Chapter 4
Energetics of Covalent Compounds

4 Bond energies

In the preceding chapter it was seen that the structures of certain compounds can be conveniently represented as non-molecular assemblages of oppositely charged ions. In other cases, such an ionic model is unacceptable, either because the ions postulated would be chemically improbable (for example, \( Si^{++}C^{4-} \) as the components of silicon carbide) or because the properties of the substance are consistent with the presence of molecular units; the compound in such cases is described as predominantly covalent.

In the case of ionic substances, the energy quantity of primary interest is the energy change for the separation of the ions in the crystalline lattice into ions in the gas phase, that is the lattice energy.

Thus for sodium chloride, \( \Delta U_0 \) for the process

\[
\text{NaCl}(s) \rightarrow \text{Na}^+(g) + \text{Cl}^-(g)
\]

is 766 kJ mol\(^{-1}\), and is a measure of the strength of the predominantly ionic bonds in the crystal. \( \Delta U_0 \) represents the amount by which the energy of one mole of \( \text{Na}^+(g) \) ions and one mole of \( \text{Cl}^-(g) \) ions, in the ideal gas state and lacking translational or rotational energies, is greater than the energy of one mole of crystalline NaCl, possessing only the zero-point vibration energy. If the zero-point energy (for NaCl, 7 kJ mol\(^{-1}\)) is added to \( \Delta U_0 \), the result (773 kJ mol\(^{-1}\)) represents the 'pure' binding energy in the crystal, in that it is free of any vibrational energy contribution whatsoever.

The room-temperature enthalpy change \( \Delta H_{298} \) for the same process differs from \( \Delta U_0 \) in that it incorporates a small \( P \Delta V \) term together with the small difference between the translational energy of the gaseous ions \( \text{Na}^+(g) \) and \( \text{Cl}^-(g) \), and the vibrational energy of the crystal sodium chloride. Thus \( \Delta H_{298} \) is not as 'pure' a measure of bond strength as \( \Delta U_0 \), but the difference between the two quantities is commonly very small, and lattice enthalpies deduced from 298 K Born–Haber cycles are freely used as measures of ionic bond strength.

Turning now to covalent compounds, the corresponding quantity of theoretical interest is the energy change for the dissociation of the basic structural unit (commonly the molecule) into its component atoms, in the ideal gas state. In the course of dissociating in this way, the covalent bonds within the molecules are broken, and the energies involved are therefore known as bond energies. The general term 'bond energy' is, however, one which must be examined closely.

Bond-dissociation energy \( D \)

For a diatomic molecule such as \( \text{H}_2 \), the change in internal energy \( \Delta U_0 \) at 0 K for the dissociation

\[
\text{H}_2(g) \rightarrow 2\text{H}(g),
\]

where the reactant molecules and product atoms are in their ground states, is called the bond-dissociation energy, \( D \). As discussed in section 1.2.4, it represents the amount by which the internal energy of two moles of hydrogen atoms (without translational, rotational or vibrational energy) is greater than the internal energy of one mole of hydrogen molecules (without translational or rotational energy, and possessing only the zero-point vibrational energy); \( \Delta U_0 = 432 \text{ kJ (mol H}_2\text{)}^{-1} \). If the zero-point energy (26 kJ mol\(^{-1}\)) is added to \( \Delta U_0 \), the result (458 kJ mol\(^{-1}\)) is the energy increase for the hypothetical dissociation \( \text{H}_2 \rightarrow 2\text{H} \) in which all forms of thermal energy, and the zero-point energy as well, are absent in both reactants and products. The quantity 458 kJ mol\(^{-1}\) is therefore a 'pure' bond energy, in that it is the measure solely of the electrostatic interactions which distinguish the \( \text{H}_2 \) molecule from its component atoms. It is usual, however, to use the term 'bond-dissociation energy' to describe \( \Delta U_0 \) itself.

For polyatomic molecules, there will be more than one bond-dissociation energy \( D \). Thus for ammonia,

\[
\begin{align*}
\text{NH}_3(g) & \rightarrow \text{NH}_2(g) + \text{H}(g) \quad \Delta U_0 = D_1 = 448 \text{ kJ mol}^{-1}, \\
\text{NH}_3(g) & \rightarrow \text{NH}(g) + \text{H}(g) \quad \Delta U_0 = D_2 = 368 \text{ kJ mol}^{-1}, \\
\text{NH}(g) & \rightarrow \text{N}(g) + \text{H}(g) \quad \Delta U_0 = D_3 = 356 \text{ kJ mol}^{-1}.
\end{align*}
\]

and for water,

\[
\begin{align*}
\text{H}_2\text{O}(g) & \rightarrow \text{OH}(g) + \text{H}(g) \quad \Delta U_0 = D_1 = 497 \text{ kJ mol}^{-1}, \\
\text{OH}(g) & \rightarrow \text{O}(g) + \text{H}(g) \quad \Delta U_0 = D_2 = 421 \text{ kJ mol}^{-1}.
\end{align*}
\]

It is clear from these data that the dissociation energy of a bond between two specified atoms (e.g. N and H) is not a constant quantity, and that its value depends on the molecular environment of the atoms considered. It is necessary therefore to specify the bond involved in the symbol used,

e.g. \( D_{\text{H-N-H}} = 448 \text{ kJ mol}^{-1} \).

Sometimes \( \Delta H_{298} \) is measured instead of \( \Delta U_0 \); the difference between the two quantities (discussed in section 1.3.1) is usually not very great,

e.g. \( \text{Cl}_2(g) \rightarrow 2\text{Cl}(g) \)
\[
\Delta U_0 = 239 \text{ kJ mol}^{-1} \quad \Delta H_{298} = 242 \text{ kJ mol}^{-1}.
\]
Table 27—continued

<table>
<thead>
<tr>
<th>X—Halogens bonds (continued;)</th>
<th>P—P</th>
<th>S—S</th>
</tr>
</thead>
<tbody>
<tr>
<td>(NCl₃)</td>
<td>(P₄)</td>
<td>(S₈)</td>
</tr>
<tr>
<td>193</td>
<td>209</td>
<td>226</td>
</tr>
<tr>
<td>319</td>
<td>489</td>
<td>427</td>
</tr>
<tr>
<td>490</td>
<td>264</td>
<td>184</td>
</tr>
<tr>
<td>317</td>
<td>243</td>
<td>180</td>
</tr>
<tr>
<td>Sb—Cl</td>
<td>(SbCl₅)</td>
<td>312</td>
</tr>
<tr>
<td>Bi—Cl</td>
<td>(BiCl₃)</td>
<td>280</td>
</tr>
<tr>
<td>O—F</td>
<td>(F₂O)</td>
<td>190</td>
</tr>
<tr>
<td>205</td>
<td>255*</td>
<td></td>
</tr>
<tr>
<td>S—F</td>
<td>(SF₆)</td>
<td>326</td>
</tr>
<tr>
<td>160*</td>
<td>146*</td>
<td></td>
</tr>
<tr>
<td>255*</td>
<td>312</td>
<td></td>
</tr>
<tr>
<td>Se—F</td>
<td>(SeF₆)</td>
<td>285</td>
</tr>
<tr>
<td>243</td>
<td>335</td>
<td></td>
</tr>
</tbody>
</table>

