The Periodic Table -
The Transition Metals

*First-row d-block elements*
*Coloured complexes*
Topic 13.1
First-row d-block elements

• Transition elements have variable oxidation states, form complex ions with ligands, have coloured compounds, and display catalytic and magnetic properties.
• Zn is not considered to be a transition element as it does not form ions with incomplete d orbitals.
• Transition elements show an oxidation state of +2 when the s-electrons are removed.
First-row d-block elements

Nature of science

• Looking for trends and discrepancies - transition elements follow certain patterns of behaviour. The elements Zn, Cr, and Cu do not follow these patterns and are therefore considered anomalous in the first-row d-block.
First-row d-block elements

• **Transition elements** have an incomplete d-sublevel, and can form positive ions with an incomplete d-sublevel
• Found in first row in period 4 from scandium (Sc) to copper (Cu)
• The **Lanthanoids** are the elements from Z=57 to Z=71 and the **actinoids** are elements from Z=89 to Z=103.
  • Lanthanum and Actinium are the only two elements in that period that do not contain an f-orbital.
  • Other f-block elements are **group 3** but they form a separate f-block in the periodic table.
• Group 12 elements (Zn, Cd, Hg, and Cn) are **not** classified as transition elements according to IUPAC as they all have full d-sublevels containing 10 electrons. Zn = [Ar]4s^23d^{10}
First-row d-block elements

• Anomolies with electron configurations: Cr & Mo
  • [Ar]3d⁴4s² While most would say this is the configuration - it is NOT!  

• As you recall, orbitals are MORE stable when they are half full, full, or empty...As you can see the d-orbital is partially full -- UNSTABLE!

• So what does the electron configuration really look like for Cr?
  [Ar]3d⁵4s¹

  WHY!?
First-row d-block elements

- Anomalies with electron configurations: Cu & Ag
  - $[\text{Ar}]3d^94s^2$ While most would say this is the configuration - it is NOT!  
  
  ![d-block elements]

- For Cu and Ag - they prefer FILLED sublevels
- So what does the electron configuration really look like for Cu?

  $[\text{Ar}]3d^{10}4s^1$

  WHY!?  
  
  ![d-block elements]
First-row d-block elements

• Though those explanations are far too simplistic and the true extent is beyond the scope of this course
  • Must take into consideration the nuclear charge effect on the 4s and 3d orbitals and interactions of electrons within the same orbital
  • A different energy must be considered, pairing energy, $p$, which arises from the electrostatic repulsion of like charges.
  • As nuclear charge increases, there is greater attraction of the electrons: d orbitals are not shielded from nucleus to same extent as other orbitals.
  • As a result electrons will occupy lowest available orbitals
# Periodic table of elements

<table>
<thead>
<tr>
<th>Main-group elements</th>
<th>group 1 (excluding H), group 2, and groups 13-18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Transition elements</td>
<td>groups 3-11 (the f-block elements are sometimes described as inner transition elements)</td>
</tr>
<tr>
<td>s-block elements</td>
<td>groups 1 and 2 and He</td>
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<tr>
<td>p-block elements</td>
<td>groups 13-18 (excluding He)</td>
</tr>
<tr>
<td>d-block elements</td>
<td>groups 3-12 (including La and Ac), but excluding Ce to Lu and Th to Lr, which are classified as f-block elements</td>
</tr>
<tr>
<td>f-block elements</td>
<td>elements Ce to Lu and from Th to Lr</td>
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<tr>
<td>Lanthanoids</td>
<td>elements La to Lu</td>
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<tr>
<td>Actinoids</td>
<td>elements Ac to Lr</td>
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</table>
First-row d-block elements

Electron configuration of first-row d-block elements and their ions

Know how to write full and condensed electron configurations for the first 36 elements (\(Z = \text{Kr}\)).

When removing electrons to form cations (positive ions) electrons are always removed from the level of the highest principal quantum number, \(n\). In the case of the first-row d-block elements this will be the 4s level.
Practice Problem

... You Do ...

Write the full and condensed electron configurations for the first 36 elements. Be sure to keep in mind the anomalies we discussed.

When you are finished - compare your work with another classmate that has finished.

