Transition Elements

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Definition

- What is transition metal? One of which forms one or more stable ions which have incompletely filled $d$ orbitals.

$Zn_{30}$
Definition

• Zink is not transition elements
  – Zn → has fully filled $d$ orbital
Electronic configuration

- charge (atomic number) $\gg$, stability of $(n-1)d \gg ns$

- ionization energy of $(n-1)d \gg ns$

- filled orbital energy of $(n-1)d \ll ns$

- electronic configuration writing
  $-(n-1)d \ ns \ not \ ns \ (n-1)d$
Electronic configuration

Electronic structures of the d block elements
Electronic configuration

- $^{21}\text{Sc}$ : [18Ar] 3d$^1$4s$^2$
- $^{22}\text{Ti}$ : [18Ar] 3d$^2$4s$^2$
- $^{23}\text{V}$ : [18Ar] 3d$^3$4s$^2$
- $^{24}\text{Cr}$ : [18Ar] 3d$^5$4s$^1$
- $^{25}\text{Mn}$ : [18Ar] 3d$^5$4s$^2$
- $^{26}\text{Fe}$ : [18Ar] 3d$^6$4s$^2$
- $^{27}\text{Co}$ : [18Ar] 3d$^7$4s$^2$
- $^{28}\text{Ni}$ : [18Ar] 3d$^8$4s$^2$
- $^{29}\text{Cu}$ : [18Ar] 3d$^{10}$4s$^1$
- $^{30}\text{Zn}$ : [18Ar] 3d$^{10}$4s$^2$
Several energy terms to think about

• The amount of energy needed to ionize the metal

• The amount of energy released when the compound formed (as lattice enthalpy in solids, or the hydration enthalpies of the ions in solution)
Several energy terms to think about

• Charged the ion >>, electrons to be removed >> ionization energy >>

• Charged the ion >>, energy to be released (as lattice enthalpy or the hydration enthalpy of the metal ion) >>
Several energy terms to think about

• The more energy released, the more stable the compound
Oxidation state

1. $^{21}\text{Sc}$: $+1, +2, +3 \rightarrow +3$ is the most stable oxidation state

2. $^{22}\text{Ti}$: $+1, +2, +3, +4 \rightarrow +4$ is the most stable oxidation state
Oxidation state

- Iron

- Iron has two common oxidation states (+2 and +3), for example, Fe$^{2+}$ or \([\text{Fe(H}_2\text{O)}_6]\)^{2+} and Fe$^{3+}$ or \([\text{Fe(H}_2\text{O)}_6]\)^{3+}

- It also has a less common +6 oxidation state in the ferrate(VI) ion, FeO$_4^{2-}$. 
Manganese has a very wide range of oxidation states in its compounds. For example:

+2 ($\text{Mn}^{2+}$),
+3 ($\text{Mn}_2\text{O}_3$),
+4 ($\text{MnO}_2$),
+6 ($\text{MnO}_4^{2-}$),
+7 ($\text{MnO}_4^{-}$)
The origin of magnetism

- Electron (as particle → mass) → spinning on its axis → magnetism → magnet elemental
The origin of magnetism

electron magnetism

dominant

rotation on its axis

revolution on its orbit

neglected
Diamagnetic

- All materials have a diamagnetic effect
  → masked by larger “para or ferro” magnetic term
- All electron are paired
- Atoms have no net magnetic moment (no applied field)
- The spinning electrons produce a magnetization (M) in the opposite direction to that of the applied field (applied field)
Diamagnetic

opposite direction to applied field

magnetic moment cancelled each other

not attracted by a magnetic filed

diamagnetic
Diamagnetic

• Magnetic moment alignment
  – Has no magnetic moment
Paramagnetic

- Permanent magnetism from the spinning of unpaired electron

\[ \text{Paramagnetism} \approx \text{unpaired electron} \]
Paramagnetic

electronic configuration of central atom / cation

paramagnetism

influenced by ligand
Paramagnetic

The strength of ligands

I⁻ < Br⁻ < Cl⁻ < OH⁻ < H₂O
< NCS⁻ < NH₃ < en < CO < CN⁻
Paramagnetic

- Magnetic moment alignment
  - Randomly magnetic moment alignment
Paramagnetic vs. Diamagnetic

What is the magnetism of each compound below?

\[ \text{[NiCl}_4\text{]}^{2-} \quad ? \quad \text{[Ni(CN)}_4\text{]}^{2-} \]
Paramagnetic vs. Diamagnetic

- $[\text{NiCl}_4]^2-$:
  - paramagnetic
  - $\text{sp}^3$
  - tetrahedral
- $[\text{Ni(CN)}_4]^2-$
  - diamagnetic
  - $\text{dsp}^2$
  - square planar
Ferromagnetic (super magnet)

– Atoms are arranged in a lattice and the atomic magnetic moments can interact to align parallel to each other.

