Lecture Notes 5th Series: Inorganic Chemistry

THE MAIN GROUP ELEMENTS
Inorganic chemistry is the chemistry of all of the elements except one. Carbon is the domain of the organic chemist. It seems a little unfair that the split is 108 for Inorganic and 1 for Organic. However the chemistry of carbon is so rich and varied it deserves a whole discipline to itself. Besides as we’ve seen, organic chemists do sometimes include H, S, N and O in their compounds!

This leaves us with an awful lot of possible chemistry in Inorganic Chemistry. Thousands of new compounds are made every year. It’s actually impossible to keep up with the number of new compounds, even for a practicing chemist. So what chance do you have of understanding inorganic chemistry? Well, believe it or not, you have a very good chance. If we use the periodic table to its full potential then we can predict the chemistry of obscure elements such as antimony (Sb, atomic number 51) or thallium (Tl, atomic number 81) without knowing too much about them.

The Groups
The main group elements are Groups 1, 2, 13, 14, 15, 16, 17, and 18. Groups 1 and 2 are the s-block elements and Groups 13 – 18 are the p-block elements.

Groups 1 and 2
Group 1 elements are known as the alkali metals. This is due to their ability to produce alkaline solutions (basic solutions) when added to water. For instance sodium and water react thus:

\[
2 \text{Na(s)} + 2 \text{H}_2\text{O(l)} \rightarrow 2 \text{Na}^+(aq) + 2 \text{OH}^-(aq) + \text{H}_2(g)
\]

Question 5.1
The reaction above is a redox reaction. Write down the balanced \(\frac{1}{2}\)-reactions for the reduction and the oxidation taking place. How many electrons are being transferred from Na to water?

The Group 2 elements are known as the alkaline earth metals. All the elements in groups 1 and 2 are metals and all are potential reducing agents due to their capacity to form stable cations. Group 1 elements form mono-cations and Group 2 elements form di-cations. We can therefore predict that these elements will form ionic compounds with non-metals. The exception is beryllium which forms covalent compounds due to the undesirable charge density on Be\(^{2+}\) (charge density is the charge per unit volume and the volume of the Be\(^{2+}\) ion is very small).

The metals however can also form covalent compounds with non-metals depending on the difference in electronegativity. AlF\(_3\) for instance is ionic (\(\Delta\text{EN} = 2.5\)) but AlCl\(_3\) is covalent (\(\Delta\text{EN} = 1.5\)).

Group 13
Group 13 contains one non-metal, namely boron, and the other elements are metals. Boron is also the only element which does not form a stable trication (B\(^{3+}\) again will have too high a charge density to be stable).

Q. Why do the other elements form trications?
A. Because they have the valence electronic configuration ns\(^2\)np\(^1\) and when three electrons are lost they have a full valence shell.

Group 14
Group 14 contains one non-metal, carbon, two metalloids, silicon (Si) and germanium (Ge), and two metals, tin (Sn) and lead (Pb). However they do have in common the fact that they can all exhibit an oxidation number of
+4 in their compounds. Only tin and lead form ions, the other elements preferring to share electrons in covalent compounds. Tin and lead are also happy in the +2 oxidation state.

**Group 15**

These elements are called the **pnicogens** (terrible name!). Nitrogen and phosphorus are non-metals. Arsenic (As) and antimony (Sb) are metalloids and bismuth (Bi) is a metal. They all exhibit the maximum oxidation state in the group, and their chemistry is largely covalent. Many other oxidation states can be exhibited by these elements (see the periodic table in tutorial 1), especially -3.

**Question 5.2**

What is the maximum oxidation state possible for the group 15 elements?

The maximum oxidation state is also known as the group valency.

**Group 16**

These elements are known as the **chalcogens**. Oxygen, sulfur and selenium (Se) are non-metals, tellurium (Te) is a metalloid, and polonium (Po) is radioactive and has no stable isotopes. Their chemistry is dominated by the formation of the -2 oxidation state but sulfur in particular can exhibit a variety of oxidation states.

**Question 5.3**

What is the oxidation number of sulfur in each of the following species?

(a) \( \text{SO}_4^{2-} \)  
(b) \( \text{S}_2\text{O}_3^{2-} \)  
(c) \( \text{SO}_3 \)  
(d) \( \text{SO}_2 \)  
(e) \( \text{H}_2\text{S} \)

**Group 17**

These elements are all non-metals and are called the **halogens**. Formation of stable mono-anions is the most common chemistry displayed by these elements. However, they also display the +7, +5, +3 and +1 oxidation states, when bonded to oxygen.

**Group 18**

The **noble gases** already have a full valence shell and therefore don’t get themselves involved in too much chemistry!

**The Periods**

The chemistry of the p-block elements does depend to some extent on which period the elements occur in. In particular the second period elements have a different chemistry from their heavier congeners (a congener is simply an element in the same group). We have touched on this difference before when talking about the octet rule in the 1st semester. The heavier elements, periods 3, 4, 5 and 6, all have vacant d-orbitals which allow them to expand their octet whereas period 2 elements have no vacant d-orbitals and cannot accommodate more than 8 valence electrons.

**Question 5.4**

Why do the second period elements not have any energetically available d-orbitals?

The second period elements B, C, N and O have a different chemistry from their congeners.
Periodic and Group Trends

Many physical properties of the elements exhibit a striking periodicity (that is, the physical properties change in a regular fashion as we go across a period). These properties include atomic size and the energies required to remove electrons from atoms. These properties also show definite trends as we go down a particular group in the periodic table. Before we talk about the trends, however, we must be sure we know exactly what the physical properties are that we will be talking about.

Atomic Radius \((r)\): This is half the distance between the centres of neighbouring atoms in the pure element. Atomic radii are usually measured in picometres, pm. (Remember a picometre is \(10^{-12}\) m). For instance, the distance between the two chlorine nuclei in \(\text{Cl}_2\) is 198 pm. Hence the atomic radius of chlorine is 99 pm.

Ionic Radius: The ionic radius of an element is its contribution to the distance between neighbouring ions in a solid ionic substance. Ionic radii are also measured in pm.

The atomic radius of an element is not the same as its ionic radius. Consider for example the element sodium. The atomic radius of \(\text{Na}\) is 180 pm, whereas the ionic radius of \(\text{Na}^+\) is 95 pm. Why is there such a large difference?

Question 5.5
(a) What is the electronic configuration of sodium?
(b) What is the electronic configuration of the sodium cation?

Generally when an element loses its valence electrons when forming cations, then only the core electrons remain. These core electrons are closer to the nuclei than the valence electrons and are thus tightly bound. Cations are always considerably smaller than their parent atoms.

How about anions? The atomic radius of chlorine is 100 pm. The ionic radius of chlorine is 181 pm.

Question 5.6
a) What is the electronic configuration of chlorine?
b) What is the electronic configuration of the chloride anion?

When we form anions we are adding electrons into the valence shell. The “extra” electrons are repelled by the existing electrons (since like charges repel) and the space taken up by the electrons expands. Thus anions are always substantially larger than their parent atoms.

Question 5.7
Explain the following observations.
(a) The atomic radius of aluminium is 125 pm while the ionic radius of the same element is only 50 pm.
(b) The ionic radius of oxygen is 140 pm, 80 pm larger than its atomic radius.

Question 5.8
The internuclear distance in solid magnesium oxide is 205 pm. The internuclear distance in solid magnesium chloride is 246 pm. Given that the ionic radius of \(\text{O}^2-\) is 140 pm, calculate the ionic radius of \(\text{Cl}^-\).
**Ionisation Energy ($I$):** The ionisation energy of an element is the minimum energy required to remove an electron from the ground state of a gaseous atom.

\[ X(g) \rightarrow X^+(g) + e(g) \]

It should be noted here that we are actually removing the electron from the atom in a physical process. This is different from when we were dealing with $\frac{1}{2}$-reactions in the redox chemistry section. Half-reactions are hypothetical i.e. the electrons do not exist as separate species in solution.

