH\(^-\), S\(^2-\)) or complexing agents (CN\(^-\))) lead to disproportionation

**Application of Hg in:**
- Hg-low pressure discharge lamps (1 – 5 mg)
  - Fluorescent tubes, compact fluorescent lamps
- Hg-high pressure discharge lamps (> 10 mg)
  - Street lighting, projector, head lights
- Thermo- and barometer
- Hg-switch
- Amalgams
10. Chemistry of Transition Metals

Zinc Group

Mercury(I)-compounds

- \( \text{Hg}_2(\text{NO}_3)_2 \) is soluble

- Halides: \( \text{Hg}_2\text{X}_2 \) (with X = Cl, Br, I) are poorly soluble

\[
\begin{align*}
\text{Hg}_2(\text{NO}_3)_2 & \quad \text{dil. HNO}_3 \quad \rightarrow \quad [\text{H}_2\text{O-Hg-Hg-OH}_2]^2+ \\
\text{Mercury(I)-nitrate} & \quad \text{Diaquamercury(I)-complex} \nearrow \text{Mercury(I)-chloride}
\end{align*}
\]

- Mercury(I)-chloride is also called calomel (deep black), since a black colour arises upon treatment with \( \text{NH}_3 \)

\[
\begin{align*}
\text{Hg}_2\text{Cl}_2 + 2 \text{NH}_3 & \quad \rightarrow \quad [\text{HgNH}_2]\text{Cl} + \text{Hg}↓ + \text{NH}_4^+ + \text{Cl}^- \\
\text{white} & \quad \text{(black)}
\end{align*}
\]

- The calomel electrode (\( \text{Hg}/\text{Hg}_2\text{Cl}_2/\text{Cl}^- \)) is a regularly used reference electrode in electrochemistry
Zinc Group

Mercury(II)-compounds
- Hg(II)-salts are highly covalent and thus poorly soluble
- Only HgF$_2$ and Hg(NO$_3$)$_2$ are built ionicly
- Hg + O$_2$ → HgO (red)
- Hg$^{2+}$ + 2 OH$^-$ → H$_2$O + HgO (yellow) ⇒ smaller particles
- HgCl$_2$ (sublimate) is white, melts at 280 °C and boils at 303 °C!
  ⇒ molecular lattice consists of linear Cl-Hg-Cl molecules
- HgI$_2$ is dimorphous: α-HgI$_2$(red) ⇄ β-HgI$_2$(yellow) at T = 127 °C
  It reacts with excess I$^-$ to the tetraiodomercurate anion:
  HgI$_2$ + 2 I$^-$ → [HgI$_4$]$^{2-}$
- Nessler’s reagent: solution of K$_2$HgI$_4$ in potash lye
  for the detection of ammonia: 2 K$_2$HgI$_4$ + NH$_3$ → [Hg$_2$N]I + 4 KI + 3 HI
  (orange to brown)
- [HgI$_4$]$^{2-}$ + 2 Ag$^+$ → Ag$_2$[HgI$_4$]$\downarrow$ (yellow)
  35 °C ⇄ Ag$_2$[HgI$_4$] (orange-red)
- [HgI$_4$]$^{2-}$ + 2 Cu$^+$ → Cu$_2$[HgI$_4$]$\downarrow$ (red)
  70 °C ⇄ Cu$_2$[HgI$_4$] (black) ⇒ thermochromism
Titanium Group

4. Sub group / group 4 \((n-1)d^2 ns^2\) with \(n = 4, 5, 6\)

Those elements are highly reactive and do react with \(N_2\) and \(H_2\) at elevated temperatures

Properties of the elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Density [g/cm(^3)]</th>
<th>(T_m^\circ) [°C]</th>
<th>(T_b^\circ) [°C]</th>
<th>Oxidation state</th>
<th>(r(M^{4+})) [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>4.54</td>
<td>1670</td>
<td>~3350</td>
<td>+II, +III, +IV</td>
<td>61</td>
</tr>
<tr>
<td>Zr</td>
<td>6.51</td>
<td>1850</td>
<td>~4400</td>
<td>+IV</td>
<td>72</td>
</tr>
<tr>
<td>Hf</td>
<td>13.31</td>
<td>2230</td>
<td>~4700</td>
<td>+IV</td>
<td>71</td>
</tr>
</tbody>
</table>

Zr and Hf resemble one another in terms of chemistry, which is why they are often associated with one another

Ti-alloys (DIN 17851)

<table>
<thead>
<tr>
<th>Element</th>
<th>Oxidation state</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>+II, +III, +IV</td>
</tr>
</tbody>
</table>

\(\Rightarrow\) Aviation industry, ship building, chemical plant construction, engines, implants….
## 10. Chemistry of Transition Metals

### The Titanium Group

**Occurrence**

Titanium (Titans)  
*Gods/giants in Greek myth.*  
\[ \text{TiO}_2 \] (Rutile)  
\[ \text{FeTiO}_3 \] (Ilmenite)  
\[ \text{CaTiO}_3 \] (Perovskite)  
\[ \text{CaTiO}[\text{SiO}_4] \] (Titanite)

Zirconium (name of mineral)  
*Named after the mineral zircon*  
\[ \text{ZrO}_2\text{(monoclinic)} \] (Baddeleyite)  
\[ \text{ZrO}_2\text{(tetragonal)} \]  
> 1100 °C  
\[ \text{ZrO}_2\text{(cubic)} \]  
> 2350 °C  
\[ \text{ZrSiO}_4 \] (Zircon)

Hafnium (Hafnia)  
*Copenhagen*  
*(lat.: Hafnia)*  
always a companion in Zr-minerals
10. Chemistry of Transition Metals

The Titanium Group

Synthesis

Lab synthesis: \[ \text{TiO}_2 + 2 \text{CaH}_2 \rightarrow \text{Ti} + 2 \text{H}_2 + 2 \text{CaO} \]
Kroll process: \[ \text{TiCl}_4 + 2 \text{Mg} \rightarrow \text{Ti} + 2 \text{MgCl}_2 \]

• Titanium is separated from the blend of Titanium, Magnesium dichloride, and Magnesium residues by high temperature vacuum sintering

• Magnesium dichloride is cleaved into Mg and Cl\(_2\) by electrolysis

• The resulting material is brittle and porous \(\rightarrow\) Titanium sponge

Arkel-de Boer process: \(\text{TiI}_4 \Leftrightarrow \text{Ti} + 2 \text{I}_2\) (hot W-wire) \(\Rightarrow\) Highly purified Titanium

Zirconium Zr and Hafnium Hf

More or less analogue to Titanium
10. Chemistry of Transition Metals

The Titanium Group

Titan(IV)-compounds

- [Ar]-configuration ⇒ most stable oxidation state, colourless
- Ti⁴⁺ is small and highly charged ⇒ strongly polarising (high ionic charge density)
  \[ \text{Ti}^{4+} + 6 \text{H}_2\text{O} \rightarrow 2 \text{H}^+ + [\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+} \text{“cation base“} \]

In aqueous solution, there are thus no Ti⁴⁺ cations but aquahydroxo complexes that can be verified by the reaction with H₂O₂:
  \[ [\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+} + \text{H}_2\text{O}_2 \rightarrow [\text{Ti(O)}_2(\text{OH})_2]^{2+} + 2 \text{H}_2\text{O} \]
  (orange-yellow)

- Treatment of TiO₂ with HNO₃ or H₂SO₄ yields double salts
  \[ \text{TiO}_2 + \text{H}_2\text{SO}_4 \rightarrow \text{TiO(SO}_4) + \text{H}_2\text{O} \]
  \[ \text{TiO}_2 + 2 \text{HNO}_3 \rightarrow \text{TiO(NO}_3)_2 + \text{H}_2\text{O} \]
  that contain polmeric Ti-O-Ti-O-Ti zig-zag chains

- However, the reaction of Ti⁴⁺-containing solutions with oxalates yield tetraters
  \[ 4 [\text{Ti(OH)}_2(\text{OH}_2)_4]^{2+} + 8 \text{C}_2\text{O}_4^{2-} \rightarrow [\text{Ti}_4\text{O}_4(\text{C}_2\text{O}_4)_8]^{8-} \]
10. Chemistry of Transition Metals

The Oxide Ion $O^{2-}$ as Ligand

1. Terminal oxo groups
   - Vanadyl cation: $[V=O]^+$
   - Permanganate anion: $[MnO_4]^-$

2. $\mu_2$-oxo-groups
   - $M - O - M$ or $M \ M \ M$
   - $[L_2Fe_2(catecholate)_2(\mu_2-O)]$ with $L = 1,4,7$-trimethyl-1,4,7-triazacyclononane
   - $[Cr_2O_6(\mu_2-O)]^{2-}$

3. $\mu_3$-oxo-groups
   - $[Mn_3(\mu_3-O)(\mu_2-CH_3COO)_6]^+$
   - $[Hg_3Cl_3(\mu_3-O)]^+$

4. $\mu_4$-oxo-groups
   - $[Be_4(\mu_4-O)(\mu-CH_3COO)_6]$
   - $[Be_4(\mu_4-O)(\mu-NO_3)_6]$
10. Chemistry of Transition Metals

The Titanium Group

Titandioxid TiO$_2$

Synthesis → see presentations

Structure

• Ti is coordinated octahedrally by O
• 3 modifications: rutile, brookite, anatase
  ⇒ Different connectivity of TiO$_2$-octahedra

Properties

• Photocatalytic activity
  TiO$_2$ + hv → TiO$_2$*(e$^-$ + h$^+$)
  TiO$_2$*(e$^-$ + h$^+$) + A + D → TiO$_2$ + A$^-$ + D$^+$
• High refractive index:

<table>
<thead>
<tr>
<th>Modification</th>
<th>$E_g$ [eV]</th>
<th>$E_g$ [nm]</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anatase</td>
<td>3.5</td>
<td>360</td>
<td>2.55</td>
</tr>
<tr>
<td>Rutile</td>
<td>3.2</td>
<td>390</td>
<td>2.79</td>
</tr>
</tbody>
</table>
Excursion: Ferroelectrics and Perowskites

Perowskites $\text{ABX}_3$

$\Rightarrow$ CaTiO$_3$, SrTiO$_3$, BaTiO$_3$, PbTiO$_3$, KIO$_3$, LaCoO$_3$, ...