Multiple bonds (Single bond energies are shown for comparison;)

<table>
<thead>
<tr>
<th>C—C</th>
<th>N—N</th>
<th>O—O</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₄H₄</td>
<td>N₂H₄</td>
<td>H₂O₂</td>
</tr>
<tr>
<td>346*</td>
<td>160*</td>
<td>146*</td>
</tr>
<tr>
<td>C≡C</td>
<td>N≡N</td>
<td>&quot;O≡O&quot;</td>
</tr>
<tr>
<td>C₄H₄</td>
<td>C₄H₄N₂</td>
<td>O₂</td>
</tr>
<tr>
<td>598*</td>
<td>418*</td>
<td>498</td>
</tr>
<tr>
<td>C≡C</td>
<td>N≡N</td>
<td></td>
</tr>
<tr>
<td>C₄H₂</td>
<td>N₂</td>
<td></td>
</tr>
<tr>
<td>813*</td>
<td>946</td>
<td></td>
</tr>
</tbody>
</table>

The experimental heat of atomization of hydrazine, viz \( \Delta H_{298} \) for the reaction

\[
\text{N}_2\text{H}_4(g) \rightarrow 2\text{N}(g) + 4\text{H}(g),
\]

is known and is equal to 1724 kJ mol⁻¹. This is the enthalpy change which occurs when four N—H bonds and one N—N bond are broken. Is it possible to assign a proportion of \( \Delta H_{298} \) for the total atomization process to each of the bonds? This can be done, but only in a rather arbitrary way. It may be assumed, for example, that \( \Delta H_{298} \) for the fission of the four N—H bonds is four times \( E_{N—H} \) for the \( \text{NH}_3 \) molecule, viz \( 4 \times 91 = 1564 \) kJ mol⁻¹, and that \( \Delta H_{298} \) for the fission of the N—N bond is thus \( 1724 - 1564 = 160 \) kJ mol⁻¹. This is in fact the only technique for assigning a value to \( E_{N—N} \) since there is no molecule – for example, a nitrogen analogue (\( \text{N}_2 \)) of white phosphorus – which contains only N—N single bonds. Many bond energies must be obtained in this indirect way.

Some thermochemical bond energies are listed in Table 27. The substances from whose heat of atomization the \( E \) value was derived are also shown. Values of \( E \) which are 'secondary' in the sense that they depend on an assumed energy for other bonds present in the molecule under consideration are marked with an asterisk.

The extent to which bond energies may be summed to give a value for the heat of atomization of a molecule for which thermochemical data are lacking is discussed in section 4.5.2.

4.4 Factors contributing to bond energies

It has been established in the foregoing discussion that the individual bond energies for the stepwise dissociation of a molecule – for example \( D_{N—N} \),

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107 Factors Contributing to Bond Energies
$D_{H-H}$ and $D_{N-H}$ are not necessarily the same, and it will be seen in section 4.5.2 that the mean thermochemical bond energies for molecules in which the central atom exhibits different oxidation states — for example $PCl_3$ and $PCl_5$ — may also be different. The possible reasons for these departures from constancy can be appreciated by considering the factors which contribute to the energy changes which occur when bonds are formed or broken.

Consider for example the group 4 elements carbon, silicon, germanium, tin and lead, which form tetravalent compounds $MX_4$ such as halides and hydrides. The total bond-formation process

$$M(g) + 4X(g) \rightarrow MX_4(g),$$

where $M = C$, $Si$, $Ge$, $Sn$, $Pb$ and $X = H$, $F$, $Cl$

involves the combination of gas-phase atoms in their ground states. In particular $M(g)$ is an atom whose valence-shell configuration is $ns^2np^3$, that is the valence-shell comprises a pair of electrons occupying a spherically symmetrical $ns$ orbital, together with two unpaired electrons which occupy, singly, two of the $np$ orbitals. In order for such an atom to form four covalent bonds with hydrogen or halogen atoms, it is necessary first that the $ns$ electron pair be uncoupled and one electron of the pair promoted to the vacant $np$ orbital, giving an atom with four unpaired electrons and configuration $ns^2np^3np^1$. There is in general more than one spectroscopically identifiable stationary state corresponding to this configuration, but that of lowest energy is the stationary state with term symbol $^3S$, which in the case of carbon $C$ lies at 3373.5 mm$^{-1}$ or 404 kJ mol$^{-1}$ above the ground ($^3P$) state, and in the case of silicon $Si$ at 3332.6 mm$^{-1}$ or 399 kJ mol$^{-1}$ above the ground state. The first step in the bond-formation process is thus the energy-absorbing transition

(i) $M(^3S_p^3p_1^1)(g) \rightarrow M(^3S_p^2p_1^1)(g).$

In the product of this transition, however, the four unpaired electrons are distributed among three $p$-orbitals which are mutually at right angles, and one $s$-orbital which has no preferred spatial orientation. Since the product molecules $MX_4$ have tetrahedral symmetry, the next step in the bond-formation process may be envisaged as the energy-absorbing rearrangement of the orbitals of the excited $M^*$ atom to produce an atom in its 'valence state', a state in which the orbitals have the correct spatial distribution (i.e. tetrahedral $sp^3$ hybrids), and the electrons in them are free of any interactions involving their spins or orbital motions:

(ii) $M(^3S_p^2p_1^1)(g) \rightarrow M(^3S_p^3p_1^1)(g).$

The resulting state is not a stationary state of the atom, that is it is not observable spectroscopically, and hence the excitation energy involved cannot be determined experimentally — nor can it be rigorously calculated. But approximate values have been obtained from weighted averages of empirical promotion energies.

The final step is the energy-releasing combination of the 'prepared' atom $M(^3S_p^3p_1^1)(g)$ with the atoms $4X(g)$ (which may also have been involved in suitable preliminary excitation processes) to give the product molecule $MX_4(g)$:

(iii) $M(^3S_p^3p_1^1)(g) + 4X(g) \rightarrow MX_4(g).$

**Figure 16.** Spectroscopic energy levels of $C(g)$ and $Si(g)$ atoms. The energies necessary to excite an electron from the ground state $sp^3$ configuration ($^3S$) to the lowest-lying $sp^3$ configuration ($^3P$) are: $C: 4.18$ eV or $404$ kJ mol$^{-1}$ and $Si: 4.13$ eV or $399$ kJ mol$^{-1}$. 

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109 Factors Contributing to Bond Energies
It is in this final step that the bonds are actually formed, and the energy released thereby has been called the "intrinsic bond energy".