Check with three before you check with me

If you have discrepancies - discuss them and try to come to an agreement on which configuration is correct and why
First-row d-block elements

Characteristics of transition elements

• L to R Periodic table: Nuclear charge \( Z \) increases and atomic radii decrease
  • First ionization increases (IE) will increase across a period.
  • For transition elements IE is much more gradual and rate of increase is much lower compared compared to main-group elements.
  • Electrons of transition elements enter an inner shell instead of a valence shell orbital -- greater shielding effect

• Transition metals have numerous key characteristics:
  • variable oxidation states
  • compounds of transition elements and their ions are often coloured
  • for complexes with ligands
  • magnetic properties depend on their oxidation states and coordination number
**First-row d-block elements**

**Variable oxidation states**

- Often have different oxidation states unlike alkali and alkaline 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>
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</tbody>
</table>

**Type A:** Sc, Ti, and V  
**Type B:** Cr and Mn  
**Type C:** Fe, Co, Ni, Cu, and Zn  

**Most common oxidation state**
**First-row d-block elements**

### Characteristics of Type A

- stable high oxidation states
  - i.e. V is +5 in VO$_3^-$
- unstable low oxidation states

<table>
<thead>
<tr>
<th>Sc</th>
<th>Ti</th>
<th>V</th>
</tr>
</thead>
<tbody>
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<td></td>
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<td>+5</td>
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</tbody>
</table>

Type A: Sc, Ti, and V
First-row d-block elements

Characteristics of Type B

- stable high oxidation states
  - i.e. Mn is +7 in MnO$_4^-$, Cr is +6 in Cr$_2$O$_7^{2-}$
- stable low oxidation states
  - i.e. Mn is +2 in [Mn(H$_2$O)$_6$]$^{2+}$, Cr is +3 in [Cr(H$_2$O)$_6$]$^{3+}$
First-row d-block elements

Characteristics of Type C

- unstable high oxidation states
- stable low oxidation states
  - i.e. Fe is +2 in \([\text{Fe(H}_2\text{O)}_6]^{2+}\)

Type C:
Fe, Co, Ni, Cu, and Zn
First-row d-block elements

Variable oxidation states

- Potassium manganate (VII) reduced from +7 oxidation state (purple) to +2 (colourless)
  - $\text{Mn}^{7+} + 5\text{e}^- \rightarrow \text{Mn}^{2+}$
- Chromium reduced from +6 oxidation state (orange/yellow) to +3 (green)
  - $\text{Cr}^{6+} + 3\text{e}^- \rightarrow \text{Cr}^{3+}$
- Breathalyzers and Blood Alcohol Concentration (BAC) tests use redox reactions involving potassium dichromate (VI), ethanol being oxidized to ethanoic acid then carbon dioxide and water, or gas liquid chromatography (GLC).
First-row d-block elements

Coloured compounds of transition elements and their ions

• Transition metal compounds and ions are usually coloured - some examples:
  
  KMnO\(_4\)                  burgundy
  [MnO(H\(_2\)O)\(_6\)]^{2+}   almost colourless (faint pink)
  K\(_2\)Cr\(_2\)O\(_7\)        orange
  [Cr(H\(_2\)O)\(_6\)]^{3+}    green
  CuSO\(_4\)\:\:5H\(_2\)O       blue
  [NH\(_4\)]\(_2\)[Fe(H\(_2\)O)\(_6\)][SO\(_4\)]\(_2\) pale green

• Zn(II) compounds are typically colourless unless the ligands in the complex have a chromophore (group of atoms responsible for the absorption of electromagnetic radiation) which can absorb in the visible region.
First-row d-block elements

Coloured compounds of transition elements and their ions

• Complexes of transition metals:
  • Compounds that contain transition elements and the central atom is a metal ion, $M^{n+}$, that is bonded (via coordinate covalent bonding) to a group of molecules or ions (ligands) are called complexes of transition metals. aka coordinate compounds

A ligand is an atom, molecule, or ion that contains a lone pair of electrons that coordinates to a central transition metal ion to form a complex.
First-row d-block elements

Coloured compounds of transition elements and their ions

• Classification of ligands:
  • The number of coordinate bonds formed by one ligand with a metal ion depends on the number of donor centres (atoms with lone electron pairs)
  • Monodentate ligands are able to only form one coordinate bond with a metal ion
  • Polydentate ligands (chelate ligands) are able to form two or more coordinate bonds.
First-row d-block elements

Coloured compounds of transition elements and their ions

- **Monodentate ligands** are able to only form one coordinate bond with a metal ion
  - Contain a single donor atom and have one lone pair contributing to the coordinate bond in a complex.
  - *i.e. water, ammonia, and halides (Cl)*
First-row d-block elements

Coloured compounds of transition elements and their ions

- Polydentate ligands are able to only form two or more coordinate bonds
  - Contain two or more donor atoms that form coordinate bonds with transition metal centre.
- 1,2 ethanediamine (en), $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$ is a bidentate ligand as it has two donor atoms

\[
\begin{array}{c}
\text{H}_2\text{N} \\
\text{Cu}^{2+} \\
\text{H}_2\text{N}
\end{array}
\]

\[
\begin{array}{c}
\text{NH}_2 \\
\text{H}_2\text{N} \\
\text{NH}_2
\end{array}
\]
**First-row d-block elements**

