Carbon Monoxide

• A colourless and very dangerously toxic gas - it has no smell - boiling point -190 °C.
• It is thermodynamically unstable with respect to carbon and carbon dioxide, but the equilibrium is only established at high temperature:

\[
2\text{CO}(g) \\
\text{C}(s) + \text{CO}_2(g)
\]

• An important primary industrial chemical, involved in several reaction sequences:

\[
\text{CH}_4 + 2\text{H}_2\text{O} \\
\text{CO}_2 + 4\text{H}_2 \\
\text{C} + \text{H}_2\text{O} \\
\text{CO} + \text{H}_2 (+ \text{H}_2\text{O}) \text{ "water gas"}
\]

CO + H₂O

CO₂ + H₂ the "water gas shift" reaction

Mixtures of carbon monoxide and hydrogen are called "synthesis gas" or "syngas".
• Formally CO is the anhydride of formic acid, HCCH, but CO does not react at room temperature with water.
• Carbon monoxide is unique in that it is a weak Lewis base (s-donor through carbon) but a very strong p-acceptor. As a ligand it stabilizes transition metals in low zero or negative oxidation states.

Carbon Dioxide and Carbonic Acid

• Carbon dioxide makes up about 0.03% (300 ppm) of the earth's atmosphere. It is mainly produced from volcanic activity, fermentation of organic matter and fires of all types.
• Solid carbon dioxide sublimes at -78 °C at atmospheric pressure, making it a useful refrigerant ("dry ice").
• Carbonic acid H₂CO₃ is produced only very slowly when CO₂ is dissolved in water. The equilibrium constants usually quoted are:

\[
[\text{H}^+][\text{HCO}_3^-]/[\text{H}_2\text{CO}_3] = 4.16 \times 10^{-7} \\
[\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] = 4.84 \times 10^{-11}
\]

but the first is incorrect because the real [H₂CO₃] is much lower than what is calculated based on dissolved CO₂. The real constant is probably closer to 2x10⁻⁴ more in keeping with a compound with a C=O bond - see Chapter 7 section 12.
Compounds with C-N Bonds: Cyanides and Related Compounds

Cyanogen (NºC--CºN) is a poisonous and flammable gas (bp -21 °C. Although its heat of formation is strongly endothermic 297 kJ mol⁻¹ is is fairly stable. Impure cyanogen polymerizes to form "paracyanogen":

Cyanogen is prepared by nitrogen dioxide catalysed oxidation of hydrogen cyanide by oxygen:

\[
\begin{align*}
2\text{HCN} &+ \text{NO}_2 \\
(\text{CN})_2 &+ \text{NO} + \text{H}_2\text{O} \\
\text{NO} &+ \frac{1}{2}\text{O}_2 \\
\text{NO}_2 &
\end{align*}
\]

It is also formed by oxidation of CN⁻ with Cu²⁺:

\[
\begin{align*}
\text{Cu}^{2+} &+ 2\text{CN}⁻ \\
\text{CuCN} &+ \frac{1}{2}(\text{CN})_2
\end{align*}
\]

Notice the similarity between the above reaction and the one below:

\[
\begin{align*}
\text{Cu}^{2+} &+ 2\text{I}⁻ \\
\text{CuI} &+ \frac{1}{2}(\text{I})_2
\end{align*}
\]

The term "pseudo halogen/halide" is often applied to molecules and derived ions such as (CN)₂ and CN⁻. Notice also the existence of HCN which has its parallel in the hydrohalic acids and the reaction of cyanogen with base:

\[
\begin{align*}
(\text{CN})_2 &+ 2\text{OH}⁻ \\
\text{CN}⁻ &+ \text{OCN}⁻ + \text{H}_2\text{O}
\end{align*}
\]

Compare:
(Cl)₂ + 2OH⁻

Cl⁻ + OCl⁻ + H₂O

The reaction of cyanogen with oxygen produces one of the hottest flames known at about 5000 °C.

