In a series of papers, we have examined the variations in the enthalpies of the following processes across the first transition series [1–4]:

\[
\text{M}^{2+}(g) + \text{aq} \rightarrow \text{M}^{2+}(\text{aq})
\]

\[
\text{M}^{2+}(g) + 2\text{X}^-(g) \rightarrow \text{MX}_2(s) \quad (\text{X} = \text{F}, \text{Cl}, \text{I})
\]

\[
\text{M}^{3+}(g) + \text{aq} \rightarrow \text{M}^{3+}(\text{aq})
\]

\[
3\text{K}^+(g) + \text{M}^{3+}(g) + 6\text{F}^-(g) \rightarrow \text{K}_3\text{MF}_6(s)
\]

We found that the variations are fully accounted for if consideration is given to (1) the stabilization energy resulting from the splitting of the 3d orbitals in the ligand field (\(\Delta E_{\text{orb}}\)); (2) the loss of energy arising from the reduction of metal-ligand distance accompanying the stabilization (the energy of contraction against the force constant, \(\Delta E_{\text{ctr}}\)) [5]; (3) the irregular, stabilizing decrease in interelectronic repulsion energy, over and above the values for spherical ions, arising from the expansion of the 3d shell in the ligand field (the ‘nephelauxetic’ effect)(\(\Delta E_{\text{rep-irreg}}\)) [6]; and (4) the reduction in spin-orbit coupling energy associated with the splitting of the 3d orbitals (\(\Delta E_{\text{so}}\)). When these quantities (per mole) are subtracted from the enthalpies of the above reactions, smooth curves are obtained through the points for 3d\(^1\) to 3d\(^{10}\) ions (see, e.g., Fig. 1).

![Figure 1](https://www.arjonline.org)

**Fig1.** Lattice enthalpies of \(\text{K}_3\text{MF}_6\) plotted against number of 3d electrons. Blue circles, experimental values; red squares, residual values after subtracting the energies listed in the text. Data from ref. 1. The equation and correlation factor refer to the residual curve.
Inter-Subshell Break in the Lattice Enthalpies of First-Row Transition-Metal Trichlorides

This analysis revealed an unexpected feature. Previous and long-standing ligand field treatments of such problems [7,8] had assumed the existence of a smooth baseline from 3d⁰ to 3d¹⁰. Ours revealed a discontinuity between the values for 3d⁰ and 3d¹. Since 3d⁰ is actually 3p⁶, this amounts to an inter-subshell break. The magnitude of this break varies as shown in Table 1. For M⁺ ions, the values are in the order (aq, F⁻) < Cl⁻ < I⁻; for M²⁺ ions, aq < F⁻, and comparing M³⁺ ions with M²⁺ ions, M³⁺ > M²⁺. These sequences follow approximately the nephelauxetic order for ligands and ions [9], which made us think that the inter-subshell break may be related to the nephelauxetic effect. To test this hypothesis, we have extended our analysis to the trichlorides, for which the nephelauxetic effect is greater than for M³⁺(aq) and K₃MF₆(s).

Table 1. Inter-subshell breaks (/kJ mol⁻¹)

<table>
<thead>
<tr>
<th>Species</th>
<th>Break</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>M⁰⁺(aq)</td>
<td>10</td>
<td>2</td>
</tr>
<tr>
<td>MF₆(s)</td>
<td>0</td>
<td>3</td>
</tr>
<tr>
<td>MCl₃(s)</td>
<td>80</td>
<td>3</td>
</tr>
<tr>
<td>MI₃(s)</td>
<td>90</td>
<td>3</td>
</tr>
<tr>
<td>M³⁺(aq)</td>
<td>42</td>
<td>4</td>
</tr>
<tr>
<td>K₃MF₆(s)</td>
<td>117</td>
<td>See Fig. 1</td>
</tr>
</tbody>
</table>

Calculations and Results

We have analysed the enthalpy of the process

M³⁺(g) + 3Cl⁻(g) → MCl₃(s)

in the same way as in our previous studies using the data in Table 2. The results are set out in Table 3 and plotted in Fig 2. A complication is that the experimental value for gallium trichloride is for tetrahedral coordination whereas all the other trichlorides have octahedral structures. To allow for this, we have estimated the enthalpy of transition to the octahedral form to be about 10 ± 10 kJ mol⁻¹. The low value reflects the fact that weak bonds in the structure complete a distorted octahedron [10]. Comparison between the lattice enthalpies of the trichlorides and corresponding trifluorides also suggest a low value [11]. The uncertainty does not significantly affect the extrapolation to 3d⁰, which gives an inter-subshell break of 24 ± 10 kJ mol⁻¹. This is less than for M³⁺(aq) and K₃MF₆(s), contrary to our expectations. The inter-subshell break is not therefore related to the nephelauxetic effect, and must have another origin.