- Cubic primitive unit cell
  i.e. $\alpha = \beta = \gamma = 90^\circ$, $a = b = c$
- Corner connected TiO$_6$-octhedra
- Me$^+$, Me$^{2+}$, Me$^{3+}$ occupy twelvefold coordinate voids

Ferroelectrics

$\Rightarrow$ Possess areas (domains) in the crystal which are uniformly polarised in one spatial dimension
- These domains exhibit a permanent dipole moment
- Throughout the whole crystal, the differently polarized domains are distributed statistically $\Rightarrow$ compensation dipole moments
- When introduced to an electrical field, the dipole moments are going to align themselves
  $\Rightarrow$ The orientation partly persists even after the cut-off of the electrical field (storage effect)

$\Rightarrow$ Ferroelectricity (cooperative phenomenon)
- BaTiO$_3$ is particularly ferroelectric ($\varepsilon \sim 1000$) $\Rightarrow$ application in capacitors
The Titanium Group

Zirconium- and Hafnium-compounds

• In compounds, Zr and Hf are mostly tetravalent
• ZrO$_2$ and HfO$_2$ possess high melting points and are poorly soluble (only in H$_2$SO$_4$):
  \[ \text{ZrO}_2 + 2 \text{H}_2\text{SO}_4 \rightarrow \text{Zr(SO}_4)_2 + 2 \text{H}_2\text{O} \]
• ZrX$_4$ and HfX$_4$ with X = F, Cl, Br, I known
• ZrX$_4$ + H$_2$O $\rightarrow$ ZrOCl$_2$·8 H$_2$O (tetramer: [Zr$_4$(OH)$_8$(H$_2$O)$_{16}$]$^{8+}$ 8Cl$^{-}$·12H$_2$O)

Application of Zirconium and Hafnium

• ZrO$_2$/CaO, MgO fire-resistant tools (crucibles, furnaces)
• ZrO$_2$/Y$_2$O$_3$ $\lambda$-probe (→ presentations)
  fuel cell
  Nernst-stick: IR-radiation source
• La$_2$Hf$_2$O$_7$·Ce Scintillators
10. Chemistry of Transition Metals

The Vanadium Group

5. Sub group or group 5 ⇒ 5 valence electrons

Vanadium [Ar]3d^34s^2
Niobium [Kr]4d^45s^1
Tantalum [Xe]4f^145d^36s^2

Properties of the elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Density [g/cm^3]</th>
<th>T_m [° C]</th>
<th>T_b [° C]</th>
<th>Oxidation state</th>
<th>r(M^{5+}) [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>6.11</td>
<td>1910</td>
<td>3407</td>
<td>+II, +III, +IV, +V</td>
<td>54</td>
</tr>
<tr>
<td>Nb</td>
<td>8.58</td>
<td>2477</td>
<td>4744</td>
<td>(+III, +IV), +V</td>
<td>64</td>
</tr>
<tr>
<td>Ta</td>
<td>16.65</td>
<td>3017</td>
<td>5458</td>
<td>(+III, +IV), +V</td>
<td>64</td>
</tr>
</tbody>
</table>

Stability of the oxidation state +V strongly increases from V to Ta!

Alloys

- Vanadium steel
  Fe + V (up to 0.5%) tool steel
- Ferro-Niobium
  Nb + Fe (28 – 33.5%) steel construction
- Tantalum-Niobium-steel
  Ta + Fe rocket engines
- Tantalumcarbide
  Ta + C cutting tool
10. Chemistry of Transition Metals

The Vanadium Group

Occurrence
Vanadium (Vanadis)  VS₄  Patronite
Byname of Nordic goddess Freya  Pb₅(VO₄)₃  Vanadinite

Niobium (Niobe)  (Fe,Mn)(Nb,Ta)₂O₆ Columbite
Daughter of Tantalus

Tantalum (Tantalus)  (Fe,Mn)(Nb,Ta)₂O₆ Tantalite
Greek saga figure

Vanadium synthesis and purification
4 VS₄ + 2 Na₂CO₃ + 21 O₂ → 4 NaVO₃ + 16 SO₂ + 2 CO₂
NaVO₃ + H₂O → polyvanadates + NaOH
Heating of polyvanadates upon 700° C → V₂O₅
V₂O₅ + 5 Ca → 2 V + 5 CaO
Arkel-de Boer process
2 V + 5 I₂ ⇄ 2 VI₅ ⇒ high purity Vanadium
10. Chemistry of Transition Metals

The Vanadium Group

Properties and reactions of Vanadium

• Four stable oxidation states

⇒ Versatile redox chemistry:

\[
[(\text{H}_2\text{O})_4\text{V(O)}_2]^+ + e^- + 2 \text{H}^+ \rightleftharpoons [(\text{H}_2\text{O})_5\text{V=O}]^{2+} \quad E^0 = +1.0 \text{ V} \quad \text{by SO}_2
\]

(cis, colourless) \quad (deep blue)

\[
[(\text{H}_2\text{O})_5\text{V=O}]^{2+} + e^- + 2 \text{H}^+ \rightleftharpoons [\text{V(H}_2\text{O)}_6]^{3+} \quad E^0 = +0.36 \text{ V} \quad \text{by Zn}
\]

(deep blue) \quad (grey green)

\[
[\text{V(H}_2\text{O)}_6]^{3+} + e^- \rightleftharpoons [\text{V(H}_2\text{O)}_6]^{2+} \quad E^0 = -0.26 \text{ V} \quad \text{by Zn under Ar}
\]

(grey green) \quad (violet)

• \text{VO}_4^{3-} \text{ in aqueous solution:}

\begin{align*}
\text{pH} > 13 & \quad \text{VO}_4^{3-} \\
\text{pH} 6 – 13 & \quad 2 \text{HVO}_4^{2-} \rightleftharpoons \text{V}_2\text{O}_7^{4-} + \text{H}_2\text{O} \\
& \quad 3 \text{H}_2\text{VO}_4^- \rightleftharpoons \text{V}_3\text{O}_9^{3-} + 3 \text{H}_2\text{O} \\
& \quad 4 \text{H}_2\text{VO}_4^- \rightleftharpoons \text{V}_4\text{O}_{12}^{4-} + 4 \text{H}_2\text{O} \\
\text{pH} 2 – 6 & \quad \text{formation of V}_6\text{O}_{16}^{2-} \text{ and V}_{10}\text{O}_{28}^{6-} \text{-anions}
\end{align*}
10. Chemistry of Transition Metals

The Vanadium Group

Isopoly acids
- Oxo acids of transition metals that contain only one kind of metal
- Formation through condensation of metal anions
- Built up by corner or edge connected metal-oxo-polyhedra

Examples: $[\text{V}_{10}\text{O}_{28}]^{6-}$, $[\text{Cr}_2\text{O}_7]^{2-}$, $[\text{Mo}_7\text{O}_{24}]^{6-}$, $[\text{H}_2\text{W}_{12}\text{O}_{42}]^{10-}$

Heteropoly acids
- Isopoly acids where the central atom is an hetero atom
- They form through intercalation of hetero atoms in tetrahedra and octahedra voids
- The hetero atom can be a non-metal or a transition metal

<table>
<thead>
<tr>
<th>Class</th>
<th>X:M</th>
<th>Hetero Group</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{X}^{n+}\text{M}<em>{12}\text{O}</em>{40}]^{(8-n)-}$ “α-Keggin-structures“</td>
<td>1:12</td>
<td>XO$_4$</td>
<td>$[\text{PMo}<em>{12}\text{O}</em>{40}]^{3-}$</td>
</tr>
<tr>
<td>$[\text{X}^{n+}\text{M}<em>6\text{O}</em>{24}]^{(12-n)-}$</td>
<td>1:6</td>
<td>XO$_6$</td>
<td>$[\text{IW}<em>6\text{O}</em>{24}]^{5-}$</td>
</tr>
</tbody>
</table>

with M = V, Cr, Mo, W and X = B, P, Si, I
The Vanadium Group

Properties and reactions of Niobium and Tantalum

- The oxidation state +V is most stable
- In low oxidation states, preferably clusters are formed

\[
14 \text{NbCl}_5 + 16 \text{Nb} + 20 \text{NaCl} \rightarrow 5 \text{Na}_4[\text{Nb}_6\text{Cl}_{18}] \quad (12 \text{h at } 850 \, ^\circ \text{C})
\]

"octahedral Nb\textsubscript{6}-cluster"

Definition of Cluster:
Higher molecular aggregates of transition metal compounds, where the metal centres are linked by M-M-bonds

