For the most part, the introduction to this chapter is about why inorganic chemistry tends to be more complicated to understand and learn than organic:

- Number of elements
- Variation of properties (size, $\Delta H$, $D_{HE}$, c) even among similar ones
- Covalency, electrovalency and multiple valencies
- Physical state, molecular aggregation and stability range (temperature) and solubility
- Air and water stability
- Coordination number and respect for the octet rule
- $s$, $p$-$p$, $p$-$d$ and $d$-$d$ bonding possibilities

Much order can be introduced into this potential chaos by relating the properties of the elements to their position in the periodic table (or, as was originally done by Mendeleev et al, arranging the elements into the periodic table according to their properties.

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**Heavier Elements**

There is little chemistry to learn about for many of the transuranium elements especially the newest (104 - 108) because of their extremely short half-lives. In some cases only one or two atoms have been made!

The rest of the chapter is divided into sections A and B which, respectively, describe the pure elements themselves and then the general group trends and non-trends.

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**Part A - The Nature and types of the Elements**

**Monatomic Elements**

Includes all the noble gases and many metal vapours. The noble gases do not form bonds to each other because of their closed valence shell configuration, and the metals have their own kind of bonding which does not work in the gas phase (see below).

**Diatomic Elements**

These are $H_2$, the simplest of all neutral molecules, the halogens which also have single bonds, and $N_2$ and $O_2$ which have multiple $p$-$p$ bonding.

**Discrete (Small) Polyatomic Molecules: $S_n$ and $Se_8$, $P_4$.**

Since $p$-$p$ bonding is not a very useful option for elements below the first short period because of core-core repulsion at useful $p$-bonding distances, P, S and Se can form clusters (or chains - see the next group).
Sulphur, which can form two single bonds to itself, comes in various ring sizes up to $S_{20}$, $S_8$ being the most stable ("orthorhombic" sulphur).

White phosphorus, which can form three, comes as $P_4$ with P-P at 2.21 Å, which is more or less normal. A particularly strained P-P, i.e. "bent" would be longer. Nevertheless, $P_4$ is the most reactive form of phosphorus, for example, spontaneously inflaming in air.

Boron and carbon, capable of forming 3 and 4 bonds, respectively, could have been included here too, but see below.

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**Elements with Extended Structures**

Boron is a somewhat anomalous case because it is electron deficient. The allotropic forms of boron are all based on the icosahedral $B_{12}$ unit. In this unit, each boron has 5 nearest neighbours, and since the units are weakly bonded to form more extended 3-frameworks, the borons that will have more remote neighbours as well. There are nowhere near enough electrons and atomic orbitals to do this using localized 2-electron - 2-centre Lewis type bonds. As usual molecular orbital theory comes to the rescue, but the $B_{12}$ cage alone is a rather complex system to use as an example. The topic of the boranes (boron hydrides), to be covered later, might help shed some light on how the molecular orbitals might be set up. The allotropes of crystalline boron are the most complex of the structures of the elements, and their study has been further complicated by the presence of small (but stoichiometric) amounts of carbon or nitrogen leading to some false ones.

The basic icosahedral $B_{12}$ unit

Depending on the number of bonds that they can form the following elements can form chain, sheet, or three dimensional structures:

- C  P  S
- Si  As  Se
- Ge  Sb  Te
- Sn  Bi

"Plastic" sulphur ($S_n$) has a rubbery texture and is thermally unstable at room temperature with respect to conversion to $S_8$. Selenium also forms chains, but infinite spirals in an ordered (crystalline) structure. Tellurium is similar and the solid has semiconductor properties.
Crystalline black phosphorus has a “double sheet” structure. This structure is shared by its cogeners (members of the same group) but they are metals. Red phosphorus, the other common form, contains chains of phosphorus tetrahedra.

Graphite has 2-dimensional sheets of trigonal sp$^2$ carbon atom arranged in aromatic six membered rings. Because of the extended delocalized orbitals, graphite is a conductor, especially parallel to the sheets.