Table 2. Data used in the calculations

<table>
<thead>
<tr>
<th>Trichloride</th>
<th>Config.</th>
<th>ΔH₀°</th>
<th>r</th>
<th>Δ</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScCl₃[6]</td>
<td>3d⁰</td>
<td>−945 ± 2</td>
<td>258⁵</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TiCl₃[6]</td>
<td>3d¹</td>
<td>−722 ± 5</td>
<td>247⁷</td>
<td>12,900⁶⁰</td>
<td></td>
<td></td>
</tr>
<tr>
<td>VCl₃[6]</td>
<td>3d²</td>
<td>−584 ± 3</td>
<td>245⁷</td>
<td>13,900⁶⁰</td>
<td>563⁶⁰</td>
<td></td>
</tr>
<tr>
<td>CrCl₃[6]</td>
<td>3d³</td>
<td>−544 ± 2</td>
<td>234.3⁸</td>
<td>13,700⁶⁰</td>
<td>550⁸⁰</td>
<td>3400⁶⁹</td>
</tr>
<tr>
<td>FeCl₃[6]</td>
<td>3d⁵</td>
<td>−396 ± 2</td>
<td>235.9⁹</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GaCl₃[4]</td>
<td>3d¹⁰</td>
<td>−525 ± 10</td>
<td>220m</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>——[6]</td>
<td></td>
<td>(−515 ± 15)⁶</td>
<td>(232)⁹</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

American Research Journal of Chemistry
Inter-Subshell Break in the Lattice Enthalpies of First-Row Transition-Metal Trichlorides


Table 3. Results of calculations (/kJ mol⁻¹)

<table>
<thead>
<tr>
<th>Trichloride</th>
<th>ΔH_latt</th>
<th>ΔE_orb</th>
<th>ΔE_rep-irreg</th>
<th>ΔE_ctr</th>
<th>ΔE_so</th>
<th>ΔH_res</th>
</tr>
</thead>
<tbody>
<tr>
<td>ScCl₃</td>
<td>-4895</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-4895</td>
</tr>
<tr>
<td>TiCl₃</td>
<td>-5132</td>
<td>-62</td>
<td>(-37)ᵇ</td>
<td>5⁶</td>
<td>2⁷</td>
<td>-5040</td>
</tr>
<tr>
<td>VCl₃</td>
<td>-5308</td>
<td>-120</td>
<td>(-48)ᵇ</td>
<td>5⁶</td>
<td>3⁷</td>
<td>-5148</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>-5490</td>
<td>-197</td>
<td>-41</td>
<td>22⁹</td>
<td>5⁶</td>
<td>-5279</td>
</tr>
<tr>
<td>FeCl₃</td>
<td>-5409</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-5409</td>
</tr>
<tr>
<td>GaCl₃[6]</td>
<td>-5625</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>-5625</td>
</tr>
</tbody>
</table>

Col. 2, enthalpy of formation from ions (lattice enthalpy); col. 3, orbital stabilization energy; col. 5, contraction energy; col. 6, spin-orbit coupling energy loss; col. 7, residual enthalpy (lattice enthalpy minus energies in cols. 2–6). Estimated by scaling the values for aqua ions and fluorides (refs. 1 and 4) according to the value for CrCl₃. Calculated from a value of about 300 cm⁻¹ for the wave number of the symmetric vibration of the [MCl₆] coordination entity in MCl₃, estimated from the values for discrete [MCl₆]²⁻ ions (K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 5th edn., Part A, Table II-8a, Wiley, New York, 1997; H.H. Eysel, Z. anorg. Chem., 1972, 390, 210). We have smoothed the experimental values of Δr by comparison with the values for aqua ions and fluorides (refs. 1 and 4). Calculated from a Boltzmann distribution over the energy levels of gaseous M³⁺ (http://physics.nist.gov/asd) and of the ion in an octahedral environment (B.N. Figgis and M.A. Hitchman, Ligand Field Theory and Its Applications, 2nd edn., Wiley Inc. UK, 2000, pp. 241–251). The latter were calculated using λ = aλ_gas with λ_gas from Figgis and Hitchman (op. cit., pp. 107–110) and a = 0.6 as for CrCl₃ (Table 2, note q). Calculated from the energy levels of the gaseous ion. To a first approximation, the ⁴A₂g ground state does not split in an octahedral field.
Inter-Subshell Break in the Lattice Enthalpies of First-Row Transition-Metal Trichlorides

![Graph showing lattice enthalpies of trichlorides plotted against number of 3d electrons. Blue circles, experimental values; red squares, residual values after subtracting the energies listed in the text (Table 3). The equation and correlation factor refer to the residual curve.]

**Fig 2.** Lattice enthalpies of trichlorides plotted against number of 3d electrons. Blue circles, experimental values; red squares, residual values after subtracting the energies listed in the text (Table 3). The equation and correlation factor refer to the residual curve.

**References**

5. In previous papers, we called this the ‘relaxation’ energy ($\Delta E_{\text{relx}}$), but this better describes the reverse process.
6. Note that this has a value for $3d^1$ ions even though there is no $3d$–$3d$ repulsion in the gaseous ion. This is because there is repulsion in the spherical ion (1/5th of that in $3d^5$ and 1/10th of that in $3d^{10}$), and hence in the energy of the gaseous ion relative to the spherical ion. The nephelauxetic effect brings down the energy of the spherical ion towards that of the gaseous ion.
11. All the trifluorides, including GaF$_3$, have an octahedral structure, enabling an approximate value for octahedral GaCl$_3$ to be obtained from a plot of the lattice enthalpies of the trichlorides against the trifluorides.

**Citation:** Peter G. Nelson, David A. Johnson “Inter-Subshell Break in the Lattice Enthalpies of First-Row Transition-Metal Trichlorides”. American Research Journal of Chemistry, 1(1); pp:37-40.

**Copyright © Peter G. Nelson, David A. Johnson, This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.**