M-M
M≡M
M≡M

In rare cases also quadruple bonds between the transition metals can be observed
10. Chemistry of Transition Metals

The Vanadium Group

Biological aspects

- **Amavadin**
  In fungus amanita muscaria (fly agaric)

- **Tunicates ("coat animals")** use vanadocytes for their oxygen transportation, that contain Vanadium ions instead of Iron(II)-ions

- **Peroxidases**, in their active form, contain Vanadium(V)-ions in trigonal-bipyramidal coordination

- **Nitrogenases**
  Some variations contain Mo-V-clusters

- **Insulin mimetics**
10. Chemistry of Transition Metals

The Chromium Group

6. Sub group or group 6 ⇒ 6 valence electrons
Chromium [Ar]3d⁵⁴s¹ Molybdenum [Kr]4d⁵⁵s¹ Tungsten [Xe]4f¹⁴d⁴⁶s²

⇒ An half-filled d-shell is reached by a change in electron configuration for Cr and Mo

Properties of the elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Density [g/cm³]</th>
<th>Tₘ [°C]</th>
<th>Tₘ [°C]</th>
<th>Oxidation state</th>
<th>r(M⁶⁺) [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cr</td>
<td>7.18</td>
<td>1903</td>
<td>2640</td>
<td>+II, +III, +VI</td>
<td>44</td>
</tr>
<tr>
<td>Mo</td>
<td>10.22</td>
<td>2620</td>
<td>4825</td>
<td>+IV, +VI</td>
<td>59</td>
</tr>
<tr>
<td>W</td>
<td>19.3</td>
<td>3410</td>
<td>5700</td>
<td>+IV, +VI</td>
<td>60</td>
</tr>
</tbody>
</table>

Lower oxidation states are accessible via π-acceptor ligands, e.g. Chromium-hexacarbonyl [Cr(CO)₆]

M-C≡O ⇔ M=C=O

σ-donor- and π-back bonding
## 10. Chemistry of Transition Metals

### The Chromium Group

<table>
<thead>
<tr>
<th>Occurrence</th>
<th>Chemical Formulas</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chromium (Chromos)</td>
<td>FeCr$_2$O$_4$</td>
</tr>
<tr>
<td>Byname of Nordic goddess Freya</td>
<td>PbCr$_2$O$_4$</td>
</tr>
<tr>
<td>Molybdenum (Molybdos)</td>
<td>MoS$_2$</td>
</tr>
<tr>
<td>Lead</td>
<td>PbMoO$_4$</td>
</tr>
<tr>
<td>Tungsten (lat.: lupi spume)</td>
<td>(Mn,Fe)WO$_4$</td>
</tr>
<tr>
<td>Wolf-foam, wolf-cream</td>
<td>CaWO$_4$</td>
</tr>
</tbody>
</table>

### Synthesis

- Chromium through thermite process:
  \[
  \text{Cr}_2\text{O}_3 + 2 \text{Al} \rightarrow \text{Al}_2\text{O}_3 + 2 \text{Cr}
  \]
- Ferrochromium (Chromium-iron-steel) by reduction with coke:
  \[
  \text{FeCr}_2\text{O}_4 + 4 \text{C} \rightarrow \text{Fe} + 2 \text{Cr} + 4 \text{CO}
  \]
- Molybdenum/Tungsten by reduction of the oxides with hydrogen:
  \[
  \text{MO}_3 + 3 \text{H}_2 \rightarrow \text{M} + 3 \text{H}_2\text{O}
  \]

Scheelit shows Blue luminescence
The Chromium Group

Properties and reactions of Chromium

Oxidation state +II
- \( \text{Cr} + 2 \text{HCl} \rightarrow \text{Cr}^{2+} + 2 \text{Cl}^- + \text{H}_2 \)
- \( \text{CrCl}_2 \) is stable in \( \text{H}_2\text{O} \) under the exclusion of air \( \Rightarrow \) Formation of \([\text{Cr(H}_2\text{O})_6]^{2+}\) (sky blue)
- \( \text{Cr}^{2+} \) is a strong reduction agent: \( \text{Cr}^{2+} \rightarrow \text{Cr}^{3+} + e^- \) \( E^0 = -0.41 \text{ V} \)
- \( \text{Cr}^{2+} \)-complexes are kinetically unstable and exhibit Jahn-Teller distortion

Oxidation state +III
- \( \text{Cr}^{3+} \) exists in aqueous solution as hexaaquochromium(III)-ion which reacts acidic
  \( [\text{Cr(H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} \Leftrightarrow [\text{Cr(H}_2\text{O})_5(\text{OH})]^{2+} + \text{H}_3\text{O}^+ \) \( pK_S = 4.0 \)
- Chromium(III)-chloride in aqueous solution is transformed into its hydration isomers
  \( [\text{CrCl}_3(\text{H}_2\text{O})_3]^{0.3\text{H}_2\text{O}} \Leftrightarrow [\text{CrCl}_2(\text{H}_2\text{O})_4]^+ + 2 \text{H}_2\text{O} + \text{Cl}^- \Leftrightarrow [\text{CrCl}(\text{H}_2\text{O})_5]^{2+} + \text{H}_2\text{O} + 2 \text{Cl}^- \) (dark green) (dark green) (light blue green)
  \( \Leftrightarrow [\text{Cr(H}_2\text{O})_6]^{3+} + 3 \text{Cl}^- \Rightarrow \) slow ligand exchange, because \( \text{Cr}^{3+} \) is kinetically inert (violet)
- \( \text{Cr}^{3+} \) is stable in acidic and neutral conditions, but is easily oxidised in basic surroundings
  \( 2 \text{Cr}^{3+} + 7 \text{H}_2\text{O} \rightarrow \text{Cr}_2\text{O}_7^{2-} + 6 \text{e}^- \) \( E^0 = +1.33 \text{ V at pH} = 0 \)
  \( 2 \text{Cr(OH)}_3 + 5 \text{OH}^- \rightarrow \text{CrO}_4^{2-} + 4 \text{H}_2\text{O} + 3 \text{e}^- \) \( E^0 = +0.13 \text{ V at pH} = 14 \)
10. Chemistry of Transition Metals

The Chromium Group

Properties and reactions of Chromium

Oxidation state +VI

- Forms from oxidising melts of Cr³⁺-salts:
  \[
  2 \text{Cr}_2\text{O}_3 + 4 \text{Na}_2\text{CO}_3 + 3 \text{O}_2 \rightarrow 4 \text{Na}_2\text{CrO}_4 + 4 \text{CO}_2
  \]
  \[
  \text{Cr}_2\text{O}_3 + 2 \text{Na}_2\text{CO}_3 + 3 \text{KNO}_3 \rightarrow 2 \text{Na}_2\text{CrO}_4 + 3 \text{KNO}_2 + 2 \text{CO}_2
  \]

- Chromate-dichromate-equilibrium:
  \[
  \text{Cr}_2\text{O}_7^{2-} + \text{H}_2\text{O} \rightleftharpoons 2 \text{HCrO}_4^{-} \rightleftharpoons 2 \text{CrO}_4^{2-} + 2 \text{H}^{+}
  \]
  \[
  \text{(orange red)} \quad \text{(yellow)}
  \]

- Chromic acid, \(\text{H}_2\text{CrO}_4\), can be drained to the anhydride:
  \[
  \text{H}_2\text{CrO}_4 + \text{H}_2\text{SO}_4 \text{(conc.)} \rightarrow \text{CrO}_3 + \text{H}_3\text{O}^{+} + \text{HSO}_4^{-}
  \]
  \[
  \text{(red)}
  \]

- Chromate oxidises primary alcohols to aldehydes:
  \[
  2 \text{CrO}_4^{2-} + 3 \text{CH}_3\text{CH}_2\text{OH} + 10 \text{H}^{+} \rightarrow 2 \text{Cr}^{3+} + 3 \text{CH}_3\text{CHO} + 8 \text{H}_2\text{O}
  \]

- Heating of dichromate with alkali metal chlorides in sulphuric acid yields chromyl chloride:
  \[
  \text{K}_2\text{Cr}_2\text{O}_7 + 4 \text{KCl} + 3 \text{H}_2\text{SO}_4 \rightarrow 2 \text{CrO}_2\text{Cl}_2 + 3 \text{K}_2\text{SO}_4 + 3 \text{H}_2\text{O}
  \]
  \[
  \text{(deep red oil)}
  \]
The Chromium Group

Properties and reactions of chromium

Oxidation state +VI
- Treatment of chromate solutions with $\text{H}_2\text{O}_2$ yields Chromium(VI)-peroxide:
  \[
  \text{HCrO}_4^- + 2 \text{H}_2\text{O}_2 + \text{H}_3\text{O}^+ \quad \rightleftharpoons \quad \text{CrO(O}_2\text{)}_2 + 4 \text{H}_2\text{O} \\
  \quad \text{(deep blue)}
  \]
- The unstable Cr(VI)-peroxide can be stabilised by the formation of an adduct with diethylether or pyridine
  \[
  \text{CrO(O}_2\text{)}_2 + \text{Et}_2\text{O} \quad \rightarrow \quad [\text{CrO(O}_2\text{)}_2(\text{Et}_2\text{O})] \\
  \quad \text{(pentagonal-pyramidal)}
  \]

