Because the elements of group 4 have a high affinity for oxygen, all three metals occur naturally as oxide ores that contain the metal in the +4 oxidation state resulting from losing all four ns\(^2\)(n − 1)d\(^2\) valence electrons. They are isolated by initial conversion to the tetrachlorides, as shown for Ti:

\[
\text{\ce{2FeTiO3(s) + 6C(s) + 7Cl2(g) \rightarrow 2TiCl4(g) + 2FeCl3(g) + 6CO(g)}} \label{1.1.1}
\]

followed by reduction of the tetrachlorides with an active metal such as Mg.

The chemistry of the group 4 metals is dominated by the +4 oxidation state. Only Ti has an extensive chemistry in lower oxidation states.

In contrast to the elements of group 3, the group 4 elements have important applications. Titanium (melting point = 1668°C) is often used as a replacement for aluminum (melting point = 660°C) in applications that require high temperatures or corrosion resistance. For example, friction with the air heats the skin of supersonic aircraft operating above Mach 2.2 to temperatures near the melting point of aluminum; consequently, titanium is used instead of aluminum in many aerospace applications. The corrosion resistance of titanium is increasingly exploited in architectural applications, as shown in the chapter-opening photo. Metallic zirconium is used in UO\(_2\)-containing fuel rods in nuclear reactors, while hafnium is used in the control rods that modulate the output of high-power nuclear reactors, such as those in nuclear submarines.

### Table \(\PageIndex{1}\): Some Properties of the Elements of Groups 4

<table>
<thead>
<tr>
<th>Element</th>
<th>Z</th>
<th>Valence Electron Configuration</th>
<th>Electronegativity</th>
<th>Metallic Radius (pm)</th>
<th>Melting Point (°C)</th>
<th>Density (g/cm(^3))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>22</td>
<td>4s(^2)3d(^2)</td>
<td>1.54</td>
<td>147</td>
<td>1668</td>
<td>4.51</td>
</tr>
<tr>
<td>Zr</td>
<td>40</td>
<td>5s(^2)4d(^2)</td>
<td>1.33</td>
<td>160</td>
<td>1855</td>
<td>6.52</td>
</tr>
<tr>
<td>Hf</td>
<td>72</td>
<td>6s(^2)5d(^2)4f(^{14})</td>
<td>1.30</td>
<td>159</td>
<td>2233</td>
<td>13.31</td>
</tr>
</tbody>
</table>

Consistent with the periodic trends, the group 4 metals become denser, higher melting, and more electropositive down the column (Table \(\PageIndex{1}\)). Unexpectedly, however, the atomic radius of Hf is slightly smaller than that of Zr due to the lanthanide contraction. Because of their ns\(^2\)(n − 1)d\(^2\) valence electron configurations, the +4 oxidation state is by far the most important for all three metals. Only titanium exhibits a significant chemistry in the +2 and +3 oxidation states, although compounds of Ti\(^{2+}\) are usually powerful reductants. In fact, the Ti\(^{2+}\)(aq) ion is such a strong reductant that it rapidly reduces water to form hydrogen gas.

Reaction of the group 4 metals with excess halogen forms the corresponding tetrahalides (MX\(_4\)), although titanium, the lightest element in the group, also forms dihalides and trihalides (X is not F). The covalent character of the titanium halides increases as the oxidation state of the metal increases because of increasing polarization of the anions by the cation as its charge-to-radius ratio increases. Thus TiCl\(_2\) is an ionic salt, whereas TiCl\(_4\) is a volatile liquid that contains tetrahedral molecules. All three metals react with excess oxygen or the heavier chalcogens (Y) to form the corresponding dioxides (MO\(_2\)) and dichalcogenides (MY\(_2\)). Industrially, TiO\(_2\), which is used as a white pigment in paints, is prepared by reacting TiCl\(_4\) with oxygen at high temperatures:
The group 4 dichalcogenides have unusual layered structures with no M–Y bonds holding adjacent sheets together, which makes them similar in some ways to graphite (Figure \(\text{Figure \(\PageIndex{1}\)}\)). The group 4 metals also react with hydrogen, nitrogen, carbon, and boron to form hydrides (such as TiH\(_2\)), nitrides (such as TiN), carbides (such as TiC), and borides (such as TiB\(_2\)), all of which are hard, high-melting solids. Many of these binary compounds are nonstoichiometric and exhibit metallic conductivity.

Figure \(\text{Figure \(\PageIndex{1}\)}\): The Layered Structure of TiS\(_2\). Each titanium atom is surrounded by an octahedral arrangement of six sulfur atoms that are shared to form extended layers of atoms. Because the layers are held together by only van der Waals forces between adjacent sulfur atoms, rather than covalent bonds, the layers slide past one another relatively easily when a mechanical stress is applied.