The contributions, $\Delta H_{\text{int}}$ (kJ mol$^{-1}$), of steps (i, ii and iii) above for the M–H bonds in CH$_4$ and SiH$_4$ are as follows:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) $M(s^2 p^1 p^1)(g) \rightarrow M^*(s^2 p^2 p^1)(g)$</td>
<td>404</td>
<td>399</td>
</tr>
<tr>
<td>(ii) $M^*(g) \rightarrow M^+_\text{a}(g)$</td>
<td>228</td>
<td>85</td>
</tr>
<tr>
<td>(iii) $M^+_\text{a}(g) + 4H(g) \rightarrow MH_4(g)$</td>
<td>-2294</td>
<td>-1777</td>
</tr>
<tr>
<td>(iv) $M(g) + 4H(g) \rightarrow MH_4(g)$</td>
<td>-1662</td>
<td>-1283</td>
</tr>
</tbody>
</table>

Thermochemical bond energy $E_{\text{M–H}}$

<table>
<thead>
<tr>
<th></th>
<th>(from step iv)</th>
<th>(from step iii)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>416</td>
<td>574</td>
</tr>
<tr>
<td>Si</td>
<td>321</td>
<td>444</td>
</tr>
</tbody>
</table>

The data for step (i) were derived from the appropriate spectroscopic promotion energies (see Figure 16); those for step (ii) are estimated values of J. Hinze and H. H. Jaffé (1962); those for step (iv) were obtained from the following enthalpies of formation, $\Delta H^\circ_f$ (kJ mol$^{-1}$):

- C(g), 715; Si(g), 452; H(g), 218; CH$_4$(g), -75; SiH$_4$(g), 31.

Those for step (iii) were then obtained by difference.

If the estimated energies for excitations to valence states are correct, then it seems that this process occurs more readily for silicon than for carbon, and that the intrinsic energy of the C–H bond is actually 130 kJ higher than that of the Si–H bond, whereas the thermochemical bond energy is only 93 kJ higher. The weakest link in this argument is obviously the estimated valence state energy – it is not a rigorously calculable quantity, and furthermore any contribution that the silicon atom 3d orbitals may make to the imagined valence state hybrids has been ignored.

The corresponding data for the M–Cl bonds in CCl$_4$(g) and SiCl$_4$(g), derived as in the previous example together with the enthalpies of formation, $\Delta H^\circ_f$ (kJ mol$^{-1}$), of CCl$_4$(g) (-107) and SiCl$_4$(g) (-628), are as follows:

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) $M(s^2 p^1 p^1)(g) \rightarrow M^*(s^2 p^2 p^1 p^1)(g)$</td>
<td>404</td>
<td>399</td>
</tr>
<tr>
<td>(ii) $M^*(g) \rightarrow M^+_\text{a}(g)$</td>
<td>228</td>
<td>85</td>
</tr>
<tr>
<td>(iii) $M^+_\text{a}(g) + 4Cl(g) \rightarrow MCl_4(g)$</td>
<td>-1938</td>
<td>-2048</td>
</tr>
<tr>
<td>(iv) $M(g) + 4Cl(g) \rightarrow MCl_4(g)$</td>
<td>-1306</td>
<td>-1564</td>
</tr>
</tbody>
</table>

4.3 Periodic trends in $\Delta G_f^\circ$ and $\Delta H_f^\circ$ for covalent compounds

In this section the factors responsible for the trends in the free energies and enthalpies of formation of covalent compounds are examined. It is difficult to generalize in a field as extensive as this, and the following three examples have been chosen to illustrate the problems which arise.

4.3.1 The gaseous hydrogen halides, HX (X = F, Cl, Br, I)

The enthalpies and free energies of formation of the gaseous hydrogen halides at 298 K are as follows:

<table>
<thead>
<tr>
<th></th>
<th>HF</th>
<th>HCl</th>
<th>HBr</th>
<th>HI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_f^\circ$ (kJ mol$^{-1}$)</td>
<td>-269</td>
<td>-92.3</td>
<td>-36.2</td>
<td>+26</td>
</tr>
<tr>
<td>$\Delta G_f^\circ$ (kJ mol$^{-1}$)</td>
<td>-271</td>
<td>-95.3</td>
<td>-53.2</td>
<td>+1.3</td>
</tr>
</tbody>
</table>

Both $\Delta H_f^\circ$ and $\Delta G_f^\circ$ become less negative in passing along the series from HF to HI; in the case of hydrogen iodide both quantities are actually positive. The contributions of the entropy term $T \Delta S$ are as follows:

111 Periodic Trends in $\Delta G_f^\circ$ and $\Delta H_f^\circ$ for Covalent Compounds
of the group nitrogen, phosphorus, arsenic, antimony and bismuth at 298 K are as follows. The contribution of the entropy term \( T \Delta S \) is also shown:

- \( \Delta H_{T}^{\circ}(kJ \text{ mol}^{-1}) \):
  - NCl3: +258
  - PCl3: -279
  - AsCl3: -299
  - SbCl3: -315
  - BiCl3: -271

- \( \Delta G_{T}^{\circ}(kJ \text{ mol}^{-1}) \):
  - NCl3: +258
  - PCl3: -279
  - AsCl3: -299
  - SbCl3: -315
  - BiCl3: -271

*estimated by calculating \( S_{298}^\circ \). NCl3(g) as approximately 297 J K^{-1} mol^{-1} (see section 4.5.4).

The most notable feature of these data is the high positive value of \( \Delta H_{T}^{\circ} \) and \( \Delta G_{T}^{\circ} \) for NCl3(g). For the other compounds, the values are all negative; the trends from PCl3 to BiCl3 are irregular, the values of both \( \Delta H_{T}^{\circ} \) and \( \Delta G_{T}^{\circ} \) becoming more negative from PCl3 to SbCl3 and then falling again at BiCl3. In all cases the entropy contribution \( T \Delta S \) to \( \Delta G \) is small compared to the enthalpy term, and is largest in the case of NCl3. The fact that \( T \Delta S_{T} \) for NCl3 is about twice that for PCl3 stems largely from the fact that elementary nitrogen in its standard state is a gas, whereas elementary phosphorus is a solid; the individual entropies of the reactants and products in the formation reactions

\[
\frac{1}{2}N_{2}(g) + \frac{3}{2}Cl_{2}(g) \rightarrow NCl_{3}(g);
\]

\[
\Delta S_{298}^{\circ} = 96 \quad 334 \quad 297,
\]

\[
\Delta S_{298}^{\circ} = -133 \text{ J K}^{-1} \text{ mol}^{-1}
\]

and

\[
P(s) + \frac{1}{2}Cl_{2}(g) \rightarrow PCl_{3}(s);
\]

\[
\Delta S_{298}^{\circ} = 44 \quad 334 \quad 312,
\]

\[
\Delta S_{298}^{\circ} = -66 \text{ J K}^{-1} \text{ mol}^{-1}
\]

show clearly the effect of the large entropy of gaseous \( N_{2} \) compared to the smaller entropy of solid phosphorus.