Removing an electron from an atom **always** requires energy. This energy is termed the **enthalpy of ionisation**, or the ionisation energy. All ionisation energies are positive enthalpies. Perhaps we’d better be a little more precise in our terminology. The **first** ionisation energy of an element, $X$, is the energy required to remove an electron from a neutral gaseous atom.

\[ X(g) \rightarrow X^+(g) + e(g) \]

The **second** ionisation energy of an element $X$ is the energy required to remove an electron from $X^+$

\[ X^+(g) \rightarrow X^{2+}(g) + e(g) \]

The third ionisation energy is the energy required to do the following

\[ X^{2+}(g) \rightarrow X^{3+}(g) + e(g) \]

and so on.

It is evident that $I_2$ will be a bigger energy than $I_1$. It will be progressively more difficult to remove electrons stepwise from a species because the more positive the species is the more tightly it will hold onto the remaining electrons. Let’s take aluminium as an example.

\[
\begin{align*}
I_1 & = 577 \text{ kJ mol}^{-1} \\
I_2 & = 1820 \text{ kJ mol}^{-1} \\
I_3 & = 2740 \text{ kJ mol}^{-1} \\
I_4 & = 11600 \text{ kJ mol}^{-1}
\end{align*}
\]

We can see that $I_4 > I_3 > I_2 > I_1$ as we would expect. Of particular mention, however, is the large jump between $I_3$ and $I_4$ i.e. 2 740 kJ mol$^{-1}$ to 11 600 kJ mol$^{-1}$. How do we account for this? Whenever dealing with ionisation energies, always ask yourself “which particular electrons are we dealing with?” or, in other words, what is the electronic configuration of the species involved? For aluminium and its ions we have the following electronic configurations.

\[
\begin{align*}
\text{Al} & : 1s^22s^22p^63s^23p^1 \\
\text{Al}^+ & : 1s^22s^22p^6 \\
\text{Al}^{2+} & : 1s^22s^22p^63s^1 \\
\text{Al}^{3+} & : 1s^22s^22p^6 \\
\text{Al}^{4+} & : 1s^22s^22p^5
\end{align*}
\]

Therefore when forming $\text{Al}^{4+}$ we have had to remove a core electron, as all the valence electrons have already been removed. Core electrons are closer to the nucleus and, consequently, are at much more negative energy than the valence electrons. It therefore takes much more energy to remove them from the atom.

**Question 5.9**

Explain the following trend in ionisation energies for magnesium:

$I_1 = 736$ kJ mol$^{-1}$; $I_2 = 1450$ kJ mol$^{-1}$; $I_3 = 7740$ kJ mol$^{-1}$.
Electron affinity ($E_a$): The electron affinity of an element is a measure of the change in energy that occurs when an electron is added to an atom or an ion of the element.

$$X(g) + e^-(g) \rightarrow X^-(g)$$

Trends in Atomic Radii
What would you expect to happen to atomic size as we proceed down a group in the periodic table? This is one of the easier questions to answer. As we proceed down a group the principal quantum number, $n$, increases. Therefore as we proceed down a group the valence electrons are becoming progressively further away from the nucleus (i.e. they are at less negative energies). Therefore as we go down a group the atomic size would be predicted to increase. The table below shows the atomic radii (pm) for the main group elements.

<table>
<thead>
<tr>
<th></th>
<th>1</th>
<th>2</th>
<th>13</th>
<th>14</th>
<th>15</th>
<th>16</th>
<th>17</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n = 2$</td>
<td>Li</td>
<td>Be</td>
<td>B</td>
<td>C</td>
<td>N</td>
<td>O</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td>145</td>
<td>105</td>
<td>85</td>
<td>70</td>
<td>65</td>
<td>60</td>
<td>50</td>
</tr>
<tr>
<td>$n = 3$</td>
<td>Na</td>
<td>Mg</td>
<td>Al</td>
<td>Si</td>
<td>P</td>
<td>S</td>
<td>Cl</td>
</tr>
<tr>
<td></td>
<td>180</td>
<td>150</td>
<td>125</td>
<td>110</td>
<td>100</td>
<td>100</td>
<td>100</td>
</tr>
<tr>
<td>$n = 4$</td>
<td>K</td>
<td>Ca</td>
<td>Ga</td>
<td>Ge</td>
<td>As</td>
<td>Se</td>
<td>Br</td>
</tr>
<tr>
<td></td>
<td>220</td>
<td>180</td>
<td>130</td>
<td>125</td>
<td>125</td>
<td>115</td>
<td>115</td>
</tr>
<tr>
<td>$n = 5$</td>
<td>Rb</td>
<td>Sr</td>
<td>In</td>
<td>Sn</td>
<td>Sb</td>
<td>Te</td>
<td>I</td>
</tr>
<tr>
<td></td>
<td>235</td>
<td>200</td>
<td>155</td>
<td>145</td>
<td>145</td>
<td>140</td>
<td>140</td>
</tr>
<tr>
<td>$n = 6$</td>
<td>Cs</td>
<td>Ba</td>
<td>Tl</td>
<td>Pb</td>
<td>Bi</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>266</td>
<td>215</td>
<td>190</td>
<td>180</td>
<td>160</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

As we proceed down any of the groups the atomic radius is seen to increase.

What happens to the atomic size as we proceed across the periodic table from left to right? You will notice that there is a general decrease in atomic size across a period. Why is this? At first sight we might think that as we proceed across a period the atomic number is increasing and therefore the size should be increasing because we have more electrons present. But this is clearly not the case. Again we have to think exactly where the electrons are going. As we proceed across a period we are gradually filling up a given valence shell i.e. a given value of $n$. As each electron is added we are also increasing the number of protons in the nucleus by one. This means that the nucleus has got a greater positive charge to attract the valence electrons. This can be shown in the diagram below.

![Diagram showing the increase in atomic size down a group and the decrease across a period.](image)

Each electron now experiences a greater positive charge and is more attracted to the nucleus. Thus the electrons are pulled closer to the nucleus and the atomic size decreases. The valence electrons are said to experience a greater effective nuclear charge as we go across a period from left to right.
Shielding

Why in the previous section did we use the term “effective nuclear charge” when describing nuclear charge? The answer to this question is very important when discussing the chemistry of the elements. As we have said before, the chemistry of an element depends upon its electronic configuration and thus on the relative energies of the electrons within the atom. The energy of one electron within the atom depends upon the energies of the other electrons present. This is, in fact, why the orbital energy diagram for hydrogen is different from that of the other elements. Hydrogen only has one electron and therefore there are no electron-electron interactions. All of the other elements have electron-electron interactions and these interactions depend on the shape of the orbital that each of the electrons is in. You will recall that the energy of the electrons in multi-electron atoms depends on both the quantum numbers n and l (l determines the shape of the orbital). Electron-electron interactions take the form of repulsions (as like charges repel). These interactions tend therefore to oppose the attractive forces between the nucleus and the electrons. If we consider the following two scenarios

Here the electron experiences the full nuclear charge. However if we now add some more electrons to the atom:

then we can see that the valence (outer) electron no longer experiences the full nuclear charge. It experiences only the difference between the attractive and repulsive forces. It is said to experience only the effective nuclear charge. The core electrons are said to shield the valence electrons from the nuclear charge. Why does this ability of the core electrons to shield the valence electrons depend on the shape of the orbital that the core electron is in? It’s a simple case of geometry. The closer a core electron is to the nucleus the better is will be at shielding the valence electrons. Which electrons are closest to the nucleus for a given value of n? The answer is the s-electrons. That is why the s-orbital is of a more negative energy than the p-orbitals in the orbital diagram of the multi-electron atoms. Thus the ability to shield valence electrons is greatest for an s-electron. The full order of shielding ability is –

\[ s > p > d > f \]

i.e. the same order of stabilities of the orbitals for a given n value. The f-electrons for instance are in very diffuse orbitals away from the nucleus and are very poor at shielding valence electrons from the nuclear charge.

When more than one valence electron is present then it must be remembered that they are very poor at shielding each other from the nuclear charge. Thus as we go across a period adding valence electrons, the effective nuclear charge experienced by the valence electrons increases because the nuclear charge has increased and the added electrons are poor at shielding each other.
There are (of course!) exceptions to the trends stated above. If we look at the ionisation energies for the second period:

<table>
<thead>
<tr>
<th></th>
<th>Li</th>
<th>Be</th>
<th>B</th>
<th>C</th>
<th>N</th>
<th>O</th>
<th>F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_1$ (kJ mol$^{-1}$)</td>
<td>519</td>
<td>900</td>
<td>799</td>
<td>1 090</td>
<td>1 400</td>
<td>1 310</td>
<td>1 680</td>
</tr>
</tbody>
</table>

You will notice that in general the trend is as we predicted; an increase from left to right. However two values seem to ignore our reasoning. $I_1$ for boron is less than that for Be and $I_1$ for O is less than that for N. Again, these discrepancies can be explained by looking at the electronic configuration of the elements involved.