Coloured compounds of transition elements and their ions

- **Polydentate ligands** are able to only form two or more coordinate bonds
  - Contain two or more donor atoms that form coordinate bonds with transition metal centre.
  - Ethanedioate (ox - oxalate), \((C_2O_4)^{2-}\) is a **bidentate** and dianionic ligand as it has two donor atoms
First-row d-block elements

Coloured compounds of transition elements and their ions

- **Polydentate ligands** are able to only form two or more coordinate bonds
  - Contain two or more donor atoms that form coordinate bonds with transition metal centre.
  - Ethylenediaminetetraacetate, (EDTA)$^{4-}$ is a **polydentate** ligand that can form up to six coordinate bonds
  - Wraps itself around transition metals in an octahedral complex
    - EDTA is used in heavy metal removal, chelation therapy, water softening, food preservation, and restorative sculpture, and cosmetics.
Coloured compounds of transition elements and their ions

• Coordination numbers
  • The majority of transition metal complexes have **coordination numbers** of six (octahedral geometry) or six (tetrahedral or square planar geometries)

<table>
<thead>
<tr>
<th>Stereochemistry</th>
<th>Bond angles / °</th>
<th>Coordination number</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>octahedral</td>
<td>90 (and 180)</td>
<td>6</td>
<td>[Fe(H₂O)₆]Cl₂</td>
</tr>
<tr>
<td>tetrahedral</td>
<td>109.5</td>
<td>4</td>
<td>K₂[CoCl₄]</td>
</tr>
<tr>
<td>square planar</td>
<td>90 (and 180)</td>
<td>4</td>
<td>K₂[Ni(CN)₄]</td>
</tr>
</tbody>
</table>

• VSEPR theory cannot be used to deduce the geometry of transition metal complexes because of the incomplete d-sublevels of the transition metal ions. Must use x-ray crystallography if single crystals are available.
First-row d-block elements

Transition metals as catalysts

- Often used as catalysts in chemical reactions.
  - **Haber process:**
    \[
    \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)
    \]
    catalyst: Fe(s)
  - **Decomposition of hydrogen peroxide:**
    \[
    2\text{H}_2\text{O}_2(aq) \rightarrow 2\text{H}_2\text{O}(l) + \text{O}_2(g)
    \]
    catalyst: MnO_2(s)
  - **Hydrogenation of alkenes:**
    \[
    \text{H}_2\text{C} = \text{CH}_2(g) + \text{H}_2(g) \rightarrow \text{CH}_3\text{CH}_3(g)
    \]
    catalyst: Ni(s), Pd(s), or Pt(s)
  - **Hydrogenation of oils:**
    \[
    \text{RCH} = \text{CHR}' + \text{H}_2(g) \rightarrow \text{RCH}_2\text{CH}_2\text{R}'
    \]
    catalyst: Ni(s)

Unsaturated oils can be hydrogenated (add hydrogen atoms). These form solids rather than liquids at room temperature and is less likely to become oxidized and go rancid. However, mono- and polyunsaturated fats are best for the heart and trans fatty acids are known to be a leading cause of heart disease.
First-row d-block elements

Transition metals as catalysts

- **Catalytic converters** in cars turn oxides of nitrogen, carbon monoxide, and hydrocarbons into nitrogen, carbon dioxide, and water.
- Play an important role in **green chemistry** - ensures we reduce the amount of substances hazardous to human health and the environment.
- **Enzymes** are biological catalysts that speed up reactions in the body. i.e. heme in hemoglobin carries oxygen.
- **Homogenous vs heterogenous catalysts**
  - Homogenous catalysts are in same phase or physical state as the substance involved in the reaction it is catalyzing.
  - Heterogenous catalysts is in a different phase to the substance involved in the chemical reaction that it is catalyzing. Usually involve transition metals for industrial catalysts.
First-row d-block elements

Magnetic properties of transition metals

• Depend on many factors: oxidation state of metal, coordination number, and geometry of the complex
  • **Paramagnetic materials** contain unpaired electrons that behave as tiny magnets and are attracted by an external magnetic field
  • **Diamagnetic materials** do not contain unpaired electrons and therefore are repelled by external magnetic fields
Transition elements have variable oxidation states, form complex ions with ligands, have coloured compounds, and display catalytic and magnetic properties.

Zn is not considered to be a transition element as it does not form ions with incomplete d orbitals.

Transition elements show an oxidation state of +2 when the s-electrons are removed.