The terms contributing to \( \Delta H_{T}^{\circ} \) are evident from the following reaction sequence:

(1) \( X(s.s.) \rightarrow X(g) \)

\[
N \quad P \quad As \quad Sb \quad Bi
\]

\[
\begin{array}{cccccc}
+47 & +31 & +28 & +255 & +20; \\
+36 & +36 & +36 & +363 & +362 \\
-578 & -957 & -95 & -937 & -841
\end{array}
\]

(2) \( \frac{1}{2}Cl_{2}(g) \rightarrow 3Cl(g) \)

(3) \( X(g) + 3Cl(g) \rightarrow XCl_{3}(g) \)

\[
\Delta H_{T}^{\circ}(kJ \text{ mol}^{-1}) \]

\[
+258 \quad -279 \quad -360 \quad -315 \quad -271
\]

4.3.7 The gaseous trichlorides, XCl3 (X = N, P, As, Sb, Bi)

The enthalpies and free energies of formation of the gaseous trichlorides:

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In Figure 17, the energies of Gai, Afi, and Af iron compounds are compared to the standard of 1.25. The data is presented in a graph with the x-axis representing the compound and the y-axis representing the energy difference from the standard. The compounds are categorized into different groups based on their energy differences. The data points are connected to show the trends and patterns among the compounds. The graph also includes a legend and annotations to provide additional context.

The data for the compounds is as follows:

<table>
<thead>
<tr>
<th>Compound</th>
<th>Energy Difference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gai</td>
<td>-1.25</td>
</tr>
<tr>
<td>Afi</td>
<td>-0.85</td>
</tr>
<tr>
<td>Af</td>
<td>-1.49</td>
</tr>
</tbody>
</table>

The graph shows a clear trend with the compounds grouped by their energy differences. The compounds are plotted on the graph with their respective energy differences, allowing for a visual comparison of their relative positions.
<table>
<thead>
<tr>
<th>Substance</th>
<th>m.p./K</th>
<th>$\Delta H_{\text{m.p.}}$ /kJ mol$^{-1}$</th>
<th>$\Delta H_{\text{fus.}}$ /kJ K$^{-1}$ mol$^{-1}$</th>
<th>b.p./K</th>
<th>$\Delta H_{\text{vap.}}$ /kJ mol$^{-1}$</th>
<th>$\Delta S_{\text{vap.}}$ /kJ K$^{-1}$ mol$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He</td>
<td>3</td>
<td>0.02</td>
<td></td>
<td>107</td>
<td>0.08</td>
<td>21</td>
</tr>
<tr>
<td>Ne</td>
<td>24</td>
<td>0.33</td>
<td></td>
<td>107</td>
<td>1.76</td>
<td>65</td>
</tr>
<tr>
<td>Ar</td>
<td>84</td>
<td>1.18</td>
<td></td>
<td>107</td>
<td>6.5</td>
<td>75</td>
</tr>
<tr>
<td>Kr</td>
<td>116</td>
<td>1.64</td>
<td></td>
<td>107</td>
<td>9.0</td>
<td>75</td>
</tr>
<tr>
<td>Xe</td>
<td>161</td>
<td>2.30</td>
<td></td>
<td>107</td>
<td>12.6</td>
<td>77</td>
</tr>
<tr>
<td>Rn</td>
<td>202</td>
<td>2.67</td>
<td></td>
<td>107</td>
<td>16.4</td>
<td>78</td>
</tr>
<tr>
<td>H$_2$</td>
<td>14</td>
<td>0.12</td>
<td></td>
<td>107</td>
<td>0.90</td>
<td>45</td>
</tr>
<tr>
<td>N$_2$</td>
<td>68</td>
<td>0.72</td>
<td></td>
<td>107</td>
<td>5.57</td>
<td>72</td>
</tr>
<tr>
<td>O$_2$</td>
<td>54</td>
<td>0.44</td>
<td></td>
<td>107</td>
<td>6.8</td>
<td>75</td>
</tr>
<tr>
<td>HF</td>
<td>190</td>
<td>3.9</td>
<td></td>
<td>107</td>
<td>3.26</td>
<td>112</td>
</tr>
<tr>
<td>HCl</td>
<td>159</td>
<td>2.0</td>
<td></td>
<td>107</td>
<td>16.2</td>
<td>86</td>
</tr>
<tr>
<td>HBr</td>
<td>186</td>
<td>2.4</td>
<td></td>
<td>107</td>
<td>17.6</td>
<td>85</td>
</tr>
<tr>
<td>HI</td>
<td>222</td>
<td>2.9</td>
<td></td>
<td>107</td>
<td>19.7</td>
<td>83</td>
</tr>
<tr>
<td>H$_2$S</td>
<td>187</td>
<td>2.5</td>
<td></td>
<td>107</td>
<td>19.8</td>
<td>83</td>
</tr>
<tr>
<td>H$_2$Se</td>
<td>207</td>
<td>2.5</td>
<td></td>
<td>107</td>
<td>19.8</td>
<td>83</td>
</tr>
<tr>
<td>PCl$_3$</td>
<td>317</td>
<td>2.5</td>
<td></td>
<td>107</td>
<td>19.8</td>
<td>83</td>
</tr>
<tr>
<td>PCl$_5$</td>
<td>317</td>
<td>2.5</td>
<td></td>
<td>107</td>
<td>19.8</td>
<td>83</td>
</tr>
<tr>
<td>SiCl$_4$</td>
<td>139</td>
<td>1.1</td>
<td></td>
<td>107</td>
<td>14.6</td>
<td>79</td>
</tr>
<tr>
<td>SiH$_4$</td>
<td>88</td>
<td>0.7</td>
<td></td>
<td>107</td>
<td>13.8</td>
<td>77</td>
</tr>
<tr>
<td>CCl$_4$</td>
<td>250</td>
<td>2.5</td>
<td></td>
<td>107</td>
<td>30.0</td>
<td>86</td>
</tr>
<tr>
<td>MoF$_6$</td>
<td>290</td>
<td>4.4</td>
<td></td>
<td>107</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>F$_2$</td>
<td>53</td>
<td>1.6</td>
<td></td>
<td>107</td>
<td>6.3</td>
<td>74</td>
</tr>
<tr>
<td>Cl$_2$</td>
<td>172</td>
<td>6.4</td>
<td></td>
<td>107</td>
<td>20.4</td>
<td>86</td>
</tr>
<tr>
<td>Br$_2$</td>
<td>266</td>
<td>10.5</td>
<td></td>
<td>107</td>
<td>31.0</td>
<td>94</td>
</tr>
<tr>
<td>I$_2$</td>
<td>387</td>
<td>15.8</td>
<td></td>
<td>107</td>
<td>41.7</td>
<td>91</td>
</tr>
<tr>
<td>PCl$_3$</td>
<td>182</td>
<td>4.5</td>
<td></td>
<td>107</td>
<td>31.0</td>
<td>88</td>
</tr>
<tr>
<td>S$_8$</td>
<td>392</td>
<td>10.0</td>
<td></td>
<td>107</td>
<td>63.0</td>
<td>83</td>
</tr>
<tr>
<td>SiCl$_4$</td>
<td>203</td>
<td>7.7</td>
<td></td>
<td>107</td>
<td>28.7</td>
<td>87</td>
</tr>
<tr>
<td>GeCl$_4$</td>
<td>223</td>
<td>7.7</td>
<td></td>
<td>107</td>
<td>30.0</td>
<td>83</td>
</tr>
<tr>
<td>SnCl$_4$</td>
<td>240</td>
<td>9.2</td>
<td></td>
<td>107</td>
<td>34.9</td>
<td>86</td>
</tr>
<tr>
<td>TiCl$_4$</td>
<td>250</td>
<td>9.4</td>
<td></td>
<td>107</td>
<td>36.0</td>
<td>88</td>
</tr>
<tr>
<td>HgCl$_2$</td>
<td>550</td>
<td>18.1</td>
<td></td>
<td>107</td>
<td>59.0</td>
<td>102</td>
</tr>
<tr>
<td>BF$_3$</td>
<td>144</td>
<td>4.2</td>
<td></td>
<td>107</td>
<td>19.0</td>
<td>112</td>
</tr>
<tr>
<td>AsF$_3$</td>
<td>267</td>
<td>10.4</td>
<td></td>
<td>107</td>
<td>30.0</td>
<td>90</td>
</tr>
<tr>
<td>AsCl$_3$</td>
<td>257</td>
<td>10.0</td>
<td></td>
<td>107</td>
<td>31.0</td>
<td>78</td>
</tr>
<tr>
<td>SO$_2$</td>
<td>197</td>
<td>7.4</td>
<td></td>
<td>107</td>
<td>25.0</td>
<td>95</td>
</tr>
<tr>
<td>B$_2$H$_6$</td>
<td>108</td>
<td>4.5</td>
<td></td>
<td>107</td>
<td>14.3</td>
<td>79</td>
</tr>
<tr>
<td>OsO$_4$</td>
<td>313</td>
<td>14.3</td>
<td></td>
<td>107</td>
<td>39.5</td>
<td>98</td>
</tr>
<tr>
<td>Ni(CO)$_4$</td>
<td>254</td>
<td>13.8</td>
<td></td>
<td>107</td>
<td>29.0</td>
<td>93</td>
</tr>
<tr>
<td>Fe(CO)$_5$</td>
<td>252</td>
<td>13.6</td>
<td></td>
<td>107</td>
<td>37.0</td>
<td>99</td>
</tr>
<tr>
<td>Fe(CO)$_5$(NO)$_2$</td>
<td>291</td>
<td>10.5</td>
<td>38.3</td>
<td>38.3</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>Fe(C$_5$H$_7$)$_2$</td>
<td>459</td>
<td>23.0</td>
<td>522</td>
<td>47</td>
<td>96</td>
<td></td>
</tr>
<tr>
<td>Pb(CH$_3$)$_4$</td>
<td>243</td>
<td>10.8</td>
<td>376</td>
<td>38.0</td>
<td>101</td>
<td></td>
</tr>
</tbody>
</table>
4.4 Melting points and boiling points of non-ionic crystals