(i) **Boron and Beryllium**

Be $1s^2 2s^2$

B $1s^2 2s^2 2p^1$

For beryllium we are removing a 2s electron during ionisation. For boron a 2p electron is removed. The 2p orbital is at a higher (less negative) energy than the 2s orbital and we would therefore expect that it would be easier to remove and that is borne out by the numbers.

(ii) **Nitrogen and Oxygen**

A more subtle explanation is required for these elements as in both cases we are removing a 2p electron. We will in fact have to go to the orbital diagram for each of the elements.

![Orbital Diagrams](image)

When ionising oxygen which electron will be removed? The answer is the one marked ↓. This electron is paired with another electron in a p-orbital and will thus experience a repulsive interaction from that other electron. This repulsive interaction results in it being easier to remove that electron than would be expected from the more simplistic atomic-size approach. The result is that oxygen has a lower ionisation energy than expected and in fact it is less than the $I_1$ value of nitrogen.

**Question 5.10**

(a) Which element in each of the following pairs of electrons has the higher $I_1$ value?

(i) Na or Mg

(ii) Mg or Al

(iii) As or Sn

(b) Predict which of the following ions has the larger ionic radius: Mg$^{2+}$ or Al$^{3+}$.

(c) Predict which of the following elements has the more exothermic (i.e. the most negative) electron affinity: fluorine or sodium.
INTRAMOLECULAR BONDING

We have seen previously that there are two types of covalent bonds that can form in molecules. These are σ bonds and π bonds. We have also added to this the fact that the second period elements have a distinctly different chemistry from their heavier congeners. One reason for this is that the heavier elements have d-orbitals available to expand the octet of electrons that are available from the s-orbital and three p-orbitals.

There is another reason why the 2nd period elements have a different chemistry and that is their size. We have seen that atomic size increases as one goes down a group in the periodic table and that it decreases as we go across a period from left to right. Thus elements such as carbon nitrogen and oxygen are amongst the smallest of the elements. This has an important consequence in the bonding that occurs in molecules containing these elements.

We have seen that N₂ is a molecule which contains one σ bond and two π bonds. The π bonds form from p-orbitals which overlap in the following manner.

As nitrogen is a small atom the two nitrogens can approach very close to each other. This allows the p-orbitals to overlap and form π bonds. The same is true for oxygen and carbon. Therefore compounds containing oxygen, nitrogen and carbon often contain π bonds to those atoms.

If we now go down Group 15 to the next element, which is phosphorus, an increase in atomic size results.

<table>
<thead>
<tr>
<th>Atomic radius/pm</th>
<th>N</th>
<th>65</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>P</td>
<td>100</td>
</tr>
</tbody>
</table>

When two phosphorus atoms come together they cannot therefore approach each other as closely as two nitrogen atoms can. This then results in a very poor overlap of the p-orbitals and a π bond cannot form.

Phosphorus therefore does not exist as a P₂ molecule with a triple bond between the phosphorus atoms. However it still needs to form three bonds to complete its octet. Phosphorus therefore forms three σ bonds to other phosphorus atoms, thus:
Each phosphorus atom now has eight electrons in its valence shell. $P_4$ is called **white phosphorus**.

A similar case arises when considering oxygen and sulfur. Oxygen occurs as $O_2$ which has one $\sigma$ bond and one $\pi$ bond between the oxygen atoms.

Sulfur being much larger than oxygen would rather form two $\sigma$ bonds. Elemental sulfur occurs in the form shown below

```
S S S S
S S S S
```

This is known as crown sulfur for obvious reasons.

**THE SOLID STATE**

We have already seen that the physical properties of the elements depend upon intermolecular interactions. When a substance is in the solid state there is one other thing which is important and that is how the atoms or molecules are packed together. There are five categories of solids

- Metallic
- Atomic
- Ionic
- Molecular covalent
- Polymeric covalent

**Metallic Bonding**

Metals adopt a close-packed crystal structure. If we imagine the metal atoms as being identical spheres then the packing of the spheres are such that the atoms occupy the smallest total volume with the least empty space. The 1$^{\text{st}}$ layer of atoms pack as follows:

```
  O  O  O
  O  O  O
  O  O  O
```

Then the 2$^{\text{nd}}$ layer sits in the holes created by the 1$^{\text{st}}$ layer and the 3$^{\text{rd}}$ layer sits in the holes created by the 2$^{\text{nd}}$ layer, etc.
Metallic bonding is special in that it is best envisaged as metal cations sitting in a ‘sea’ of electrons. This is due to the electrons not being confined just to one metal atom. Rather, they are free to roam all over the crystal. The electrons are said to be delocalised (as opposed to localised on one atom). This movement of electrons within a crystal results in metals being very good conductors of electricity. Due to the electrostatic interaction between the metal cations and the sea of electrons, metallic bonding is very strong and, consequently, the melting point temperatures of metals are very high. The metal with the highest melting point temperature, tungsten (W), has a melting point of about 3400 °C!

The Group 1 elements are atypical for metals in that they are, in the main, soft metals with low melting point temperature. Sodium, for instance, is easily cut with a knife and has a melting point temperature of 98 °C. We can explain this using our ‘sea’ of electrons model. Group I metals have only one valence electron and therefore the electrostatic interaction between the cations and the sea of electrons is not as great as, say, for aluminium which has three valence electrons it can donate to the ‘sea’.

**Bonding in Atomic Solids**

Another group of elements also exhibits close-packed crystal structures. These structures however have very different physical properties from metallic structures and thus we will separate them out into a different category. The noble gases (Group 18), also exhibit close-packing in their solid state. Here, however, the electrons stay within their parent atoms i.e. they are localised. This results in only weak intermolecular London forces between the adjoining atoms. We would therefore expect these types of solid to have much lower melting point temperatures than the metals. The melting point temperatures of the group 18 elements are shown below.
A molecular solid is one which contains discrete molecules packed together.

Molecular Solids

What type of solids do elements such as nitrogen and fluorine adopt? We must remember that these elements occur as diatomic molecules and thus these diatomic molecules are the building-blocks for the solid.
As only dipole-dipole interactions (for polar molecules) and London forces (for all molecules) hold the molecules together molecular solids have low melting point temperatures as shown for some elements overleaf.

<table>
<thead>
<tr>
<th></th>
<th>Melting point temperature/°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{O}_2 )</td>
<td>-218</td>
</tr>
<tr>
<td>( \text{N}_2 )</td>
<td>-210</td>
</tr>
<tr>
<td>( \text{P}_4 )</td>
<td>44</td>
</tr>
<tr>
<td>( \text{S}_6(\alpha) )</td>
<td>113</td>
</tr>
</tbody>
</table>

Again we can see that, as the number of atoms increases in the molecule, the higher the melting point temperature will be, due to the increased London forces present.

**Polymeric Covalent Solids**

These are sometimes known as network solids as they consist of giant molecules which contain hundreds (or even thousands or even millions!) of atoms. An example is the diamond structure of carbon. In this molecule carbon is \( \sigma \) bonded to four other carbons in a huge 3-dimensional structure of carbon atoms.

![Diamond structure of carbon](image)

This type of crystal is quite different from the molecular covalent solids. Here we have each atom covalently bonded to the other atoms. Therefore if we were to melt these substances we would need to break covalent bonds and thus we would expect a lot of energy to be required. The melting point temperature of the diamond structure of carbon is 3547°C, even higher than that of tungsten (3400°C), the metal with the highest melting point temperature.

**Allotropy and Polymorphism**

In the previous section we referred to the diamond structure of carbon. This implies that there are other structures of carbon that occur, and this is indeed the case. Carbon can also occur in the solid state as graphite, the “lead” in pencils:
or as the more exotic buckminsterfullerene.