Oxidation state +V
- Known are: Li$_3$CrO$_4$, Na$_3$CrO$_4$ and CrF$_5$
- Reaction of $\text{H}_2\text{O}_2$ with alkaline alkali metal chromate solutions results in peroxochromate(V) M$_3$CrO$_8$
  \[
  [\text{Cr(O}_2\text{)}_4]^{3-} + 2 \text{H}_3\text{O}^+ \quad \rightleftharpoons \quad [\text{CrO(O}_2\text{)}_2(\text{OH})]^{\text{+}} + 1.5 \text{H}_2\text{O}_2 + \text{H}_2\text{O} \\
  \quad \text{(red brown, dodecahedral) (blue violet)}
  \]
## 10. Chemistry of Transition Metals

### The Chromium Group

#### Solubility of Chromium compounds

<table>
<thead>
<tr>
<th>Charge</th>
<th>Compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>+II</td>
<td>CrCl$_2$</td>
</tr>
<tr>
<td>+III</td>
<td>CrCl$_3$·6H$_2$O (complex salts)</td>
</tr>
<tr>
<td>+VI</td>
<td>Na$_2$CrO$_4$, K$_2$Cr$_2$O$_7$</td>
</tr>
</tbody>
</table>

Poorest soluble Chromium(III)-salts can be transformed into more readily soluble compounds by oxidation or reduction:

- $\text{CrCl}_3 + \text{e}^- \rightleftharpoons \text{CrCl}_2 + \text{Cl}^-$
- $\left[\text{Cr(H}_2\text{O)}_6\right]^{3+} + \text{e}^- \rightleftharpoons \left[\text{Cr(H}_2\text{O)}_6\right]^{2+}$

$d^3$ kinetically stable $\rightarrow$ $d^4$ kinetically labile

Similar is true for poorly soluble Iron(III)- and Manganese(IV)-compounds:

$\Rightarrow$ Of importance for the assimilation of Fe (Fe$_2$O$_3$) and Mn (MnO$_2$) from soil

**Trick:** Addition of $M^{2+}$-salts to poorly soluble $M^{3+}$-salts increases the solubility through the transfer of electrons on the crystal surfaces
10. Chemistry of Transition Metals

The Chromium Group

Optical spectra of Chromium(III)-compounds

\[
\begin{align*}
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
-2 & -1 & 0 & 1 & 2 \\
3d \\
S & = \Sigma s = 3/2 \\
L & = |\Sigma l| = 1 \\
\uparrow & \uparrow & \uparrow & \uparrow & \uparrow \\
-2 & -1 & 0 & 1 & 2 \\
3d \\
S & = \Sigma s = 3/2 \\
L & = |\Sigma l| = 3 \\
\end{align*}
\]

<table>
<thead>
<tr>
<th>Complex</th>
<th>10 Dq [cm(^{-1})]</th>
<th>en = ethylenediamine</th>
<th>ox = oxalate (C_2O_4^{2-})</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Cr(CN)}_6]^{3-})</td>
<td>26700</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Cr(en)}_3]^{3+})</td>
<td>21900</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{Cr(ox)}_3]^{3-})</td>
<td>17500</td>
<td></td>
<td></td>
</tr>
<tr>
<td>([\text{CrF}_6]^{3-})</td>
<td>14900</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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

\([\text{Cr(ox)}_3]^{3-}\)

\([\text{CrF}_6]^{3-}\)
10. Chemistry of Transition Metals

The Chromium Group

Optical spectra of with Cr(III) doped solid state materials (oxides)

- $\text{Al}_2\text{O}_3$:$\text{Cr}$ (693 nm) $\Rightarrow$ ruby $\sim$ 0.1% Cr$^{3+}$ $\Rightarrow$ ruby-LASER
- $\text{Y}_3\text{Al}_5\text{O}_{12}$:$\text{Cr}$ (688 nm)
- $\text{LiAlO}_2$:$\text{Cr}$ (690 nm)
- $\text{BaMgAl}_{10}\text{O}_{17}$:$\text{Cr}$ (695 nm)
- $\text{Lu}_3\text{Al}_5\text{O}_{12}$:$\text{Cr}$ (704 nm)
- $\text{Y}_3\text{Ga}_5\text{O}_{12}$:$\text{Cr}$ (730 nm)
- $\text{LaAlO}_3$:$\text{Cr}$ (735 nm)
- $\text{Gd}_3\text{Ga}_5\text{O}_{12}$:$\text{Cr}$ (745 nm)

Weak influence of the crystal field on the exact position of the 3d-3d emission lines!
10. Chemistry of Transition Metals

The Chromium Group

Properties and reactions of Molybdenum and Tungsten

- MoO$_3$ and WO$_3$ are insoluble in water and acids, but soluble in alkaline lyes:
  \[ \text{MoO}_3 + 2 \text{OH}^- \rightarrow \text{MoO}_4^{2-} + \text{H}_2\text{O} \]

- At pH 6 and below isopoly anions are formed:
  
  \[
  \begin{align*}
  7 \text{MoO}_4^{2-} + 8 \text{H}^+ & \rightarrow \text{Mo}_7\text{O}_{24}^{6-} + 4 \text{H}_2\text{O} \\
  8 \text{MoO}_4^{2-} + 12 \text{H}^+ & \rightarrow \text{Mo}_8\text{O}_{26}^{4-} + 6 \text{H}_2\text{O} \\
  36 \text{MoO}_4^{2-} + 64 \text{H}^+ & \rightarrow \text{Mo}_{36}\text{O}_{112}^{8-} + 32 \text{H}_2\text{O}
  \end{align*}
  \]

- Isopoly anions can incorporate hetero atoms:
  \[
  12 \text{MoO}_4^{2-} + \text{HPO}_4^{2-} + 23 \text{H}^+ \rightarrow [\text{PMo}_{12}\text{O}_{40}]^{3-} + 12 \text{H}_2\text{O}
  \]
  (yellow) \(\Rightarrow\) detection of phosphate

- Reduction of sodiumpolytungstate with H$_2$ yields
  Tungstic bronzes Na$_n$WO$_3$ (0 < n < 1)

- Reduction of MoO$_4^{2-}$ with Zn/Hg \(\Rightarrow\) diamagnetic Mo$^{3+}$-complex:

  \[
  2 \text{MoO}_4^{2-} + 2 \text{H}_2\text{O} + 3 \text{Zn} + 12 \text{H}^+ \rightarrow [(\text{H}_2\text{O})_4\text{Mo} \equiv \text{Mo(\text{H}_2\text{O})}_4]^{2+} + 3 \text{Zn}^{2+}
  \]
10. Chemistry of Transition Metals

The Chromium Group

Metal-metal-bonds

- Chromium(II)-acetate contains one Cr-Cr-quadruple bond
  \[2 \text{[Cr(OH}_2\text{)]}_6^{2+} + 4 \text{CH}_3\text{COO}^- \rightarrow \text{[Cr}_2\text{(H}_2\text{O})_2(\mu-\text{OOCCCH}_3)_4]\]
  + 10 H_2O

- Molybdenum(II)-acetate also contains one Mo-Mo-quadruple bond
  \[2 \text{[Mo(CO)}_6]_0 + 4 \text{CH}_3\text{COOH} \rightarrow \text{[Mo}_2(\mu-\text{OOCCCH}_3)_4]+ 12 \text{CO} + 4 \text{H}^+ + 4 \text{e}^-\]

\[\sigma\text{-bonds} \quad 0 \text{ nodal plane}\]
(s + s, \(p_z + p_z\), \(d_z^2 + d_z^2\))

\[\pi\text{-bonds} \quad 1 \text{ nodal plane}\]
(p_x + p_x, p_y + p_y, d_{xz} + d_{xz}, d_{yz} + d_{yz})

\[\delta\text{-bonds} \quad 2 \text{ nodal plane}\]
(d_{xy} + d_{xy})

Cr(I) also forms Cr-Cr-quintuple bonds, e.g. in \([\text{PhCrCrPh}]\)
The Chromium Group

Biological aspects

Chromium

- Chromium(VI) acts carcinogenic, because it can oxidise OH-groups of the DNA
- Chromium(III) regulates the blood sugar level, together with insulin and glucagon

Molybdenum

- Only element of 2nd transition metal series of biological significance!
- In the form of molybdate MoO$_4^{2-}$ soluble und thus readily available from sea water
- Biochemically relevant oxidation states: IV, V, VI $\Rightarrow$ electron transfer reactions
- Coordination by O-, S-, and N-ligands
- Enzymes: nitrogenases, nitrate reductases, aldehyde oxidases

Tungsten

- Only element of 3rd transition metal series of biological relevance!
- Metalloenzymes in hypothermal archaeabacteria are stable up to 110 °C, due to strong metal-ligand interactions, stabilising the enzyme
10. Chemistry of Transition Metals

The Manganese Group

7. Sub group or group 7 ⇒ 7 valence electrons
Manganese [Ar]3d⁵⁴s²  Technetium [Kr]4d⁵⁵s²  Rhenium [Xe]4f¹⁴⁵d⁵⁶s²

- Manganese is one of the most abundant heavy metals, second only to Iron
- ⁹⁹Tc* → ⁹⁹Tc + γ: τ₁/₂ = 6 h ⁹⁹Tc → ⁹⁹Ru + β⁻: τ₁/₂ = 2.1·10⁻⁵ a