The melting and boiling points of ionic crystals have been described in section 3.6, where a brief comparison with molecular crystals was also given. The latter class will now be discussed in more detail. Before doing so, however, it is worth noting that certain substances in which the bonding is predominantly covalent may have the same characteristically high melting points associated with ionic compounds - such substances are those in which individual molecules cannot be distinguished, and typical examples are those shown in the following tabulation:

<table>
<thead>
<tr>
<th>Substance</th>
<th>m.p./K</th>
<th>b.p./K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Silicon carbide, SiC</td>
<td>3000*</td>
<td></td>
</tr>
<tr>
<td>Diamond</td>
<td>3800</td>
<td></td>
</tr>
<tr>
<td>Graphite</td>
<td>3925*</td>
<td>1725*</td>
</tr>
<tr>
<td>Silicon dioxide, SiO₂</td>
<td>1986</td>
<td></td>
</tr>
<tr>
<td>Boron nitride, BN</td>
<td>3300*</td>
<td>3960*</td>
</tr>
</tbody>
</table>

*sublimes

The fusion of such crystals must, of course, involve extensive disruption of the strong covalent bonds which extend throughout the crystal, and high temperatures are necessary to achieve this. Most predominantly covalent substances, however, form molecular crystals in which the strong covalent bonds are found only within small molecular units, which themselves are bound together by the much weaker van der Waals forces of attraction. These weak intermolecular forces constitute the points of structural weakness in such a crystal, and the temperature at which fusion occurs is usually low.

At the conventional melting and boiling points,

\[ T/\text{K (m.p.)} = \frac{\Delta H_{\text{fusion}}}{\Delta S_{\text{fusion}}} \quad \text{and} \quad T/\text{K (b.p.)} = \frac{\Delta H_{\text{vap}}}{\Delta S_{\text{vap}}} \]

so that the actual melting point (or boiling point) is a constant to whose magnitude both an enthalpy and an entropy change contribute. The appropriate data for a number of representative molecular substances are shown in Table 28, and these will now be discussed.

4.4.1 Melting points of molecular substances

The lowest melting points are displayed by the noble gases (these are, of course, atomic rather than molecular substances), and are clearly a consequence of the small enthalpies of fusion. The entropy of fusion in each case (except for helium) is about 14 J K⁻¹ mol⁻¹, and it is noteworthy that entropies of fusion of about this magnitude are also observed for a number of diatomic and polyatomic molecules, for example, H₂, N₂, O₂, HCl, HBr, HI, H₂S, H₂Se, P₄, PH₅, SiH₄, CCl₄, and MoF₆. There are many molecular substances, however, whose entropies of fusion are distinctly higher - in the range 25-50 J K⁻¹ mol⁻¹, and it seems that the occurrence of 'low' entropies of fusion (8-12 J K⁻¹ mol⁻¹) may be associated with the fact that melting is preceded by solid-phase transitions involving entropy increases. For example, the melting of solid oxygen, O₂, at 54 K is preceded by two transitions in the solid:

- transition at 23.7 K \( \Delta S = 4 \)
- transition at 43.8 K \( \Delta S = 17 \)
- fusion at 54.4 K \( \Delta S = 29 \ J \ K⁻¹ \ mol⁻¹. \)

If the entropy changes are added, the total is 29 J K⁻¹ mol⁻¹. For a similar diatomic molecule such as Cl₂, however, there are no solid-phase transitions and the entire entropy increase (for Cl₂, 37 J K⁻¹ mol⁻¹) occurs when the solid melts.

The heats of fusion are difficult to systematize; their magnitudes depend heavily on the strengths of the intermolecular van der Waals forces in the solid, and the largest values of \( \Delta H_{\text{fusion}} \) are observed for large, polarizable molecules like I₂ (15.8 kJ mol⁻¹) and HgCl₂ (18 kJ mol⁻¹).