Diamond, graphite and buckminsterfullerene are said to be allotropic forms of the element carbon.

Each allotrope has unique physical properties due to the different types of bonding within the structure. Graphite for instance is soft and conducts electricity whereas diamond is very hard (the hardest substance known) and is an electrical insulator. Same element, but different structures, and therefore different properties!

The properties of graphite arise from the fact that each carbon is sp$^2$-hybridised i.e. it forms only three σ bonds to three other carbons. This results in sheets of carbon atoms covalently bonded to each other.

Each carbon still has one more electron which is in a p-orbital of π symmetry. These π-electrons form a delocalised π bond over the whole sheet of carbon atoms. Thus we have a case where the π electrons can move within the crystal and thus the crystal conducts electricity.

**Question 5.13**
(a) What is the hybridisation of the carbon atoms in the diamond structure?
(b) Are there any delocalised π electrons in the diamond structure?
(c) Will the diamond structure conduct electricity?

What about the difference in hardness between the graphite and diamond allotropes? Again this results directly from the difference in bonding. The sheet structure of graphite contains covalently–bonded carbons.

However between these sheets there are no covalent bonds. Only London forces hold the sheets together and therefore these bonds are easily broken. This results in the sheets ‘slipping’ along the plane of the sheets and thus graphite is soft. Diamond on the other hand is a three dimensional covalent structure and is thus very hard.

> If more than one allotrope exists for an element, be sure to specify which one you are talking about.

Phosphorus is another element which has more than one allotrope. We have met white phosphorus, P$_4$, previously. However there is another allotrope known as red phosphorus. You will recall that white phosphorus has the following structure:
where each phosphorus had to form three σ bonds in order to obey the octet rule. There is however another way that we can draw three σ bonds to each phosphorus. If we break the bond marked in bold in the above structure and form two new bonds to those phosphorus atoms we will end up with the following structure.

![Phosphorus structure diagram]

Long chains form and we end up with a polymeric structure known as red phosphorus.

**Question 5.14**

(a) What type of crystal structure would you expect for red phosphorus?

(b) Which allotrope of phosphorus would you expect to have the higher melting point temperature?

**Allotropes are different structural units of an element.**

Previously we quoted the melting point temperature for sulfur, \( S_8 \). When we did this we wrote it as \( S_8(\alpha) \). You might be wondering what the \( (\alpha) \) was for? It is actually used to describe the way the \( S_8 \) units are packed together in the crystal. Why do we need to specify \( (\alpha) \)? Because there is another, different way, to pack the \( S_8 \) molecules. This is quite different from allotropy where the structural unit was different. Here the structural unit is constant and the packing is different. The \( \alpha \)-form is called rhombic sulfur and the \( \beta \)-form is known as monoclinic sulfur. They are different polymorphs of sulfur.

Polymorphism does affect the physical properties. For instance monoclinic sulfur melts at \( 119^\circ \text{C} \) while the rhombic form melts at \( 113^\circ \text{C} \). They also have different densities and different thermodynamic properties. It is obvious therefore that the different structural units that elements can form (allotropy) affects their chemical and physical properties, while even the packing of a given structural unit within a crystal lattice (polymorphism) can affect the physical properties of a substance.

**INORGANIC ACIDS AND BASES**

We have seen previously that HCl in the gaseous state is a covalent molecule. However when we put HCl in water the following occurs.

\[
\text{HCl(g)} + \text{H}_2\text{O(l)} \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{Cl}^-(\text{aq})
\]

HCl donates a proton to water to form the hydronium ion. The other product is the chloride ion. HCl is therefore an acid and water is acting as a base. HCl is said to be a strong acid. A strong acid is one which dissociates completely in water to form ions.

Some acids do not dissociate completely in water. These are known as weak acids. Examples of weak acids are the carboxylic acids. Some other acids are listed below.

<table>
<thead>
<tr>
<th>Strong acids</th>
<th>Weak acids</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO(_3) (nitric acid)</td>
<td>HF (hydrofluoric acid)</td>
</tr>
<tr>
<td>HClO(_4) (perchloric acid)</td>
<td>HCN (hydrogen cyanide)</td>
</tr>
<tr>
<td>HBr (hydrobromic acid)</td>
<td>HCOOH (methanoic acid or formic acid)</td>
</tr>
<tr>
<td>HI (hydroiodic acid)</td>
<td>HClO (hypochlorous acid)</td>
</tr>
</tbody>
</table>

Some strong and weak bases are listed below.
Polyprotic Acids

Some acids can donate more than one proton and are thus called polyprotic acids. An example is sulfuric acid, H₂SO₄. Polyprotic acids lose their protons in a stepwise manner i.e. one at a time. Thus for H₂SO₄:

\[
\begin{align*}
\text{H}_2\text{SO}_4(\text{aq}) + \text{H}_2\text{O}(\text{l}) & \rightarrow \text{H}_3\text{O}^+(\text{aq}) + \text{HSO}_4^-(\text{aq}) \\
\text{HSO}_4^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) & \rightleftharpoons \text{H}_3\text{O}^+(\text{aq}) + \text{SO}_4^{2-}(\text{aq})
\end{align*}
\]

You will note that H₂SO₄ behaves as a strong acid when it loses its first proton but as a weak acid when it loses its second proton.

Other weak polyprotic acids include H₂SO₃ (sulfurous acid), H₂C₂O₄ (oxalic acid) and H₃PO₄ (phosphoric acid).

Oxo-Acids

The aforementioned polyprotic acids all have one thing in common. The acidic protons are all attached to oxygen atoms.

\[
\begin{align*}
\text{H–O–P–O–H} & \quad \text{H–O–C–O–H} & \quad \text{O–S–O–H} \\
\text{phosphoric acid (triprotic)} & \quad \text{oxalic acid (diprotic)} & \quad \text{sulfurous acid (diprotic)}
\end{align*}
\]

In fact all hydrogens attached to oxygens in a covalent molecule are acidic. Species which contain such hydrogens are known as oxo-acids.

An example of a simple monoprotic oxo-acid is hypochlorous acid, HOCl. HOCl contains a polar oxygen-hydrogen bond thus:

\[
\delta^+ \quad \delta^- \\
\text{H–O–Cl}
\]

When, therefore, we put HOCl in water, the hydrogen is attracted to a lone pair on the oxygen atom in water as shown below.
The reaction then results in the following.

Water has accepted a proton and is thus a base and HOCl has donated a proton and is thus an acid. The products are H$_3$O$^+$, the hydronium ion, and OCl$^-$, the hypochlorite ion.

**Question 5.15**

(a) What is the oxidation number of chlorine in HOCl?
(b) What is the oxidation number of chlorine in OCl$^-$?
(c) What is the correct IUPAC name for the OCl$^-$ ion?

HOCl is a weak acid and thus the correct way of writing the reaction is with the double arrow between the reactants and products.

\[
\text{HOCl(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+(aq) + \text{OCl}^-(aq)
\]

The strength of an acid is a measure of how many of the acid molecules donate protons to water i.e. how many hydronium ions are formed in solution. What factors affect the strengths of oxo-acids? We can answer this question by considering the nature of the oxygen-hydrogen bond. The greater the tendency of the acid to donate a proton, the stronger the acid will be. This, in turn, will depend upon the polarity of the oxygen-hydrogen bond. The greater the polarity of the oxygen-hydrogen bond in the oxo-acids, the greater will be the tendency for the water molecule to form a bond to the hydrogen atom, thus breaking the oxygen-hydrogen bond in the acid.

What factors can affect the polarity of the oxygen-hydrogen bond in an oxo-acid? Easy(!)- the rest of the molecule.

Firstly let’s consider varying the atom attached to the oxygen atom in the acid. Which of the following will be the stronger acid?

```
\begin{align*}
\text{H—O—Cl—O} & \quad \text{H—O—I—O} \\
\text{chloric acid} & \quad \text{iodic acid}
\end{align*}
```

The easiest way to answer this problem is to consider which of the chlorine or the iodine is the more electronegative. The more electronegative the atom attached to the oxygen the more electron density will be withdrawn from the hydrogen and the more polar will be the oxygen-hydrogen bond. Chlorine is more electronegative than iodine, therefore chloric acid is a stronger acid than iodic acid.