**Hydrogen cyanide** boils at 25.6 °C. It is very poisonous and has an odour of almonds which not everyone can smell. It is a very good solvent due to its high dielectric constant, \( \varepsilon = 107 \). It is made on an industrial scale (~300 000 tons in 1980) as follows:

\[
\text{CH}_4 + 3\text{O}_2 + 2\text{NH}_3 \rightarrow 2\text{HCN} + 6\text{H}_2\text{O} \quad (\text{Pt/Rh or Pt/Ir catalyst and } 800 \degree\text{C})
\]

or

\[
\text{CH}_4 + \text{NH}_3 \rightarrow \text{HCN} + 3\text{H}_2 \quad (\text{Pt catalyst and } 1200 \degree\text{C})
\]

**Cyanides** are made industrially via the calcium cyanamide salt by the processes:

\[
\text{CaC}_2 + \text{N}_2 \rightarrow \text{CaNCN} + \text{C} \quad (1100 \degree\text{C})
\]

\[
\text{CaNCN} + \text{C} + \text{Na}_2\text{CO}_3 \rightarrow \text{CaCO}_3 + 2\text{NaCN}
\]

or

\[
\text{NaNH}_2 + \text{C} \rightarrow \text{NaCN} \quad (500-600 \degree\text{C})
\]

(NCN²⁻ which yields cyanamide itself, H₂NCN, by hydrolysis of the salt, is isoelectronic with CO₂.)

Cyanide is important, among other things, as a very good p-acceptor ligand like CO.
Compounds with C-S bonds

Carbon disulphide is perhaps the most important as a solvent and a synthetic reagent. It gives rise to other carbon sulphur compounds such as:

\[ \text{RO}^- + \text{CS}_2 \]

\[ \text{ROCS}_2^- \text{(xanthates)} \]

\[ \text{HS}^- + \text{CS}_2 \]

\[ \text{CS}_3^{2-} \text{(thiocarbonate)} \]

\[ \text{R}_2\text{HN} + \text{CS}_2 \]

\[ \text{R}_2\text{NCS}_2^- \text{(dithiocarbamates)} \]

These ions are important ligands for transition metals, and the dithiocarbamtes are sued as agricultural fungicides.

Allotropes of carbon

Carbon is capable of forming many allotropes in addition to the well known diamond and graphite forms.

The physical properties of carbon vary widely with the allotropic form. For example, diamond is highly transparent, but graphite is opaque and black. Diamond is the hardest naturally-occurring material known, while graphite is soft enough to form a streak on paper (hence its name, from the Greek word "γράφω" which means "to write"). Diamond has a very low electrical conductivity, while graphite is a very good conductor. Under normal conditions, diamond, carbon nanotubes, and graphene have the highest thermal conductivities of all known materials.

All carbon allotropes are solids under normal conditions, with graphite being the most thermodynamically stable form. They are chemically resistant and require high temperature to react even with oxygen.
Allotropes of Carbon

graphite
The system of carbon allotropes spans a range of extremes:

<table>
<thead>
<tr>
<th>Synthetic nanocrystalline diamond is the hardest material known.</th>
<th>Graphite is one of the softest materials known.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond is the ultimate abrasive.</td>
<td>Graphite is a very good lubricant, displaying superlubricity.</td>
</tr>
<tr>
<td>Diamond is an excellent electrical insulator, and has the highest breakdown electric field of any known material.</td>
<td>Graphite is a conductor of electricity.</td>
</tr>
</tbody>
</table>

C60-fullerene
"BuckyBall"
### Properties of Diamond and Graphite

<table>
<thead>
<tr>
<th>Diamond</th>
<th>Graphite</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diamond is the best known naturally occurring <strong>thermal conductor</strong>.</td>
<td>Some forms of graphite are used for <strong>thermal insulation</strong> (i.e. firebreaks and heat shields), but some other forms are good thermal conductors.</td>
</tr>
<tr>
<td>Diamond is highly transparent.</td>
<td>Graphite is <strong>opaque</strong>.</td>
</tr>
<tr>
<td>Diamond crystallizes in the <strong>cubic system</strong>.</td>
<td>Graphite crystallizes in the <strong>hexagonal system</strong>.</td>
</tr>
<tr>
<td>Amorphous carbon is completely <strong>isotropic</strong>.</td>
<td>Carbon nanotubes are among the most <strong>anisotropic</strong> materials ever produced.</td>
</tr>
</tbody>
</table>

- **Topic hierarchy**