4.4.2 Boiling points of molecular substances

Both the enthalpy and entropy changes which occur on vaporization of a liquid are considerably larger than the corresponding changes which accompany fusion; furthermore, the entropy of vaporization, except for substances with very low boiling points, is fairly constant within a range of about 80-95 J K⁻¹ mol⁻¹. A number of empirical rules depend on this rough constancy: for example Trouton's rule states that

\[ \Delta H_{\text{vap}} \approx 88 \ J \ K⁻¹ \ mol⁻¹, \]

and may be used to assess the heat of vaporization of a non-associated molecular liquid if its boiling point is known. Because of the relative constancy of \( \Delta S_{\text{vap}} \), the boiling point of a molecular substance is in effect largely determined by the magnitude of the heat of vaporization, that is by the strength of the intermolecular van der Waals forces which must be overcome for the liquid → gas transition to occur. For a coherent series such as the halogens X₂, \( \Delta H_{\text{vap}} \) (see Table 28) increases with increase in the size and polarizibility of the X₂ molecules. Since the variation in \( \Delta S_{\text{vap}} \) is relatively smaller, the boiling points follow the trend in \( \Delta H_{\text{vap}} \) and increase from F₂ to I₃.

An instructive comparison may be made with the hydrogen halides HX, for which the data are given in Table 28. It is clear that the heat of vaporization of liquid hydrogen fluoride (to the ideal, i.e. non-associated, gas is
an abnormally high, a consequence of the circumstance that in the liquid the intermolecular van der Waals forces are considerably reinforced by extensive HF...HF hydrogen bonding. That this hydrogen bonding in hydrogen fluoride also imposes restrictions on the translational freedom of the molecules in the liquid phase is evident from the significantly greater entropy of vaporization. The boiling point of liquid hydrogen fluoride is thus higher than that of any of the other hydrogen halides, which show the normal increase in boiling point from hydrogen chloride to hydrogen iodide. The trends in boiling points for the halogens and the hydrogen halides are shown in Figure 18.

Similar 'anomalously' high boiling points are shown by the first members of the two series H₂O, H₂S, H₂Se, H₂Te, and NH₃, PH₃, AsH₃, SbH₃.

An interesting example of structural influences on the enthalpy and entropy changes accompanying fusion and vaporization is seen in the following data for aluminium chloride and bromide:

<table>
<thead>
<tr>
<th></th>
<th>Aluminium chloride</th>
<th>Aluminium bromide</th>
</tr>
</thead>
<tbody>
<tr>
<td>m.p.</td>
<td>463 K</td>
<td>370 K</td>
</tr>
<tr>
<td>ΔHfusion/(kJ (mol AlX₃)⁻¹)</td>
<td>36</td>
<td>11</td>
</tr>
<tr>
<td>ΔSfusion/(J K⁻¹ (mol AlX₃)⁻¹)</td>
<td>77</td>
<td>31</td>
</tr>
<tr>
<td>b.p.</td>
<td>433 K</td>
<td>528 K</td>
</tr>
<tr>
<td>ΔHsub/(kJ (mol AlX₃)⁻¹)</td>
<td>20-3</td>
<td>22-8</td>
</tr>
<tr>
<td>ΔSsub/(J K⁻¹ (mol AlX₃)⁻¹)</td>
<td>47</td>
<td>43</td>
</tr>
</tbody>
</table>

Each thermodynamic quantity is calculated for 133.3 g of aluminium chloride or 266.7 g of aluminium bromide, that is for one mole based on the formula weights of AlCl₃ and AlBr₃. On this basis, the entropies of vaporization are anomalously low. The explanation lies of course in the fact that both the chloride and the bromide form dimeric molecules in the liquid and vapour phases, so that the formula weight should be based on the unit Al₃X₆. The corrected entropies of vaporization then have the unexceptionable values 94 J K⁻¹ (mol Al₃Cl₆)⁻¹ and 86 J K⁻¹ (mol Al₃Br₆)⁻¹. The second notable feature of the data listed is the fact that both the enthalpy and the entropy of fusion of aluminium chloride are much higher than the corresponding quantities for aluminium bromide. This in turn stems from the fact that while aluminium bromide consists of Al₂Br₆ molecules in both the solid and liquid states, solid aluminium chloride has a layer lattice structure in which the aluminium has sixfold coordination. On melting, the layer lattice of the solid is transformed into a molecular liquid consisting of AlCl₃ molecules in which the aluminium is involved in fourfold tetrahedral coordination. This more profound structural change is reflected in the high values of the enthalpy and entropy of fusion.

4.3 Estimation of ΔG° for covalent compounds

This section follows the treatment of ionic compounds given in section 3.7.

4.5.1 Estimation of ΔH°

The critical part of any estimation of an enthalpy of formation is the evaluation of the binding energy. If the compound under consideration is described in terms of an ionic model, then the binding energy corresponds to the lattice energy. Where a covalent model is adopted, then the covalent bond energy is the quantity in question. For example, suppose it is desired to estimate ΔH° for the hypothetical molecule

\[
\begin{align*}
\text{H} & \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

that is, ΔH°₂₈ for the reaction

\[
\text{H}_2(g) + 1\text{N}_2(g) + 2\text{Cl}_2(g) \rightarrow \text{HN}_2\text{Cl}_4(l),
\]

assuming that HN₂Cl₄ is a liquid in its standard state.

The appropriate sequence of reactions whose sum yields the formation reaction above is

\[
\begin{align*}
(\text{i}) & \quad \text{H}_2(g) \rightarrow \text{H}(g) & \Delta h_1 & + \\
(\text{ii}) & \quad 1\text{N}_2(g) \rightarrow 3\text{N}(g) & \Delta h_2 & + \\
(\text{iii}) & \quad 2\text{Cl}_2(g) \rightarrow 4\text{Cl}(g) & \Delta h_3 & + \\
(\text{iv}) & \quad \text{H}(g) + 3\text{N}(g) + 4\text{Cl}(g) \rightarrow \text{HN}_2\text{Cl}_4(g) & \Delta h_4 & - \\
(\text{v}) & \quad \text{HN}_2\text{Cl}_4(g) \rightarrow \text{HN}_2\text{Cl}_4(l) & \Delta h_5 & - \\
(\text{vi}) & \quad 3\text{H}_2(g) + 1\text{N}_2(g) + 2\text{Cl}_2(g) \rightarrow \text{HN}_2\text{Cl}_4(l) & \Delta H° & 
\end{align*}
\]

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The compound is thus likely to be highly endothermic; a major cause of this is the high enthalpy of atomization of nitrogen ($\Delta h_3$), that is, the great strength of the $N\equiv N$ triple bond relative to the bonds in the product.

4.5.2 Constancy of bond energies

It is clear from the above example that any estimation of a similar sort depends heavily on the accuracy with which the bond energy can be evaluated. There is no doubt that the energy of a particular bond will always depend to some degree on its molecular environment, and that the assumption of constancy from molecule to molecule introduces an element of uncertainty into any calculation which relies on tabulations of average bond energies. Unfortunately there is no general and straightforward way of making energetic corrections for the molecular environment of a bond, but it is often possible to recognize circumstances in which departures from constancy are likely to be marked.

For example, the energy $E$ of a bond $A-B$ is unlikely to be constant for a series of compounds in which the oxidation states of $A$ and $B$ do not remain constant.

Thus a $P-Cl$ bond energy can be derived from the following $\Delta H_f^o/(kJ \text{ mol}^{-1})$ values:

- $\text{PCl}_3(g)$, $-279$; $\text{P}(g)$, $315$; $\text{Cl}(g)$, $121$.