Another factor, closely related to the first, is which atoms are attached to the atom which is attached to the oxygen! The same reasoning is relevant. If those groups withdraw electron density then the oxygen-hydrogen bond becomes more polar and the acid strength will increase.
Consider the following acids.

\[
\begin{align*}
\text{perchloric acid} & & \text{chlorous acid} \\
\text{H} & \text{O} \quad \text{Cl} \quad \text{O} & \text{H} & \text{O} \quad \text{Cl} \quad \text{O}
\end{align*}
\]

In perchloric acid, the three oxygens double-bonded to the chlorine atom are highly electronegative. Therefore they will increase the electron-withdrawing effect on the hydrogen making it more acidic. Chlorous acid only has one such oxygen and thus the effect is less and chlorous acid is consequently a weaker acid than perchloric acid.

In general the more oxygens attached to the atom bonded to the –OH group the stronger will be the acid.

**Question 5.16**

Predict which of the following acids is the stronger - nitric acid or nitrous acid?

**Question 5.17**

Given the following names for oxo-acids:

- HClO₄: perchloric acid [chloric(VII) acid]
- HClO₃: chloric acid [chloric (V) acid]
- HClO₂: chlorous acid [chloric (III) acid]
- HClO: hypochlorous acid [chloric (I) acid]

Name the following acids.

(a) HBrO₄ (b) HIO (c) HBrO₂

**Question 5.18**

Predict, with clear reasoning, which of the acids in 5.17 is the strongest acid.

**Acidic and Basic Oxides**

As we live in an oxygen-rich planet many of the elements occur combined with oxygen in oxides. The chemistry of the oxides largely determine the movement of these elements between the geosphere (the earth), the hydrosphere (the water) and the atmosphere. It is thus very important we understand the acid-base properties of these species.

**Question 5.19**

Predict the common binary (something that contains only two elements) oxides of the following elements.

(a) sodium (b) calcium (c) aluminium (d) gallium (e) carbon (f) antimony

**Question 5.20**

Predict whether the bonding in each of the oxides in the question above is ionic or covalent.

**Basic Oxides**

The oxides of groups 1 and 2 are all solids and all are ionic (due to the large ΔEN values between the metals and oxygen atoms). How do ionic oxides behave when added to water?

Let’s look at the reaction between CaO and H₂O.

\[
\text{CaO(s)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca}^{2+}(\text{aq}) + \text{O}^2-(\text{aq})
\]
Ionic substances dissolve in water to give rise to ions. The $O^{2-}$ ion however is a very strong base (it has a very large negative charge density) and thus has a strong affinity for protons. The oxide ion, $O^{2-}$, is in fact such a strong base that it does not exist in aqueous solution. Instead it reacts with water thus.

$$O^{2-}(aq) + H_2O(l) \rightarrow 2 OH^-(aq)$$

or if we draw the Lewis structures:

\[ \text{O}^{2-} \text{extracts a proton from a water molecule, thus acting as a base. Therefore the reaction between CaO and H}_2\text{O is better written as:} \]

$$\text{CaO(aq)} + \text{H}_2\text{O(l)} \rightarrow \text{Ca}^{2+}(aq) + 2 \text{OH}^-(aq)$$

**Question 5.21**
Write a balanced reaction equation for the reaction between sodium oxide and water.

**Acidic Oxides**
When non-metals form oxides the bonding is always polar-covalent, not ionic. This results in these oxides having very different acid/base behaviour from the metal-oxides. If we take $SO_2$ as an example:

$$SO_2(g) + H_2O(l) \rightarrow H_2SO_3(aq)$$

We have thus formed sulfurous acid.

**Question 5.22**
Write balanced equations for the reaction between:
(a) $SO_3$ and $H_2O$  
(b) $CO_2$ and $H_2O$

**Amphoteric Oxides and Hydroxides**
We have seen that metal oxides are largely basic and non-metallic oxides are largely acidic. There is another class of oxides; those which can exhibit acidic or basic behaviour. These oxides can react with acids and bases and are known as **amphoteric oxides**. Aluminium oxide is an example.

<table>
<thead>
<tr>
<th>Base</th>
<th>$\text{Al}_2O_3(s)$ + 6 $H^+(aq)$ $\rightarrow$ 2 $Al^{3+}(aq)$ + 3 $H_2O(l)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid</td>
<td>$\text{Al}_2O_3(s)$ + 2 $OH^-(aq)$ + 3 $H_2O(l)$ $\rightarrow$ 2 $Al(OH)_4^-(aq)$</td>
</tr>
</tbody>
</table>

It is important to realise that the acid/base characteristics of an oxide are similar to the acid-base chemistry of the corresponding hydroxide. Therefore if a metal oxide is basic, the hydroxide of that same metal will also be basic. For example:

$$\text{Na}_2O(s) + H_2O(l) \rightarrow 2 \text{Na}^+(aq) + 2 \text{OH}^-(aq)$$
If an oxide is amphoteric then so will be the corresponding hydroxide. PbO, an amphoteric oxide, will give rise to Pb(OH)₂ upon hydration. Therefore, although Pb(OH)₂ is a hydroxide (which you might think is a base), it is actually amphoteric.

Acid  Pb(OH)₂(s)  +  2 OH⁻(aq)  →  Pb(OH)₄²⁻(aq)  plumbite ion

Base  Pb(OH)₂(s)  +  2 H⁺(aq)  →  Pb²⁺(aq)  +  2 H₂O(l)

Some other amphoteric hydroxides are listed below.

<table>
<thead>
<tr>
<th>Hydroxide</th>
<th>Acidic solution</th>
<th>Basic solution*</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al(OH)₃</td>
<td>Al³⁺</td>
<td>Al(OH)₄⁻ alumin ate ion</td>
</tr>
<tr>
<td>Cr(OH)₃</td>
<td>Cr³⁺</td>
<td>Cr(OH)₄⁻ chromite ion</td>
</tr>
<tr>
<td>Sn(OH)₂</td>
<td>Sn²⁺</td>
<td>Sn(OH)₄⁻ stannite ion</td>
</tr>
<tr>
<td>Zn(OH)₂</td>
<td>Zn²⁺</td>
<td>Zn(OH)₄⁻ zincate ion</td>
</tr>
</tbody>
</table>

*You will notice that many metals form complex ions with four hydroxides. The other common number is six.

**Question 5.23**
Write a balanced equation for the reaction of Sn(OH)₂ with:
(a) acid  (b) base

**Question 5.24**
Arrange the acids $\text{H}_2\text{SO}_4$, $\text{H}_2\text{SO}_3$ and $\text{HSO}_3⁻$ in order of decreasing strength.

**Question 5.25**
Arrange the acids HCl, HF and H₂O in order of decreasing strength.

**Question 5.26**
Arrange the bases ClCH₂COO⁻, CH₃COO⁻ and FCH₂COO⁻ in order of increasing strength.

**Question 5.27**
Which of the following oxides are basic?
(a) BaO  (b) CO₂  (c) CO  (d) Rb₂O

**Question 5.28**
Classify each of the following species as an acid, a base or an amphiprotic substance in aqueous solution
(a) $\text{H}_2\text{O}$  (b) $\text{PO}_4^{³⁻}$  (c) $\text{CH}_3\text{NH}_2$  (d) $\text{CH}_2\text{NH}_₃^⁺$

**Question 5.29**
Identify all species in the following reactions as either an acid or a base.
(a) $\text{HCO}_3(aq) + \text{H}_2\text{SO}_4(aq) \rightleftharpoons \text{HSO}_4(aq) + \text{H}_2\text{CO}_3(aq)$
(b) \( \text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{NO}_2(\text{aq}) \rightleftharpoons \text{HNO}_2(\text{aq}) + \text{HC}_2\text{O}_4(\text{aq}) \)

(c) \( \text{NH}_4(\text{aq}) + \text{HCO}_3(\text{aq}) \rightleftharpoons \text{NH}_3(\text{aq}) + \text{H}_2\text{CO}_3(\text{aq}) \)

**SOME IMPORTANT ELEMENTS**

**SULPHUR**

What do we know about sulphur? Perhaps we should summarise some of the important material we’ve covered already.