Properties of the elements

<table>
<thead>
<tr>
<th>Element</th>
<th>Density [g/cm³]</th>
<th>Tₘ [°C]</th>
<th>Tₜ [°C]</th>
<th>Oxidation state</th>
<th>r(M⁷⁺) [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mn</td>
<td>7.44</td>
<td>1247</td>
<td>2030</td>
<td>+II, +III, +IV, +VI, +VII</td>
<td>46</td>
</tr>
<tr>
<td>Tc</td>
<td>11.49</td>
<td>2250</td>
<td>4700</td>
<td>+IV, +V, +VII</td>
<td>56</td>
</tr>
<tr>
<td>Re</td>
<td>21.03</td>
<td>3180</td>
<td>5870</td>
<td>+IV, + V, + VI, +VII</td>
<td>53</td>
</tr>
</tbody>
</table>

Alloys

- Ferromanganese  Mn(>70%) + Fe + C
- Silicomanganese Mn(65%) + Si(15-20%) + C
- Manganin        Cu(84%), Cu(12%), Ni(4%)  precision resistors
- Manganese steel Fe + Mn(10-18%)  railway track, armour plates
10. Chemistry of Transition Metals

The Manganese Group

Occurrence
Manganese (Greek: manganizein) MnO₂ Pyrolustie (manganese ore)
cleaning: discolours ferrous glass MnO(OH) Manganite
Mn₃O₄ Hausmannite
MnSiO₄ Rhodonite

Technetium (Grek: technetos) Traces in uranium ores
artificial

Rhenium (Rhineland) Companion in molybdenum ores (MoS₂)
Home to the discoverer Ida Tacke

Production of Manganese
1. From Manganese ores with silicomanganese
   2 MnO + Si → 2 Mn + SiO₂
2. Electrolysis of Manganese sulphate solutions
   2 MnSO₄ + 2 H₂O → 2 Mn + 2 H₂SO₄ + O₂↑
10. Chemistry of Transition Metals

The Manganese Group

Oxidation states of Manganese

- Manganese is relatively ignoble: $\text{Mn} \rightleftharpoons \text{Mn}^{2+} + 2 \text{e}^- \quad E^\circ = -1.19 \text{ V}$
- In acidic solution $\text{Mn}^{2+}$ is the most stable oxidation state
- In alkaline solution $\text{Mn}^{4+}$ is the most stable species but also $\text{Mn}^{2+}$ and $\text{Mn}^{3+}$ experience high stability

Frost-diagram of manganese in acidic (right) and alkaline (left) solution
10. Chemistry of Transition Metals

The Manganese Group

Oxidation state +II ([Ar]3d⁵)

- Compared to other divalent TM ions, Mn²⁺ is relatively stable and no reducing agent in acidic solution:
  \[ E_0^{[V]} \text{ at pH } 0 \]
  \[
  \begin{align*}
  \text{Mn}^{2+} (d^5) & \rightleftharpoons \text{Mn}^{3+}(d^4) + e^- & 1.5 \\
  \text{Fe}^{2+} (d^6) & \rightleftharpoons \text{Fe}^{3+}(d^5) + e^- & 0.75 \\
  \text{Cr}^{2+} (d^4) & \rightleftharpoons \text{Cr}^{3+}(d^3) + e^- & -0.41
  \end{align*}
  \]

- Manganese(II)-salts and solutions are just weakly coloured, since absorption in the visible range of the spectrum is due to spin-forbidden d-d-transitions (d⁵, high-spin), only
  \[
  \begin{align*}
  \text{MnSO}_4 \cdot 7\text{H}_2\text{O} & \quad \text{Manganese(II)-sulphate-heptahydrate} \quad \text{rose} \\
  \text{MnCl}_2 \cdot 4\text{H}_2\text{O} & \quad \text{Manganese(II)-chloride-tetrahydrate} \quad \text{rose} \\
  [\text{Mn(H}_2\text{O})_6]^{2+} & \quad \text{Hexaaquamanganese(II)-ion} \quad \text{light rose}
  \end{align*}
  \]

- Strongly coloured low-spin complexes are formed solely with very strong ligands
  \[
  [\text{Mn(CN)}_6]^{4-} \\
  [\text{Mn(CN)}_5(\text{NO})]^{3-}
  \]
Oxidation state +III ([Ar]3d⁴)

- Dissolution of braunite, Mn₂O₃, in concentrated H₂SO₄
  Mn₂O₃ + 6 H⁺ + 9 H₂O ⇄ 2 [Mn(H₂O)₆]³⁺
yields a solution of garnet red hexaaquamanganese(III)-ions

- Manganese(III)-ions tend to disproportionate
  2 Mn³⁺ + 2 H₂O ⇄ Mn²⁺ + MnO₂ + 4 H⁺
if no reductive agent is present

- The stable deep red Manganese(III)-acetate is formed upon treatment of Manganese(II)acetate with permanganate in glacial acetic acid:
  3 KMnO₄ + 12 Mn(OAc)₂ + 11 HOAc + 3 H⁺ → 5 [Mn₃O(OAc)₆]OAc↓ + 7 H₂O + 3 K⁺

(HOAc = CH₃-COOH)
10. Chemistry of Transition Metals

The Manganese Group

**Oxidation state +IV ([Ar]3d\(^3\))**

MnO\(_2\)·H\(_2\)O = MnO(OH)\(_2\) is a strong oxidising agent in acidic solution

\[ \text{pH} = 0 \quad \text{Mn}^{2+} + 2 \text{H}_2\text{O} \Leftrightarrow \text{MnO}_2 + 4 \text{H}^+ + 2 \text{e}^- \quad E^\circ = +1.28 \text{ V} \]

\[ \text{MnO}_2 + 4 \text{HCl} \rightarrow \text{MnCl}_2 + \text{Cl}_2 \uparrow + 2 \text{H}_2\text{O} \]

\( \Rightarrow \) preparation of chlorine at laboratory scale

\[ \text{pH} = 14 \quad 2 \text{OH}^- + \text{Mn(OH)}_2 \Leftrightarrow \text{MnO}_2 + 2 \text{H}_2\text{O} + 2 \text{e}^- \quad E^\circ = -0.05 \text{ V} \]

\[ 4 \text{OH}^- \Leftrightarrow \text{O}_2 + 2 \text{H}_2\text{O} + 4 \text{e}^- \quad E^\circ = +0.40 \text{ V} \]

\( \Rightarrow \) O\(_2\) oxidises Manganese(II)-hydroxide to MnO\(_2\)·H\(_2\)O

**Oxidation state +VII ([Ar]3d\(^0\))**

The violet permanganate ion, MnO\(_4\)^{-}, is a very strong oxidising agent in acidic solution

\[ \text{pH} = 0 \quad \text{MnO}_4^- + 8 \text{H}_3\text{O}^+ + 5 \text{e}^- \Leftrightarrow \text{Mn}^{2+} + 12 \text{H}_2\text{O} \quad E^\circ = +1.51 \text{ V} \]

\[ \text{pH} = 5 \quad E = E^0 + \frac{0.059}{5} \log \left[ \frac{[\text{MnO}_4^-][\text{H}_3\text{O}^+]^8}{[\text{Mn}^{2+}]} \right] \quad E^\circ = +1.04 \text{ V} \]

\[ \text{pH} = 7 \quad E^\circ = +0.85 \text{ V} \]

Permanganate can be synthesised by the oxidation of Mn\(^{2+}\) with PbO\(_2\) in acidic surroundings

\[ 2 \text{Mn}^{2+} + 5 \text{PbO}_2 + 4 \text{H}^+ \Leftrightarrow 2 \text{MnO}_4^- + 5 \text{Pb}^{2+} + 2 \text{H}_2\text{O} \]
10. Chemistry of Transition Metals

The Manganese Group

Oxidation state +VII ([Ar]3d⁰)

- Permanganate can be dehydrated to Manganeseheptoxide, using sulphuric acid:
  \[ \text{KMnO}_4 + \text{H}_2\text{SO}_4 \rightarrow 2 \text{Mn}_2\text{O}_7 + \text{K}_2\text{SO}_4 + \text{H}_2\text{O} \]
- \( \text{Mn}_2\text{O}_7 \) is highly oxidising: \( 2 \text{Mn}_2\text{O}_7 \rightarrow 4 \text{MnO}_2 + 3 \text{O}_2 \) “lightning under water“

Redox chemistry and colours of Manganese

<table>
<thead>
<tr>
<th>Mn</th>
<th>-2e⁻</th>
<th>( \leftrightarrow )</th>
<th>Mn²⁺</th>
<th>-e⁻</th>
<th>( \leftrightarrow )</th>
<th>Mn³⁺</th>
<th>-e⁻</th>
<th>( \leftrightarrow )</th>
<th>MnO₄⁴⁻</th>
</tr>
</thead>
<tbody>
<tr>
<td>grey</td>
<td>+2e⁻</td>
<td>rose</td>
<td>+e⁻</td>
<td>red</td>
<td>+e⁻</td>
<td>brown</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Redox enzymes and photosystem II

\[ \Rightarrow \text{Manganese complexes} \]

Model complex for Mn-species, that cleaves \( \text{O}_2 \) during photosynthesis
The Manganese Group

Rhenium compounds

Oxides and oxychlorides
- Re₂O₇, ReO₃, Re₂O₅, ReO₂,
- ReOCl₄, ReOCl₃

Halides
- ReCl₆, ReCl₅, ReCl₄, ReCl₃
- [Re^{III}_2Cl₈]²⁻ with quadruple bond
- Cp₂Re¹² with bond order 4-6!
The Manganese Group