These yield $E_{\text{PCl}} = 319 \text{ kJ mol}^{-1}$

In the $\text{P(V)}$ compound $\text{PCl}_4(g)$, however, for which $\Delta H_f^o = -371 \text{ kJ mol}^{-1}$, the formation of the two additional $P-Cl$ bonds in the process

$\text{PCl}_3(g) + 2\text{Cl}(g) \rightarrow \text{PCl}_5(g)$

evolves only $334 \text{ kJ mol}^{-1}$, so that the average energy of the two new bonds is only $167 \text{ kJ mol}^{-1}$, or little more than half of the average energy of the bonds in $\text{PCl}_3$.

Similarly, the following enthalpy data for the antimony chlorides, $\Delta H_f^o/(kJ \text{ mol}^{-1})$,

- $\text{SbCl}_3(g)$, $-315$; $\text{SbCl}_5(g)$, $-390$; $\text{Sb}(g)$, $259$

yield $E_{\text{Sb-Cl}}$ in $\text{SbCl}_3 = 312 \text{ kJ mol}^{-1}$ and for the reaction

$\text{SbCl}_3(g) + 2\text{Cl}(g) \rightarrow \text{SbCl}_5(g)$,

$\Delta H_f^o = -315 \text{ kJ mol}^{-1}$, so that $E_{\text{Sb-Cl}}$ for the two additional bonds in $\text{SbCl}_3$ is only $158 \text{ kJ mol}^{-1}$, again little more than half the value of $E_{\text{Sb-Cl}}$ in $\text{SbCl}_3$.

Again, for the fluorides of iodine, the following enthalpy data, $\Delta H_f^o/(kJ \text{ mol}^{-1})$,

$\Delta h_1$, $\Delta h_2$, and $\Delta h_3$ (which are all positive) are the enthalpies of atomization of the elements from their standard states, and experimental values of these are given in Chapter 2, Table 10 (p. 46). The two reactions for which experimental values are, of course, not available are (iv), the formation of the gaseous molecule from its gaseous atoms, and (v), the condensation of the gaseous molecule to its standard (liquid) state. Thus $\Delta h_a$ is numerically equal to the total thermochemical bond energy for the molecule, and $\Delta h_3$ is the negative of its enthalpy of vaporization; both these enthalpy contributions must be estimated.

The enthalpy of vaporization of $\text{HN}_2\text{Cl}_4$ is likely to be quite small compared with the total bond energy, and a rough value is most easily obtained from known $\Delta H_{\text{vap}}$ data for molecules of similar size, shape and polarizability. Such a molecule is 1,1,3,3-tetrachloropropane,

for which the enthalpy of vaporization (estimated by Trouton's rule from its boiling point, 453 K) is approximately $38 \text{ kJ mol}^{-1}$. The corresponding quantity ($\Delta h_3$) for $\text{HN}_2\text{Cl}_4$ is unlikely to differ significantly from this; in any case an uncertainty of a few kIloules in this quantity is small compared to the uncertainty in $\Delta h_a$ (the total bond energy) which it now remains to evaluate.

The usual procedure is to assume that the total enthalpy change for the bond-formation reaction (iv) can be divided into a number of contributions or terms representing the energies of the individual bonds.

Thus $\Delta h_a = E_{\text{total}} = 2E_{\text{N-N}} + 4E_{\text{N-Cl}} + E_{\text{N-H}}$

where $E$ is the enthalpy decrease accompanying the formation of the bond indicated, from its gaseous atoms. It is then assumed that each of these bond energy terms may be equated with the appropriate thermochemical bond energy listed in Table 27, that is it is assumed that bond energies are constant and additive. (The validity of this assumption is examined in section 4.5.2.)

Hence $\Delta h_a$ is given by

$-\Delta h_a = 2E_{\text{N-N}} + 4E_{\text{N-Cl}} + E_{\text{N-H}}$

$= (2 \times 160) + (4 \times 193) + 391$

$= 1483 \text{ kJ mol}^{-1}$.

Since (from Table 10) $\Delta h_1 = 218$, $\Delta h_2 = 1418$, and $\Delta h_3 = 485 \text{ kJ}$, $\Delta H_f^o \text{HN}_2\text{Cl}_4(l) = \Delta h_1 + \Delta h_2 + \Delta h_3 + \Delta h_a = 218 + 1418 + 485 - 1483 - 38$

$= 600 \text{ kJ mol}^{-1}$.
IF(g), −94; IF₄(g), −816; IF₃(g), −938; I(g), +107, F(g), +79, permit the calculation of enthalpy changes for the reactions

\[
\Delta H^\circ_{298} \text{(kJ mol}^{-1}\text{)}
\]

(i) \( \text{I(g)} + \text{F(g)} \rightarrow \text{IF(g)} \quad -280 \)

(ii) \( \text{IF(g)} + 4\text{F(g)} \rightarrow \text{IF}_5\text{(g)} \quad -1038 \quad \Delta \text{F} \equiv 2 \text{F} \)

(iii) \( \text{IF}_3\text{(g)} + 2\text{F(g)} \rightarrow \text{IF}_5\text{(g)} \quad -280 \quad \Delta \text{F} \equiv 0 \quad 4\text{F} \)

from which it is clear that \( E_{\text{IF}} \) in iodine(I) fluoride is 280 kJ mol\(^{-1}\), but that the average energy of the four 'new' bonds formed in reaction (ii) in iodine(VI) fluoride is \( 4 \times 1038 = 260 \text{ kJ mol}^{-1} \), while the average energy of the two 'new' bonds formed when iodine(VII) fluoride is produced in reaction (iii) is only \( 2 \times 280 = 140 \text{ kJ mol}^{-1} \). There is thus a decrease in the strength of the I—F bonds formed in the sequence

\[ \text{IF} \rightarrow \text{IF}_3 \rightarrow \text{IF} \)

Some thermochemical bond energies, \( E_b(\text{kJ mol}^{-1}) \), for chlorine–metal bonds are as follows; the consistently lower value observed for the metal in its higher oxidation state is noteworthy:

<table>
<thead>
<tr>
<th>Bond</th>
<th>( E_b(\text{kJ mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl} ) – ( \text{Cl} )</td>
<td>502</td>
</tr>
<tr>
<td>( \text{CrCl}_2 )</td>
<td>381</td>
</tr>
<tr>
<td>( \text{FeCl}_3 )</td>
<td>397</td>
</tr>
<tr>
<td>( \text{SnBr}_3 )</td>
<td>326</td>
</tr>
<tr>
<td>( \text{TiCl}_4 )</td>
<td>427</td>
</tr>
</tbody>
</table>

4.5.3 Estimation of \( \Delta H^\circ \) by Pauling’s method

One of the few attempts which have been made to systematize covalent bond energies is that of L. Pauling, who postulated that the observed decrease in bond energy along a series such as the following:

<table>
<thead>
<tr>
<th>Bond</th>
<th>( E_b(\text{kJ mol}^{-1}) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{HF} )</td>
<td>565</td>
</tr>
<tr>
<td>( \text{HCl} )</td>
<td>431</td>
</tr>
<tr>
<td>( \text{HBr} )</td>
<td>366</td>
</tr>
<tr>
<td>( \text{HI} )</td>
<td>299</td>
</tr>
</tbody>
</table>

has its basis in the diminishing electronegativity difference between the bonded atoms. His suggestion is that for a single covalent bond between two atoms \( X \) and \( Y \), the energy \( E_{X-Y} \) of the bond \( X—Y \) is greater than the arithmetic mean of the single-bond energies \( E_{X-X} \) and \( E_{Y-Y} \) by an amount \( \Delta \), which measures the extent to which the bond \( X—Y \) is stabilized by 'ionic-covalent resonance'.