- Sulphur is in group 16 and the 3\(^{rd}\) period.
- It exhibits many different oxidation numbers in its compounds, most commonly +6, +4 and −2.
- Its oxides are covalent and thus acidic.
- It can extend its octet in molecules and complex ions due to the presence of d-orbitals.

**Question 5.30**

(a) What is the full electronic configuration of sulfur?

(b) How many electrons does it require to fill its valence shell?

(c) Give an example of a compound which contains sulfur in the following oxidation states.

- (i) +6
- (ii) +4
- (iii) −2

(d) Which oxides do you know of sulfur?

(e) Which oxo-anions do you know of sulfur?

(f) Name a weak acid containing sulfur.

(g) Name a strong acid containing sulfur.

**Sulphuric Acid**

Sulphuric acid is used in more industrial processes than any other chemical (with the exception of water!). It is prepared by oxidising elemental sulphur. The reaction sequence used in industry is called the **contact process**.

\[
\begin{align*}
\text{S(s)} + \text{O}_2(\text{g}) & \rightarrow \text{SO}_2(\text{g}) \\
2 \text{SO}_2(\text{g}) + \text{O}_2(\text{g}) & \rightarrow 2 \text{SO}_3(\text{g}) \\
\text{SO}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) & \rightarrow \text{H}_2\text{S}_2\text{O}_7(\text{aq}) \\
\text{H}_2\text{S}_2\text{O}_7(\text{aq}) + \text{H}_2\text{O}(\text{l}) & \rightarrow 2 \text{H}_2\text{SO}_4(\text{aq})
\end{align*}
\]

**Question 5.31**

(a) What is the oxidation number of S on the RHS of the first and second equations above?

(b) What is being reduced in the second equation?

(c) \( \text{H}_2\text{S}_2\text{O}_7 \) is known as oleum. What is the oxidation state of sulphur in this compound?

(d) Is the fourth equation a redox equation? Explain your answer.

The acidic properties of \( \text{H}_2\text{SO}_4 \) are used widely in the industrial manufacture of fertilisers. Biomass requires nitrogen and phosphorus (as well as potassium) which often need to be supplied by the farmer using synthetic fertilisers. A common source of nitrogen is ammonium sulfate which is prepared in the following manner.

\[
2 \text{NH}_3(\text{g}) + \text{H}_2\text{SO}_4(\text{aq}) \rightarrow (\text{NH}_4)_2\text{SO}_4(\text{s})
\]

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Sulfuric acid is also used in the manufacture of phosphate fertilisers by reaction with minerals such as fluorapatite.

\[
\text{Ca}_{10}[(\text{PO}_4)_6\text{F}_2(s) + 7 \text{H}_2\text{SO}_4(aq) \rightarrow 3 \text{Ca(H}_2\text{PO}_4)_2(s) + 2 \text{HF(g)} + 7 \text{CaSO}_4(s)}
\]

The fertiliser material prepared in this way, i.e. containing both Ca(H$_2$PO$_4$)$_2$ and CaSO$_4$, is called single superphosphate.

As well as its acidic properties, H$_2$SO$_4$ is often used as an oxidising agent in chemical preparations. Concentrated H$_2$SO$_4$ oxidises most metals. For instance the following reaction is used to prepare SO$_2$ on a laboratory scale.

\[
\text{Cu(s) + 2 H}_2\text{SO}_4(aq) \rightarrow \text{CuSO}_4(aq) + \text{SO}_2(g) + 2 \text{H}_2\text{O(l)}
\]

With stronger reducing agents such as zinc, elemental sulphur is produced.

\[
3 \text{Zn(s) + 4 H}_2\text{SO}_4(aq) \rightarrow 3 \text{ZnSO}_4(aq) + \text{S(s) + 4 H}_2\text{O(l)}
\]

Another example of concentrated sulphuric acid reacting with different strengths of reducing agents is its reaction with hydrogen halides.

\[
\text{HCl(aq) + H}_2\text{SO}_4(aq) + \text{heat} \rightarrow \text{no reaction}
\]

\[
2 \text{HBr(aq) + H}_2\text{SO}_4(aq) + \text{heat} \rightarrow \text{Br}_2(aq) + 2 \text{H}_2\text{O(l) + SO}_2(g)
\]

\[
8 \text{HI(aq) + H}_2\text{SO}_4(aq) + \text{heat} \rightarrow 4 \text{I}_2(aq) + \text{H}_2\text{S(g) + 4 H}_2\text{O(l)}
\]

The above reactions, as you know, can be used to distinguish between chlorides, bromides and iodides in the laboratory when one is trying to identify an unknown salt.

Another use of H$_2$SO$_4$ in chemistry is as a dehydrating agent i.e. something which has a high affinity for water. A very spectacular demonstration of this ability is when we treat ordinary sugar (sucrose) with concentrated H$_2$SO$_4$. The following reaction takes place.

\[
\text{C}_6\text{H}_{12}\text{O}_6(s) \xrightarrow{\text{H}_2\text{SO}_4(c)} 6\text{C} - 6 \text{H}_2\text{O}
\]

The sulfuric acid extracts the water from the sugar leaving behind a black residue which dramatically “flows” out of the reaction vessel.

**NITROGEN**

Some of the important information for the element nitrogen is listed below.

- Nitrogen is in group 15 and the 2$^{nd}$ period.
- Nitrogen, like sulfur, exhibits many oxidation numbers. The oxidation states +5, +4, +3, +2, +1, 0 and −3 all occur in the natural environment.
- Nitrogen is a non-metal and thus forms covalent oxides which are acidic in nature.
- Being in the second period, nitrogen compounds and oxo ions normally obey the octet rule.

**Question 5.32**

(a) How many unpaired electrons does an atom of nitrogen have?

(b) Give an example of a species which contains nitrogen in oxidation state:

(i) +5  
(ii) +3  
(iii) 0

(c) What is the oxidation number of nitrogen in the following gases?

(i) N$_2$O  
(ii) NO  
(iii) N$_2$O$_4$
(d) Identify each of the following species as a reducing agent, an oxidizing agent or both.

(i) \( \text{HNO}_3 \)  
(ii) \( \text{NH}_3 \)  
(iii) \( \text{N}_2\text{O} \)

**Nitric Acid**

Nitric acid is prepared on a large scale in industry via the Ostwald Process.

\[
4 \text{NH}_3 (g) + 5 \text{O}_2 \rightarrow 4 \text{NO}(g) + 6 \text{H}_2\text{O} \\
2 \text{NO}(g) + \text{O}_2(g) \rightarrow 2 \text{NO}_2(g) \\
3 \text{NO}_2(g) + \text{H}_2\text{O}(l) \rightarrow 2 \text{HNO}_3(aq) + \text{NO}(g)
\]

Like sulfuric acid, nitric acid has important acid/base properties and extensive redox behaviour. Again the acid/base properties are used in fertiliser manufacture such as in the production of ammonium nitrate.

\[
\text{NH}_3(g) + \text{HNO}_3(aq) \rightarrow \text{NH}_4\text{NO}_3(s)
\]

This reaction in fact uses about 80% of the \( \text{HNO}_3 \) produced via the Ostwald process. \( \text{HNO}_3 \) can also be used (instead of \( \text{H}_2\text{SO}_4 \)) in the production of phosphate fertilisers from apatite minerals.

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2(s) + 14 \text{HNO}_3(aq) \rightarrow 3 \text{Ca}(\text{H}_2\text{PO}_4)_2(s) + 7 \text{Ca(NO}_3)_2(s) + 2 \text{HF}(g)
\]

The fertiliser material thus produced contains both phosphorus (\( \text{Ca}(\text{H}_2\text{PO}_4)_2 \)) and nitrogen (\( \text{Ca(NO}_3)_2 \)); both essential elements for plant growth.

The redox properties of \( \text{HNO}_3 \) can be very complicated for students starting out in chemistry. Due to the number of stable oxidation states available to nitrogen, the possible products upon reduction of nitric acid are numerous, and depend upon the reducing agent and (as was true for \( \text{H}_2\text{SO}_4 \)) whether the acid is dilute or concentrated.