– Only Fe, Co and Ni are ferromagnetic at and above room temperature.
Ferromagnetic (super magnet)

- As ferromagnetic materials are heated or vibrated
  - alignment of the atomic magnetic moments decreases
  - saturation magnetization also decreases
  - paramagnetic
Ferromagnetic (super magnet)

– Curie temperature, TC
  • transition temperature of ferro → para
    Fe : 770°C
    Co : 1131°C
    Ni : 358°C
Ferromagnetic (super magnet)

• Magnetic moment alignment
  – Parallel magnetic moment alignment
Ferrimagnetic

– Only observed in compounds, which have more complex crystal structures than pure elements.
– Parallel alignment of atoms in some of the crystal sites and anti-parallel alignment of others.
– Ferrimagnetic materials usually have lower saturation magnetizations than ferromagnetic materials
Ferrimagnetic

Barium ferrite (BaO.6Fe$_2$O$_3$)

• The unit cell contains 64 ions
  – barium and oxygen ions have no magnetic moment
  – 16 Fe$^{3+}$ ions have moments aligned parallel
Ferrimagnetic

Barium ferrite (BaO.6Fe$_2$O$_3$)

- 8 Fe$^{3+}$ aligned anti-parallel giving a net magnetization parallel to the applied field,

- only $\frac{1}{8}$ of the ions contribute to the magnetization of the material.
Ferrimagnetic

- Magnetic moment alignment
  - Parallel magnetic moment in one site and anti-parallel in the other site
Antiferromagnetic

– Very similar to ferromagnetic materials

– The exchange interaction between neighboring atoms are anti-parallel alignment
Antiferromagnetic

– The magnetic field cancelled out

– Appears to behave in the same way as a paramagnetic material
Antiferromagnetic

– Only chromium is antiferromagnetic at room temperature

– Néel temperature, TN.
  • transition temperature of antiferro → para

  Cr: 37°C
Antiferromagnetic

- Magnetic moment alignment
  - Anti-parallel magnetic moment with neighboring atoms
Summary of different types of magnetic behavior

<table>
<thead>
<tr>
<th>Type of Magnetism</th>
<th>Susceptibility, Example</th>
<th>Atomic Behaviour</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamagnetism</td>
<td>Small &amp; negative Au (-2.74x10^{-6})</td>
<td>Atoms have no magnetic moment</td>
</tr>
</tbody>
</table>
## Summary of different types of magnetic behavior

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<tr>
<td>Paramagnetism</td>
<td>Small &amp; positive</td>
<td>Atoms have randomly oriented magnetic moments</td>
</tr>
<tr>
<td></td>
<td>Cu (0.77x10^{-6})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>β-Sn (0.19x10^{-6})</td>
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<tr>
<td></td>
<td>Pt (21.04x10^{-6})</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mn (66.10x10^{-6})</td>
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<td>Large &amp; positive function of applied magnetic moments field, microstructure dependent Fe (~100,000)</td>
<td>Atoms have parallel aligned</td>
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<tr>
<td>Antiferromagnetism</td>
<td>Small &amp; positive Cr (3.6 \times 10^{-6})</td>
<td>Atoms have anti-parallel aligned</td>
</tr>
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<tr>
<td>Ferri-magnetism</td>
<td>Large &amp; positive function of applied magnetic moments field, microstructure dependent Ba ferrite (~3)</td>
<td>Atoms have mixed parallel and anti-parallel aligned magnetic moments</td>
</tr>
</tbody>
</table>
Problem:

- Cr, Mo and W locate in the same group (group 6 or group VIB)
- Radius of:
  - $^{24}\text{Cr} = 128 \text{ pm}$
  - $^{42}\text{Mo} = 139 \text{ pm}$
  - $^{74}\text{W} = 139 \text{ pm}$
- Explain the radius phenomena of this group.