Biological aspects

Manganese

- Manganese is the key element in the photo reaction of photosynthesis, viz. it is responsible for the cleavage of water in the oxygen-releasing cluster:

\[
\begin{align*}
\text{Mn}^{III}_4 & \quad \text{Mn}^{III}_3\text{Mn}^{IV} \quad \text{Mn}^{III}_2\text{Mn}^{IV}_2 \quad \text{Mn}^{III}\text{Mn}^{IV}_3 \quad \text{Mn}^{IV}_4 \\
\text{Mn}^{IV}_4 + 2 \text{H}_2\text{O} & \quad \rightarrow \quad \text{Mn}^{III}_4 + 4 \text{H}^+ + \text{O}_2 \\
2 \text{H}_2\text{O} & \quad \rightarrow \quad 4 \text{H}^+ + 4 \text{e}^- + \text{O}_2^{\uparrow} \\
\end{align*}
\]

(\to \text{presentations})

- Arginase: nitrogen-containing metabolite \(\rightarrow\) synthesis of urea \(\text{H}_2\text{N-CO-NH}_2\)

- Superoxide dismutase: cleavage of the superoxide radical \(\text{O}_2^-\)

\[
\begin{align*}
4 \text{O}_2^- + 4 \text{H}^+ & \quad \rightarrow \quad 3 \text{O}_2 + 2 \text{H}_2\text{O} \\
\text{Mn}, \quad \text{besides Zn, Cu, Fe, and Se, is a cofactor for enzymes, acting as antioxidants} \\
\end{align*}
\]

Technetium and Rhenium are of no biological importance
10. Chemistry of Transition Metals

The Iron Group

8. Sub group or group 8, 9 and 10 ⇒ 8, 9 or 10 valence electrons

Iron  Cobalt  Nickel  ⇒ Iron group  ignoble
Ruthenium  Rhodium  Palladium  ⇒ light platinum metals  noble
Osmium  Iridium  Platinum  ⇒ heavier platinum metals  noble

• Iron, Cobalt, and Nickel experience similar densities, boiling points, melting points, and are all ferromagnetic
• Osmium (22.59 g/cm³) and Iridium (22.56 g/cm³) are the two elements with the highest density!

Properties of the elements of the Iron group

<table>
<thead>
<tr>
<th>Element</th>
<th>Density [g/cm³]</th>
<th>T_m [° C]</th>
<th>T_b [° C]</th>
<th>Oxidation state</th>
<th>r(M^{2+}) [pm]</th>
<th>r(M^{3+}) [pm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>7.87</td>
<td>1536</td>
<td>2860</td>
<td>+II, +III</td>
<td>78(h.s.), 61(l.s.)</td>
<td>64(h.s.), 55(l.s.)</td>
</tr>
<tr>
<td>Cobalt</td>
<td>8.90</td>
<td>1499</td>
<td>2900</td>
<td>+II, +III</td>
<td>74(h.s.), 65(l.s.)</td>
<td>61(h.s.), 54(l.s.)</td>
</tr>
<tr>
<td>Nickel</td>
<td>8.90</td>
<td>1455</td>
<td>2880</td>
<td>+II, +III</td>
<td>69</td>
<td>60(h.s.), 56(l.s.)</td>
</tr>
</tbody>
</table>
10. Chemistry of Transition Metals

The Iron Group

<table>
<thead>
<tr>
<th>Occurrence</th>
<th>Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron (Latin.: ferrum)</td>
<td>Fe₃O₄</td>
<td>Magnetite</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃</td>
<td>Haematite</td>
</tr>
<tr>
<td></td>
<td>Fe₂O₃·xH₂O</td>
<td>Brown Iron ore</td>
</tr>
<tr>
<td></td>
<td>FeCO₃</td>
<td>Siderite</td>
</tr>
<tr>
<td></td>
<td>FeS₂</td>
<td>Pyrite</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Cobalt (Goblin)</th>
<th>Co₃S₄</th>
<th>Cobalt gravel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berggeist</td>
<td>CoAsS</td>
<td>Cobalt glare</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Nickel (Nickel)</th>
<th>(Fe,Ni)S</th>
<th>Iron Nickel gravel</th>
</tr>
</thead>
<tbody>
<tr>
<td>Berggeist</td>
<td>NiAs</td>
<td>Niccolite</td>
</tr>
</tbody>
</table>

Production

<table>
<thead>
<tr>
<th>Iron and steel</th>
<th>→ presentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cobalt</td>
<td>→ calcination</td>
</tr>
<tr>
<td>Nickel</td>
<td>→ calcination</td>
</tr>
</tbody>
</table>

\[
\text{Cobalt} \rightarrow \text{calcination} \rightarrow \text{CoO} \rightarrow \text{CoSO₄} \rightarrow \text{electrolysis} \rightarrow \text{Co} \\
\text{Nickel} \rightarrow \text{calcination} \rightarrow \text{NiO} \rightarrow \text{NiSO₄} \rightarrow \text{electrolysis} \rightarrow \text{Ni} + 4 \text{CO} \rightleftharpoons \text{Ni(CO)₄(g)}
\]
10. Chemistry of Transition Metals

The Iron Group

Blast-Furnace-Process

“Continuous process“

1000 – 1500 t of Iron as well as slurry per day

Iron: Fe + C, P, Si, Mn, S

Slurry: Ca-Al-silicates

Reduction with CO

\[
\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow \text{FeO} \rightarrow \text{Fe}
\]

Boudouard-equilibrium

\[
\text{C} + \text{CO}_2 \rightleftharpoons 2\text{CO}
\]
The Iron Group

Non-stoichiometric compounds
Iron(II)-oxide does not exist as FeO but Fe\textsubscript{x}O (x = 0.833 < 0.957)

Explanation
FeO crystallises in a NaCl-like structure, where part of the Fe-ions exhibit the trivalent oxidation state
⇒ Charge compensation
1. By cation vacancies (Schottky-defects)
2. By additional oxide anions on interstitials (Frenkel-defects)

Metals with a tendency for a change of valence form non-stoichiometric compounds
- MnO \( \text{Mn}_x\text{O} \) (x = 0.848 < 1.000)
- CoO \( \text{Co}_x\text{O} \) (x = 0.988 < 1.000)
- NiO \( \text{Ni}_x\text{O} \) (x = 0.999 < 1.000)
- \( \text{Ce}_2\text{O}_3 \) \( \text{CeO}_x \) (x = 1.50 < 1.52)
- TiO\textsubscript{2} \( \text{TiO}_x \) (x = 1.998 < 2.000)
10. Chemistry of Transition Metals

The Iron Group

Iron(II) and Iron(III) compounds

Acid-base chemistry

\[
\begin{align*}
[\text{Fe}^{II}(\text{H}_2\text{O})_6]^{2+} + \text{H}_2\text{O} & \rightleftharpoons [\text{FeOH}(\text{H}_2\text{O})_5]^+ + \text{H}_3\text{O}^+ \quad K = 10^{-7} \quad \text{pH of a 0.1 M solution} \sim 4 \\
[\text{Fe}^{III}(\text{H}_2\text{O})_6]^{3+} + \text{H}_2\text{O} & \rightleftharpoons [\text{FeOH}(\text{H}_2\text{O})_5]^{2+} + \text{H}_3\text{O}^+ \quad K = 10^{-7} \quad \text{pH of a 0.1 M solution} \sim 2 \\
4 \ [\text{FeOH}(\text{H}_2\text{O})_5]^{2+} & \rightarrow 2 \ [(\text{H}_2\text{O})_5\text{Fe-O-Fe}(\text{H}_2\text{O})_5]^{4+} + 2 \ \text{H}_2\text{O} \\
& \text{(yellow brown)}
\end{align*}
\]

Iron(II)-hydroxide

\[
\text{Fe}^{2+} + 2 \ \text{OH}^- \rightleftharpoons \text{Fe(OH)}_2 \\
K_L = c(\text{Fe}^{3+}) \cdot c^2(\text{OH}^-) = 2 \cdot 10^{-15} \ \text{mol}^3/\text{l}^3
\]

Iron(III)-hydroxide

\[
\text{Fe}^{3+} + 3 \ \text{OH}^- \rightleftharpoons \text{Fe(OH)}_3 \\
K_L = c(\text{Fe}^{3+}) \cdot c^3(\text{OH}^-) = 5 \cdot 10^{-38} \ \text{mol}^4/\text{l}^4
\]
10. Chemistry of Transition Metals

The Iron Group

Iron(II) and Iron(III) compounds

Redox chemistry

<table>
<thead>
<tr>
<th>Redox reaction</th>
<th>E° [V] for pH = 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe ⇌ Fe^{2+} + 2 e⁻</td>
<td>-0.41</td>
</tr>
<tr>
<td>Fe ⇌ Fe^{3+} + 3 e⁻</td>
<td>-0.036</td>
</tr>
<tr>
<td>Fe^{2+} ⇌ Fe^{3+} + e⁻</td>
<td>+0.77</td>
</tr>
</tbody>
</table>

⇒ Strongly depends on pH, since the hydroxides are insoluble in neutral and alkaline environment

Using the solubility products of Fe(OH)₃ and Fe(OH)₂, the redox potential can be calculated by means of the Nernst equation:

\[ E(\text{Fe}^{2+}/\text{Fe}^{3+}) = E^0(\text{Fe}^{2+}/\text{Fe}^{3+}) + 0.059/n \cdot \log\left(\frac{c(\text{Fe}^{3+})}{c(\text{Fe}^{2+})}\right) \]