If we look for instance at the reaction of conc. \( \text{HNO}_3 \) with some reducing agents:

(i) \( \text{S}^{2-}(aq) + 2 \text{HNO}_3(aq) + 2 \text{H}^+(aq) \rightarrow \text{S(s)} + 2 \text{NO}_2(g) + 2 \text{H}_2\text{O}(l) \)

(ii) \( 2 \text{I}^-(aq) + 2 \text{HNO}_3(aq) + 2 \text{H}^+(aq) \rightarrow \text{I}_2(s) + 2 \text{NO}_2(g) + 2 \text{H}_2\text{O}(g) \)

(iii) \( 6 \text{Fe}^{2+}(aq) + 2 \text{HNO}_3(aq) + 6 \text{H}^+(aq) \rightarrow 6 \text{Fe}^{3+}(aq) + 2 \text{NO}(g) + 4 \text{H}_2\text{O}(l) \)

Either \( \text{NO}(g) \) or \( \text{NO}_2(g) \) can result.

**Question 5.33**

Calculate the number of electrons being transferred in each of the equations above.

We can also illustrate the difference between conc. and dilute nitric acid by looking at their respective reactions with copper metal. Two equations we have seen before are:

\[
\text{Cu(s)} + 4 \text{HNO}_3(c) \rightarrow \text{Cu(NO}_3)_2(aq) + 2 \text{H}_2\text{O}(l) + 2 \text{NO}_2(g)
\]

\[
\text{Cu(s)} + \text{HNO}_3(aq) + \text{H}^+(aq) \rightarrow \text{Cu}^{2+}(aq) + \text{H}_2\text{O}(l) + \text{NO}(g)
\]

(To be quite honest the reaction of \( \text{HNO}_3 \) with copper, and in fact most metals that dissolve in \( \text{HNO}_3 \) normally leads to a mixture of \( \text{NO}(g) \) and \( \text{NO}_2(g) \). The above reactions can thus be viewed as ideal equations.)
The reason most metals dissolve in HNO₃ is that it is a very strong oxidising agent. Non-metals can also be oxidised, usually to their highest available oxidation number. Some examples are shown below using hot, concentrated HNO₃.

\[
\begin{align*}
S & \xrightarrow{\text{HNO}_3(c) \text{ hot}} \text{SO}_3 \xrightarrow{\text{H}_2\text{O}} \text{H}_2\text{SO}_4 \\
\text{P}_4 & \xrightarrow{\text{HNO}_3(c) \text{ hot}} \text{P}_4\text{O}_{10} \xrightarrow{\text{H}_2\text{O}} \text{H}_3\text{PO}_4
\end{align*}
\]

**Question 5.34**

Assuming that NO₂(g) is the by-product of the two redox reactions above, write balanced reaction equations.

**PHOSPHORUS**

Like nitrogen, phosphorus appears in many forms in soils and waters, mainly due to its use in fertilisers.

The element itself does not occur uncombined in nature; instead phosphorus is always combined with oxygen to form oxides and oxo-acids. We can get a good idea of the chemistry of phosphorus just by reminding ourselves of some basic facts.

- Phosphorus is in the 3rd period and group 15
- Phosphorus has the valence electronic configuration 3s²3p³
- Phosphorus has the common oxidation numbers +5, +3 and −3
- Phosphorus forms covalent bonds to oxygen and the halides

**Question 5.35**

Predict the shape around phosphorus in the following molecules.

(i) PCl₃ (ii) PF₅ (iii) H₃PO₄

**Phosphoric Acid**

Phosphoric acid, H₃PO₄, is a triprotic weak acid and is prepared from one of two common pathways. The first route involves treating raw phosphate rock such as Ca₃(PO₄)₂ with sulfuric acid thus:

\[
\text{Ca}_3(\text{PO}_4)_2(s) + 3 \text{H}_2\text{SO}_4(aq) \rightarrow 2 \text{CaSO}_4(s) + 2 \text{H}_3\text{PO}_4(l)
\]

The phosphoric acid made in this manner is in turn used to prepare a fertiliser material called “triple superphosphate” from phosphate rock. If we again take fluorapatite as our starting material:

\[
\text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 14 \text{H}_3\text{PO}_4 \rightarrow 10 \text{Ca(H}_2\text{PO}_4)_2 + 2 \text{HF}
\]

In this case, the phosphorus fertiliser is not “diluted” by CaSO₄ and we thus have so-called “triple superphosphate”.

The second method used to prepare phosphoric acid is employed when one requires pure H₃PO₄ if, for instance, it is to be used in food and beverages. This time we must go through an intermediate of elemental white phosphorus P₄. P₄ is generated from the reduction of phosphate rock. The reducing agent used is carbon (“coke”).

\[
2 \text{Ca}_{10}(\text{PO}_4)_6\text{F}_2 + 30 \text{C} + 18 \text{SiO}_2 \rightarrow 18 \text{CaSiO}_3 + 30 \text{CO} + 2 \text{CaF}_2 + 3 \text{P}_4
\]
**Question 5.36**

Identify which elements are changing their oxidation number in this reaction and therefore calculate the number of electrons being transferred.

The white phosphorus thus isolated can now be reoxidised to prepare pure \( \text{H}_3\text{PO}_4 \). This is done in two steps.

\[
\text{P}_4(\text{s}) + 5 \text{O}_2(\text{g}) \rightarrow \text{P}_4\text{O}_{10}(\text{s})
\]

\[
\text{P}_4\text{O}_{10}(\text{s}) + 6 \text{H}_2\text{O}(\text{g}) \rightarrow 4 \text{H}_3\text{PO}_4(\text{aq})
\]

\( \text{P}_4\text{O}_{10} \) is known as phosphorus pentoxide (this name arises from the formula \( \text{P}_2\text{O}_5 \), which is the empirical formula for \( \text{P}_4\text{O}_{10} \)).

\( \text{H}_3\text{PO}_4 \) prepared this way is added to soft drinks such as Cola to give it an acidic, sour taste.

**OXYGEN**

It is now time to look back on one of our rules when determining oxidation numbers. Previously, way back in the 1st tutorial, we determined that oxygen always exhibited an oxidation number in a compound of –2, (except when combined with fluorine). We now need to qualify that statement because in some important compounds oxygen can exhibit an oxidation number of –1! These compounds are known as peroxides. You, in fact, met hydrogen peroxide in prac 3.

**Hydrogen Peroxide**

Hydrogen peroxide has the formula \( \text{H}_2\text{O}_2 \). If we allocate hydrogen an oxidation number of +1 then oxygen must have an oxidation number of –1. \( \text{H}_2\text{O}_2 \) has the following structure.

\[
\text{H} \\
\text{O} \quad \text{O} \\
\text{H}
\]

**Question 5.37**

(a) How many lone pairs are present on each oxygen atom?

(b) Would you expect \( \text{H}_2\text{O}_2 \) to be a reducing agent or an oxidizing agent? Explain your answer.

Hydrogen peroxide can be prepared industrially from treatment of \( \text{O}_2 \) with a reducing agent. From organic chemistry we know that alcohols can be oxidized and are thus reducing agents.

\[
\text{(CH}_3\text{)_2CHOH} + \text{O}_2 \rightarrow \text{(CH}_3\text{)_2CO} + \text{H}_2\text{O}_2
\]

isopropyl alcohol

acetone

The main industrial use of \( \text{H}_2\text{O}_2 \) is as a bleaching agent. Bleaching agents act through their ability to oxidise. If \( \text{H}_2\text{O}_2 \) acts as an oxidising agent then it, itself, will be reduced. The products of reduction will depend upon whether we are in acidic or basic media.

\[
\text{Base} \quad \text{H}_2\text{O}_2(\text{aq}) + 2\text{e}^- \rightarrow 2\text{OH}^- (\text{aq})
\]

\[
\text{Acid} \quad \text{H}_2\text{O}_2(\text{aq}) + 2\text{e}^- + 2\text{H}^+ \rightarrow 2\text{H}_2\text{O}(\text{l})
\]

**Question 5.38**

Write balanced reaction equations for the following oxidations using \( \text{H}_2\text{O}_2 \)

(a) \( \text{SO}_3^{2-} \) to \( \text{SO}_4^{2-} \) in acid

(b) \( \text{Mn}^{2+} \) to \( \text{MnO}_2 \) in base
When H₂O₂ acts as a reducing agent it, itself, is oxidised and O₂(g) is always evolved.