Thus \( \Delta = E_{X-Y} - \frac{1}{2}(E_{X-X} + E_{Y-Y}). \)

Electronegativity coefficients \( \chi_X \) and \( \chi_Y \) were next assigned to \( X \) and \( Y \) in such a way as to satisfy as far as possible the relationship

\[ |\chi_X - \chi_Y| = \left( \frac{\Delta}{96} \right)^{\frac{1}{2}}. \]
The resulting coefficients are listed in Table 29. It then follows from 4.1 and 4.2 above that
\[ E_{x+y} = \frac{1}{2}(E_{x-x} + E_{y-y}) + 96 |x_y - x_y|^2 \]
and that, for a gaseous single-bonded molecule formed from gaseous single-bonded elements, the heat evolved would be approximately 96|\( x_y - x_y \)|\(^2 \) kJ mol\(^{-1} \).

For example, \( \Delta H^\circ \) for the reaction
\[ \text{P}_2(g) + 11 \text{Br}_2(g) \rightarrow \text{PBr}_3(g), \]
in which reactants and products are all single-bonded molecules, is 
\[ -3 \times 96|\text{P}_2 - \text{Br}_2|^2, \]
which, with \( x_{\text{Br}} = 2.8 \) and \( x_P = 2.1 \), is \(-141 \) kJ (mol \( \text{PBr}_3(g) \))\(^{-1} \). The experimental result is \(-209 \) kJ mol\(^{-1} \).

If the reacting elements are not single-bonded gases, corrections must be made. Thus for \( \text{NF}_3 \), the quantity \( 3 \times 96|\text{X}_F - \text{X}_N|^2 \), with \( x_F = 4.0 \) and \( x_N = 3.0 \), is \( 288 \) kJ (mol \( \text{NF}_3 \))\(^{-1} \); however, in the reaction
\[ 1 \text{N}_2(g) + 1 \text{F}_2(g) \rightarrow \text{NF}_3(g), \]
elementary nitrogen consists not of single-bonded molecules but of triplebonded \( \text{N} = \text{N} \) molecules, in which the triple bond (\( \text{N}_2(g) \rightarrow 2\text{N}(g) \), \( \Delta H^\circ \) is \( 946 \) kJ (mol \( \text{N}_2 \))\(^{-1} \)) is more stable than three \( \text{N} = \text{N} \) single bonds (\( 3E_{x-x} = 3 \times 160 = 480 \) kJ) by \( 946 - 480 = 466 \) kJ (mol \( \text{N}_2 \))\(^{-1} \); or \( 233 \) kJ for half a mole of \( \text{N}_2 \); the expected enthalpy change for reaction 4.3 is thus 
\[ -(288 - 233) = -55 \text{ kJ (mole } \text{NF}_3 \))^{-1} \]. The experimental result is \(-124 \) kJ mol\(^{-1} \).

Pauling's procedure produces results which are not very accurate, partly because of the inadequacy of his basic postulates, and partly because of difficulties in assigning satisfactory electronegativity coefficients to fit equation 4.2 above. It is useful, however, for obtaining rough measures of \( \Delta H^\circ \) in cases where more accurate estimates cannot be made.

4.5.4 Estimation of \( \Delta S^\circ \)

In order to estimate \( \Delta S^\circ \) for a covalent compound it is necessary to know the entropy \( S^\circ \) of the compound itself, and also that of each constituent element in its standard state. The latter are tabulated in Table 25 (p. 99).

The estimation of \( S^\circ \) for a molecular compound is best tackled empirically from observed trends for gaseous molecules. A plot of \( S^\circ \) against molecular weight \( M \) for known gaseous polyatomic molecules, using the data of Table 30, is shown in Figure 19, from which the entropies of new compounds can be obtained by interpolation with a fair degree of accuracy. Kubaschewski, Evans and Alcock (1967) have fitted empirical equations to curves such as these; their relationships are

(a) for diatomic gases other than hydrides,
\[ S^\circ = 225 + 0.18M - 100M^{-1}, \]
(b) for polyatomic gases of molecular weight not higher than 250,
\[ S^\circ = 163 + 1.44M - (2.6 \times 10^{-3})M^2. \]

(This equation fails for molecular weights above 250.)

There appear to be certain classes of compound for which these empirical equations, and the empirical curve of Figure 19, are quite unsuitable. For example, the following gaseous carbonyls,

\[
S^\circ_{\text{298}}/(\text{J K}^{-1} \text{ mol}^{-1}) \quad M
\]
\[
\begin{array}{ll}
\text{Fe(CO)}_5 & 444 \\
\text{Ni(CO)}_4 & 399 \\
\text{Cr(CO)}_6 & 487 \\
\text{Mo(CO)}_5 & 507
\end{array}
\]

have exceptionally high entropies. The empirical relationships, however, seem to hold extensively for binary compounds.
The energy of formation of N₂Cl₄ is:

\[
N₂Cl₄(l) → N₂Cl₂(g) + Cl₂(g)
\]

The enthalpy of formation of N₂Cl₄ is:

\[
\Delta H_f = H_f(N₂Cl₄) - H_f(N₂Cl₂) - H_f(Cl₂)
\]

The enthalpy of formation of N₂Cl₂ is:

\[
\Delta H_f = H_f(N₂Cl₂) - H_f(N₂) - H_f(Cl₂)
\]

The enthalpy of formation of Cl₂ is:

\[
\Delta H_f = H_f(Cl₂) - 2H_f(Cl)
\]

The enthalpy of formation of N₂ is:

\[
\Delta H_f = H_f(N₂) - 2H_f(N)
\]

The enthalpy of formation of H₂ is:

\[
\Delta H_f = H_f(H₂) - 2H_f(H)
\]

The enthalpy of formation of Cl is:

\[
\Delta H_f = H_f(Cl) - H_f(Cl⁻)
\]

The enthalpy of formation of N is:

\[
\Delta H_f = H_f(N) - H_f(N⁺)
\]

The enthalpy of formation of H is:

\[
\Delta H_f = H_f(H) - H_f(H⁺)
\]

The enthalpy of formation of Cl⁻ is:

\[
\Delta H_f = H_f(Cl⁻) - H_f(Cl)
\]

The enthalpy of formation of N⁺ is:

\[
\Delta H_f = H_f(N⁺) - H_f(N)
\]

The enthalpy of formation of H⁺ is:

\[
\Delta H_f = H_f(H⁺) - H_f(H)
\]