⇒ \[ E(\text{Fe}^{2+}/\text{Fe}^{3+}) = +0.77 \text{ V} + 0.059 \cdot \log\left(\frac{5 \cdot 10^{-38}}{2 \cdot 10^{-15}}\right) \text{ V} = -0.56 \text{ V} \quad \text{for } c(\text{OH}^-) = 1 \text{ mol/l} \ (\text{pH} 14) \]

Due to the considerable difference in the solubility products of Fe(OH)₃ and Fe(OH)₂, the system Fe^{2+}/Fe^{3+} becomes a strong reducing agent in alkaline milieu!
10. Chemistry of Transition Metals

The Iron Group

Iron(II) and Iron(III) compounds

Complex chemistry

- Mainly octahedral and high-spin with the exception of CN-, phen- or bipy-ligands

- Stability of the oxidation states depends on the electronic properties of the ligands

  $\text{[Fe(CN)}_6\text{]}^{4-} \rightleftharpoons \text{[Fe(CN)}_6\text{]}^{3-} + e^- \quad E^0 = +0.36 \text{ V l.s. negative charge!}$

  $\text{[Fe(H}_2\text{O)}_6\text{]}^{2+} \rightleftharpoons \text{[Fe(H}_2\text{O)}_6\text{]}^{3+} + e^- \quad E^0 = +0.77 \text{ V h.s.}$

  $\text{[Fe(bpy)}_3\text{]}^{2+} \rightleftharpoons \text{[Fe(bpy)}_3\text{]}^{3+} + e^- \quad E^0 = +0.96 \text{ V l.s.}$

  $\text{[Fe(phen)}_3\text{]}^{2+} \rightleftharpoons \text{[Fe(phen)}_3\text{]}^{3+} + e^- \quad E^0 = +1.12 \text{ V l.s. for pH = 0}$

- Fe(III)-ions $\Rightarrow$ high affinity to Oxygen-donor ligands

  $\text{[Fe(PO}_4\text{)}_3\text{]}^6-\text{, [Fe(C}_2\text{O}_4\text{)}_3\text{]}^{3-}$

- Fe(II)-ions $\Rightarrow$ high affinity to Nitrogen-donor ligands

  $\text{[Fe(NH}_3\text{)}_6\text{]}^{2+}, \text{[Fe(en)}_3\text{]}^{2+}$

- $K_4[\text{Fe(CN)}_6\text{]}$ Potassiumhexacyanoferrate(II) yellow prussiate of potash

- $K_3[\text{Fe(CN)}_6\text{]}$ Potassiumhexacyanoferrate(III) red prussiate of potash

Name: Formerly obtained through heating of blood (Fe-, C-, and N-containing) with $K_2CO_3$ and subsequent leaching of the resulting salts with water.
10. Chemistry of Transition Metals

The Iron Group

Iron(II) and Iron(III) compounds

Detection reaction

1. \( \text{Fe}^{3+} + \) yellow prussiate of potash \( \rightarrow \) Prussian blue
   \( \text{Fe}^{2+} + \) red prussiate of potash \( \rightarrow \) Prussian blue

Prussian blue = \( \text{Fe}_4[\text{Fe(CN)}_6]_3 \cdot 14\text{H}_2\text{O} \)
\( \text{Fe(NC)}_5 \)

\( \Rightarrow \) Charge-transfer complex (inter-valence band)

2. \([\text{Fe(H}_2\text{O)}_6]^{3+} + \text{SCN}^- \rightarrow \) blood red complexes

\( [\text{Fe(SCN)}(\text{H}_2\text{O})_5]^{2+} \)
\( [\text{Fe(SCN)}_2(\text{H}_2\text{O})_4]^+ \)
\( [\text{Fe(SCN)}_3(\text{H}_2\text{O})_3]^0 \rightarrow \text{Fe(SCN)}_3 \downarrow + 3\text{H}_2\text{O} \)
10. Chemistry of Transition Metals

The Iron Group

Ferrites
Magneto ceramic materials
⇒ Binary and ternary iron oxides

Soft ferrites
• Are easily and efficiently magnetised by an external magnetic field
• Magnets in writing and reading heads in audio and video recorders, hard drives etc.
• Electrical isolators, ferrimagnetic compounds with low saturation magnetisation in combination with low anisotropy in terms of the crystal structure
• MFe$_2$O$_4$ (spinel) with M = Zn$^{2+}$, Mn$^{2+}$, Ni$^{2+}$, Co$^{2+}$, Mg$^{2+}$
• Typical composition: Fe-Mn-Zn-oxide with 70% Fe, 25% Mn, and 5% Zn

Hard ferrites
• Maintain their magnetic properties after the initial magnetisation
• Permanent magnets in electric motors, speaker, generators, etc.
• MFe$_{12}$O$_{19}$ with M = Sr$^{2+}$, Ba$^{2+}$
10. Chemistry of Transition Metals

The Iron Group

Bioinorganic chemistry of Iron
Iron takes part in the transportation of Oxygen and in a number electron transfer reactions

**Haem-proteins (Iron-porphyrin-complexes)** \( E^0 [V] \)
- Haemoglobin \( \text{O}_2 \)-transport \( 0.17 \)
- Myoglobin \( \text{O}_2 \)-storage \( 0.05 \)
- Cytochromes (a,b,c) Electron transfer \( 0.04 - 0.40 \)
- Oxygenases Oxygenation
- Oxidases \( \text{O}_2 \)-reduction to \( \text{O}_2^- \), \( \text{O}_2^{2-} \), \( \text{O}^- \)
- Peroxidases Oxidation with \( \text{H}_2\text{O}_2 \)
- Katalasases \( \text{H}_2\text{O}_2 \)-disproportionation to \( \text{H}_2\text{O} \) and \( \text{O}_2 \)

**Non-Haem-proteins (Iron-Sulphur-cluster)** \( E^0 [V] \)
- Rubridoxines Electron transfer \( -0.06 \)
- Ferredoxines Electron transfer \( -0.42 \)
- Nitrogenases \( \text{N}_2 \)-reduction to \( \text{NH}_3 \)
- Transferrrines Transport of Iron
- Ferritines Storage of Iron
10. Chemistry of Transition Metals

The Iron Group

Bioinorganic chemistry of Iron
The adult human accommodates 4 g of Fe, 75% thereof being bound by erythrocytes in haemoglobin

Oxygen transportation chain $\rightarrow$ respiratory chain

Structure of myoglobin (Mb) and haemoglobin (Hb)

<table>
<thead>
<tr>
<th>Lunge</th>
<th>Blut</th>
<th>Gewebe</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>Hb(O₂)₂-₃ Mb</td>
<td>H₂O</td>
</tr>
<tr>
<td></td>
<td>Hb (Mb(O₂))</td>
<td>2H⁺</td>
</tr>
<tr>
<td></td>
<td>Cytochrome</td>
<td></td>
</tr>
</tbody>
</table>
10. Chemistry of Transition Metals

The Iron Group

Function and structure of heme

**Oxyhaemoglobin**

Fe$^{2+}$, [Ar]3d$^6$ l.s., diamagnetic

$r = 75 \text{ pm} \Rightarrow \text{in-plane structure}$

**Desoxyhaemoglobin**

Fe$^{2+}$, [Ar]3d$^6$ h.s., paramagnetic

$r = 92 \text{ pm} \Rightarrow \text{out-of-plane structure}$

---

**Free Fe$^{2+}$**

<table>
<thead>
<tr>
<th>Energy</th>
<th>e$^*_g$</th>
<th>d$^{x^2-y^2}$</th>
<th>d$^z_2$</th>
<th>t$^2_g$</th>
<th>d$^y_x$</th>
<th>d$^z_x$</th>
<th>d$^z_y$</th>
</tr>
</thead>
</table>

**Fe$^{2+}$ in oxyhaemoglobin**

O$_2$ is a $\sigma$-donor and $\pi$-acceptor ligand

**Fe$^{2+}$ in desoxyhaemoglobin**
10. Chemistry of Transition Metals

The Iron Group

Cobalt(II) and Cobalt(III) compounds

Redox chemistry

Redox reaction

\[ \text{Co} \rightleftharpoons \text{Co}^{2+} + 2 \text{e}^- \]  \[ E^0 \text{ [V]} \text{ for pH = 0} \]  
\[ \text{Co} \rightleftharpoons \text{Co}^{3+} + 3 \text{e}^- \]  \[ +0.41 \]  
\[ \text{Co}^{2+} \rightleftharpoons \text{Co}^{3+} + \text{e}^- \]  \[ +1.82 \]

\[ [\text{Co(H}_2\text{O)}_6]^{2+} \rightleftharpoons [\text{Co(H}_2\text{O)}_6]^{3+} + \text{e}^- \]

\begin{align*}
\text{rose (3d}^7) & \quad \text{blue (3d}^6) \\
\end{align*}

\[ \Rightarrow \text{In contrary to Iron, divalent Cobalt is the most stable oxidation state in water} \]

\[ \Rightarrow \text{The ligands strongly influence the electrode potentials} \]

\[ [\text{Co(NH}_3)_6]^{2+} \rightleftharpoons [\text{Co(NH}_3)_6]^{3+} + \text{e}^- \]  \[ E^0 = +0.10 \text{ V} \]

\[ [\text{Co(CN)}_5]^{3-} + \text{CN}^- \rightleftharpoons [\text{Co(CN)}_6]^{3-} + \text{e}^- \]  \[ E^0 = -0.83 \text{ V} \]

\[ \Rightarrow \text{The high ligand field stabilisation energies stabilise Co(III)-complexes, and most octahedral Co(II)-complexes are unstable against oxidation by air, which can be traced back to their redox potentials} \]
10. Chemistry of Transition Metals

The Iron Group

Cobalt(II) and Cobalt(III) compounds

Complex chemistry

- $\text{Co}^{3+}$ (isoelectronic to $\text{Fe}^{2+}$) normally forms octahedral low-spin complexes, because then, high ligand field stabilisation energies (LFSE) can be reached:

\[
\begin{align*}
\text{Co}^{3+} & \quad \left[\begin{array}{c}
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\uparrow \\
\end{array}\right] \\
\text{Fe}^{2+} & \quad \left[\begin{array}{c}
\downarrow \\
\downarrow \\
\downarrow \\
\uparrow \\
\uparrow \\
\end{array}\right]
\end{align*}
\]

- Low-spin $\text{Co}^{3+}$ complexes are kinetically inert, because antibonding $e_g^*$-orbitals are unoccupied.