**Question 5.39**
(a) Write a balanced equation for the reaction of H₂O₂ with MnO₄⁻ to form Mn²⁺ in acid solution.
(b) Write a balanced equation for the theoretical reaction of H₂O₂ with Fe²⁺ to form Fe³⁺ in a basic solution.

Hydrogen peroxide can therefore act as an oxidising agent or a reducing agent, depending upon the circumstances. Consider the following reaction.

\[2 \text{H}_2\text{O}_2(\text{l}) \rightarrow 2 \text{H}_2\text{O}(\text{l}) + \text{O}_2(\text{g})\]

**Question 5.40**
(a) Is H₂O₂ being reduced or oxidised?
(b) What name is given to this type of reaction?

Understanding this reaction is important as it could save your life! Hydrogen peroxide decomposes spontaneously and, as oxygen gas is produced, this decomposition is explosive! [Always treat hydrogen peroxide with great care. Never open a bottle of hydrogen peroxide which has been sitting around on a shelf for years].

**THE HALOGENS**
The halogens are of course the group 17 elements. They therefore readily form anions. Other important chemistry is their ability to form a range of oxo-anions and oxo-acids.

**The Elements**
The elements occur as diatomic molecules, all of which are oxidising agents.

**Question 5.41**
Would the following reaction go spontaneously to the left or to the right?

\[\text{Cl}_2(\text{g}) + 2 \text{Br}^-(\text{aq}) \rightleftharpoons \text{Br}_2(\text{l}) + 2 \text{Cl}^-(\text{aq})\]

The above equation is in fact how liquid bromine is produced on an industrial scale.

F₂(g) is not often used in chemical reactions in the laboratory as it is such a powerful oxidising agent it has to be handled with extreme care. Cl₂(g), on the other hand, is used extensively as an oxidising agent both in the lab and in industry.

**Question 5.42**
Balance the following reactions and calculate the number of electrons transferred.
(a) \(\text{NH}_3(g) + \text{Cl}_2(g) \rightarrow \text{N}_2(g) + \text{HCl}(g)\)
(b) \(\text{H}_2\text{S}(g) + \text{Cl}_2(g) \rightarrow \text{S}(s) + \text{HCl}(g)\)

Aqueous solutions of iodine are often used by analytical chemists in titrimetry.

Typical reactions involving iodine are shown below.

\[\text{I}_2(\text{aq}) + \text{S}_2\text{O}_3^{2-} \rightarrow 2 \text{I}^- + \text{S}_4\text{O}_6^{2-}\]

Thiosulphate tetrathionate

\[\text{I}_2(\text{aq}) + \text{H}_3\text{AsO}_3(\text{aq}) \rightarrow 2 \text{I}^- + \text{H}_3\text{AsO}_4(\text{aq}) + 2 \text{H}^+\]

Arsenic(III) acid (arsenous acid) arsenic(V) acid
The oxidising ability of Cl\(_2\) is often used in chemical products such as bleaches. However, because Cl\(_2\)(g) is poisonous it is converted into a less toxic material first. An example is the swimming pool bleaching agent HTH. HTH is manufactured by the following reaction.

\[
2 \text{Cl}_2(g) + 2 \text{Ca(OH)}_2(aq) \rightarrow \text{Ca(OCl)}_2(s) + \text{CaCl}_2(s) + 2 \text{H}_2\text{O}(l)
\]

HTH is thus a mixture of Ca(OCl)_2, calcium hypochlorite, and calcium chloride, CaCl_2. (HTH actually stands for High Test Hypochlorite).

The chlorine is now in the form of the hypochlorite ion, OCl\(^-\), which itself is an oxidising agent which can destroy bacteria.

**Halides**

We have already noted that the hydrogen halides, HX, are acidic.

They can be prepared from the direct reaction of the elements thus:

\[
\text{H}_2(g) + \text{X}_2(g) \rightarrow 2 \text{HX}(g)
\]

However if you attempt this reaction with F\(_2\) (g) or Cl\(_2\) (g) get ready to run! Both of these reactions are explosive. Normally in the laboratory we instead take the metal halide and react it with an acid. For example, HF can be prepared by the following reaction.

\[
\text{CaF}_2(s) + 2 \text{H}_2\text{SO}_4(aq,\text{conc}) \rightarrow \text{Ca(HSO}_4)_2(aq) + 2 \text{HF}(g)
\]

HBr and HI cannot be prepared using sulfuric acid as they themselves are oxidised by the H\(_2\)SO\(_4\) used in the preparation to form Br\(_2\) and I\(_2\) respectively.

**Question 5.43**

Write down a balanced reaction for the reaction of HBr with H\(_2\)SO\(_4\) if the products include Br\(_2\) and SO\(_2\).

[Hint: you should recognise this equation!]

HBr and HI are thus prepared from the reaction of a suitable salt with a non-oxidising acid such as H\(_3\)PO\(_4\).

\[
\text{KI}(s) + \triangle \text{H}_3\text{PO}_4(aq) \rightarrow \text{KH}_2\text{PO}_4(aq) + \text{HI}(g)
\]

**Question 5.44**

(a) In your own words explain why H\(_2\)SO\(_4\) does not oxidize HF to F\(_2\).

(b) Explain the trends of the following data

<table>
<thead>
<tr>
<th></th>
<th>Normal boiling point temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>HF</td>
<td>20</td>
</tr>
<tr>
<td>HCl</td>
<td>-85</td>
</tr>
<tr>
<td>HBr</td>
<td>-67</td>
</tr>
<tr>
<td>HI</td>
<td>-35</td>
</tr>
</tbody>
</table>
One acid worth particular mention is perchloric acid. Perchloric acid is the strongest of all the common acids. It is also a powerful oxidising agent (chlorine is in its highest possible oxidation state). Perchlorate, in the form of the ammonium perchlorate salt, is used in the booster rockets of the space shuttle in combination with aluminium powder. The aluminium is the “fuel” and the perchlorate is the “oxidant” and the products are nitrogen, water, hydrochloric acid and aluminium oxide (if you can balance this equation you’ll be able to do redox chemistry for life!). Another important industrial halogen-oxygen species is the chlorate (V) ion, ClO$_3^-$.

It is prepared by treating chlorine with a concentrated alkali in a disproportionation reaction.

$$3 \text{Cl}_2(\text{g}) + 6 \text{OH}^- (\text{aq}) \xrightarrow[\Delta]{\text{ }} \text{ClO}_3^-(\text{aq}) + 5 \text{Cl}^- (\text{aq}) + 3 \text{H}_2\text{O}(\text{l})$$

ClO$_3^-$ is again a powerful oxidant and is used as such in fireworks and safety matches.

**Question 5.45**

Chlorate salts decompose when heated. Two different reactions occur depending upon the conditions.

- (a) $\text{ClO}_3^- \rightarrow \text{ClO}_4^- + \text{Cl}^-$
- (b) $\text{ClO}_3^- \rightarrow \text{Cl}^- + \text{O}_2$  

Balance each of the above reactions.

**Halogen Oxoacids**

Chlorine, bromine and iodine can exhibit a number of different oxidation numbers when combined with oxygen. When the oxygens are also bonded to hydrogen, a whole array of different oxoacids results.

**Question 5.46**

Give the oxidation number of the halogen atom for each example in the table below and give the IUPAC name for each acid.

<table>
<thead>
<tr>
<th>known Examples</th>
<th>oxidation number</th>
<th>IUPAC Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Perhalic acid</td>
<td>HClO$_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HBrO$_4$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HIO$_4$</td>
<td></td>
</tr>
<tr>
<td>Halic acid</td>
<td>HClO$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HBrO$_3$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HIO$_3$</td>
<td></td>
</tr>
<tr>
<td>Halous acid</td>
<td>HClO$_2$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HBrO$_2$</td>
<td></td>
</tr>
<tr>
<td>Hypohalous acid</td>
<td>HFO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HClO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HBrO</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HIO</td>
<td></td>
</tr>
</tbody>
</table>

**Question 5.47**

Draw Lewis dot-cross diagrams for the following species.

(a) HClO$_4$ (b) HIO$_3$ (c) HBrO$_2$ (d) HFO