Variable oxidation states in transition elements

- is due to the small energy difference between the 4s and 3d subshells.

- Example: Iron,

\[
\text{Oxidation state} \\
\begin{align*}
\text{Fe}^{2+} & : +2 \\
\text{Fe}^{3+} & : +3 \\
\text{Fe} & : \{ \text{common} \} \\
\text{Ferrate(VI) ion, FeO}_4^{2-} & : +6 \text{ } \{ \text{less common} \}
\end{align*}
\]

- Example: Manganese,

\[
\begin{align*}
\text{Mn}^{2+} & : +2 \\
\text{Mn}_2\text{O}_3 & : +3 \\
\text{MnO}_2 & : +4 \\
\text{MnO}_4^- & : +6 \\
\text{Mn}^{7+} & : +7
\end{align*}
\]

Explaining iron has +2 & +3 oxidation states
(Magnesium has only +2)

- The first 4 successive ionisation energies (kJ mol\(^{-1}\)) for iron and magnesium are as follows:

<table>
<thead>
<tr>
<th>element</th>
<th>first</th>
<th>second</th>
<th>third</th>
<th>fourth</th>
</tr>
</thead>
<tbody>
<tr>
<td>magnesium</td>
<td>736</td>
<td>1450</td>
<td>7740</td>
<td>10500</td>
</tr>
<tr>
<td>iron</td>
<td>762</td>
<td>1560</td>
<td>2960</td>
<td>5400</td>
</tr>
</tbody>
</table>
When compounds are formed, energy must be supplied to remove electrons (the sum of the various ionisation energies) from the atoms of the elements,

- The energy for this ionisation is supplied by the energy given out when the new bonds are formed. This will be lattice energy for solid compounds (hydration enthalpies of the ions for solution).
- When Mg forms compounds, Mg$^{2+}$ ions are easily formed.
- For example, the lattice energy liberation from the Mg$^{2+}$ and O$^{2-}$ ions comes together to supply enough to supply the ionisation energy ($736 + 50 \text{ kJ mol}^{-1}$) to form Mg$^{2+}$ ions. However, this reaction will not supply the much larger amount of energy ($7740 \text{ kJ}$) needed to remove the 3rd electron, which is from an inner shell. Hence Mg only forms Mg$^{2+}$ ions and not Mg$^{3+}$ or Mg$^{4+}$ etc.

- When iron forms compounds, Fe$^{2+}$ ions are easily formed - like Mg$^{2+}$ in magnesium.
- However, there is no big increase in the amount of energy required to remove the 3rd electron (from the 3d subshell) because of the small energy difference between the 4s and 3d.