- Cobalt(III) forms a great number of stable complexes with Chromium(III), which can easily be separated into geometrical and optical isomers, due to their high kinetic stability.
10. Chemistry of Transition Metals

The Iron Group

Cobalt(II) and Cobalt(III) compounds

Complex chemistry

- \( \text{Co}^{2+} (3d^7) \) are high-spin complexes and exhibit octahedral or tetrahedral coordination

- Tetrahedral complexes are formed with monodental ligands, such as \( \text{Cl}^- \), \( \text{Br}^- \), \( \text{SCN}^- \), \( \text{OH}^- \)
- Octahedral Co(II)-complexes are generally rose to red, while tetrahedral Co(II)-complexes are blue
- \( [\text{Co(H}_2\text{O})_6]^{2+} + 4 \text{Cl}^- \rightarrow [\text{CoCl}_4]^{2-} + 6 \text{H}_2\text{O} \)

\[ \begin{align*}
\uparrow \uparrow & \quad \uparrow \uparrow \\
\text{d}_{x^2-y^2} & \quad \text{d}_z^2 \\
\downarrow \downarrow & \quad \uparrow \uparrow \\
\text{d}_{xy} & \quad \text{d}_{xz} & \quad \text{d}_{yz} \\
\end{align*} \]

\[ \begin{align*}
\uparrow \downarrow & \quad \uparrow \downarrow \\
\text{d}_{xy} & \quad \text{d}_{xz} & \quad \text{d}_{yz} \\
\uparrow \downarrow & \quad \uparrow \downarrow \\
\text{d}_{x^2-y^2} & \quad \text{d}_z^2 \\
\end{align*} \]

\( \text{LFSE} \quad -8 \text{Dq}_o \quad -8 \text{Dq}_t = -5.33 \text{Dq}_o \quad \Rightarrow \text{rel. small difference} \)
10. Chemistry of Transition Metals

The Iron Group

Bioinorganic chemistry of Cobalt
The adult human accommodates ca. 2.5 mg Cobalt, primarily bound in cobalamin (vitamin B$_{12}$)

Alkylcobalamins participate in redox reactions, alkylations, and rearrangements.
Part of one-electron reductions or oxidations can be Co$^{III}$-, Co$^{II}$- and Co$^{I}$-species

Methylationss (even of Hg$^{2+}$):

Hg$^{2+}$ → HgCH$_3^+$ → Hg(CH$_3$)$_2$
10. Chemistry of Transition Metals

The Iron Group

Nickel(II) compounds

**Hydrolysis**

\[ \text{Ni}^{2+} + 2 \text{OH}^- \rightarrow \text{Ni(OH)}_2 \downarrow \text{(green gel)} \quad K_L = 2 \cdot 10^{-16} \text{ mol}^2/\text{l}^2 \]

**Complexes**

\[ \text{Ni(OH)}_2(s) + 6 \text{NH}_3(aq) \rightarrow [\text{Ni(NH}_3)_6]^{2+}(aq) + 2 \text{OH}^-(aq) \]

\[ \text{Ni}^{2+}(aq) + 2 \text{H}_2\text{dmg}(aq) \rightarrow [\text{Ni(Hdmg)}_2](s) + 2 \text{H}^+(aq) \]

[Diagram of Dimethylglyoxime (H$_2$dmg)]

[Diagram of Bis(dimethylglyoximato)nickel(II)]

Dimethylglyoxime (H$_2$dmg)      Bis(dimethylglyoximato)nickel(II)
10. Chemistry of Transition Metals

The Iron Group

Nickel(II) compounds

Absorption spectra (octahedral complexes)

Electron configuration of Ni$^{2+}$ [Ar]3d$^8$

Ground state

| ↑ | ↓ | ↑ | ↓ | ↑ | ↑ |

Free ion

$S = \Sigma s = 1$, $L = |\Sigma l| = 3$ (F) $\rightarrow$ $^3F$

1. excited state

| ↑ | ↓ | ↓ | ↑ | ↑ |

Split term: $^3T_{1g}$

Coordinated ion

split terms: $^3A_{2g}$, $^3T_{2g}$, $^3T_{1g}$

NiCl$_2$·6H$_2$O(s) $\rightarrow$ [Ni(H$_2$O)$_6$]$^{2+}$(aq) + 2 Cl$^-$(aq)

Absorption spectra

Absorptionsstärke (a.u.)

Wellenlänge (nm)

NiCl$_2$ 0,05 mol/L

Spectrum: Marcel Kallert

Energy

$^3F$

$^3T_{1g}$

$^3T_{2g}$

$^3A_{2g}$

$\nu_1$

$\nu_2$

$\nu_3$

10 Dq
## 10. Chemistry of Transition Metals

### The Iron Group

**Nickel(II) compounds**

Typical for Nickel(II) are octahedral, square-planar and tetrahedral complexes

<table>
<thead>
<tr>
<th>Octahedral</th>
<th>Square-planar</th>
<th>Tetrahedral</th>
</tr>
</thead>
<tbody>
<tr>
<td>H$_2$O</td>
<td>Strong ligands, e.g. CN$^-$ or ligands which force a square-planar arrangement, such as Hdmg</td>
<td>Cl$^-$</td>
</tr>
<tr>
<td>NH$_3$</td>
<td></td>
<td>Br$^-$</td>
</tr>
<tr>
<td>Ethylenediamine</td>
<td></td>
<td>I$^-$</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Green, blue to violet paramagnetic</th>
<th>Yellow, red diamagnetic</th>
<th>Blue paramagnetic</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\uparrow \downarrow$ $\uparrow \downarrow$</td>
<td>$d_{x^2-y^2}$ $d_{z^2}$</td>
<td>$\uparrow \downarrow \uparrow \downarrow$</td>
</tr>
<tr>
<td>$d_{xy}$ $d_{xz}$ $d_{yz}$</td>
<td>$d_{xy}$ $d_{xz} \quad d_{yz}$</td>
<td>$d_{x^2-y^2}$ $d_{z^2}$</td>
</tr>
</tbody>
</table>
10. Chemistry of Transition Metals

The Iron Group

Bioinorganic chemistry of Nickel(II)

a) Ureases: catalyse the decomposition of urea
   \[ \text{O=C(NH}_2\text{)}_2 + \text{H}_2\text{O} \rightarrow \text{NH}_3 + \text{O=C(OH)NH}_2 \rightarrow \text{NH}_3 + \text{CO}_2 \]
   (carbamidic acid: unstable!)

b) Hydrogenases
   \[ 2 \text{H}^+ + 2 \text{e}^- \rightleftharpoons \text{H}_2 \]
   \[ \text{CO}_2 + \text{H}_2 \rightleftharpoons \text{CO} + \text{H}_2\text{O} \]

c) Acetyl-CoA-synthetases
   HS-CoA + CO + Methyl-cobalamin
   \[ \rightarrow \text{MeC(O)S-CoA} + \text{H}^+ + \text{cobalamin}^- \]
   (acetyl-CoA)

   ⇒ Acetyl-CoA = educt for acetylation reactions in biochem.
10. Chemistry of Transition Metals

The Iron-Platinum Group: Summary

- Fe, Co, and Ni are the only metals, which are ferromagnetic at room temperature
- These metals and their compounds, respectively are essential in biochemistry, mechanical and electrical engineering
- Fe fertilises marine phytoplankton and is thus a CO₂ sink with a strong impact on global climate → induced ice ages
- The noble metals Ru, Rh, Pd and Pt as well as their oxides play an important role in heterogeneous catalysis

<table>
<thead>
<tr>
<th>Iron group</th>
<th>Cobalt group</th>
<th>Nickel group</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O₄ ferrimagn.</td>
<td>Co₃O₄ antiferromagn.</td>
<td>Ni₂O₃</td>
</tr>
<tr>
<td>γ-Fe₂O₃ ferromagn.</td>
<td>Co₂O₃ antiferromagn.</td>
<td>NiO</td>
</tr>
<tr>
<td>α-Fe₂O₃ antiferromagn.</td>
<td>CoO</td>
<td>NiO₂</td>
</tr>
<tr>
<td>RuO₂</td>
<td>Rh₂O₃</td>
<td>PdO</td>
</tr>
<tr>
<td>RuO₄</td>
<td>RhO₂</td>
<td>PdO₂</td>
</tr>
<tr>
<td>OsO₂</td>
<td>Ir₂O₃</td>
<td>PtO</td>
</tr>
<tr>
<td>OsO₄</td>
<td>IrO₂</td>
<td>PtO₂</td>
</tr>
</tbody>
</table>