Diamond is a 3-dimensional lattice of tetrahedral sp$^3$ carbon atoms arranged in saturated six-membered rings all in the chair form. Diamond is an insulator.
A number of additional carbon structures have been discovered quite recently. Buckmeisterfullerene $C_{60}$, the simplest of the "bucky balls" is shown on the right. It was discovered in soot. (Its shape, like an international soccer ball, is an icosahedron with all 10 corners cut off to 1/3 of the way along each edge which generates 10 new pentagonal faces and converts the old triangular ones to hexagons.) There are a number of elongated spheroidal structures and tubes capped by hemispheres known all made by cooling carbon vapour from an arc or plasma discharge. Chemists are still trying to make them do something useful!

Heats of formation for carbon forms are: Graphite, 0; diamond, 2.9; and $C_{60}$, 38.1 kJ mol$^{-1}$.

**Metals**

The structures of many metals are based on hexagonal or cubic close packing (Chapter 4 section 7), or the less efficient body-centered cubic (Fig 8-6). Figure 8-7 shows the distribution of these structures.

Metals are sometimes described as a regular array of cations immersed in a sea of valence electrons which are completely delocalized and free to roam through the entire mass. A simplified theoretical picture of this follows:

In the molecule Li$_2$ the bond results from overlap of the 2s orbitals each of which contains 2 electrons. The diagram below shows several representations of this:
The part of the diagram on the left shows the energy levels at the observed internuclear distance marked with a vertical dotted line on the right hand diagram. A crude representation of the two molecular orbitals is also shown. (The internal spherical nodes that the 2s orbitals possess are omitted.)

The next four diagrams show orbital energies (and orbitals) for hypothetical linear molecules, Li₃, Li₄, Li₅ and Li₆.

Variation of orbital energy with internuclear separation for a hypothetical linear Li₃ molecule.

Variation of orbital energy with internuclear separation for a hypothetical linear Li₄ molecule.
Variation of orbital energy with internuclear separation for a hypothetical linear Li$_5$ molecule.

At the left is the diagram for the hypothetical Li$_5$. The infinite number of Morse curves merge together to give the "band" shown.

Because lithium has the 2s$^1$ valence shell configuration, only half of this band will be filled, and electrons can easily move into the empty orbitals accounting for the metallic conduction observed. The occupied levels/orbitals are shown by the shaded area in the diagram below:
The situation described above is not real. Real crystals are three-dimensional, and in addition to the molecular orbitals formed by the atomic s-orbitals, there will be another set formed by overlap of the atomic p-orbitals. The text figures 8.8 and 8.9 are a more realistic representation.

Cohesive Energies of the Metals

See figure 8-10. Note that the main group metals have relatively low enthalpies of atomization correlating roughly with the number of valence electrons. Maxima occur at the half-filled shell after which antibonding parts of the conduction bands begin to be populated.

Part B - The Chemistry of the Elements in Relation to their Position in the Periodic Table

Hydrogen: 1s\(^1\)

With an intermediate electronegativity and one valence electron, hydrogen might range from H\(^+\) to H\(^-\) in its compounds:

- The proton (radius = 1.5x10\(^{-13}\) cm) cannot exist in condensed states (liquid or solids) because it exerts too powerful a polarizing influence on molecules near to itself. Therefore, it is always complexed, for example as H\(_3\)O\(^+\).
- Covalent compounds are the normal situation.
- When combined with very electropositive elements e.g. Na, K, Ca it behaves as H\(^-\) (hydride ion) and is a very powerful reducing agent.
Helium (1s\(^2\)) and the noble gases (ns\(^2\)np\(^6\))

- The energy necessary to make a valence state is not compensated by bond formation above krypton which forms a few fluorides. The rest of the group have fairly extensive chemistry with fluorine, chlorine and oxygen.

(The first noble gas compound, originally thought to be Xe\(^{2+}\)[PtF\(_6\)]\(^{2-}\) by analogy with [O\(_2\)]\(^{2+}\)[PtF\(_6\)]\(^{2-}\), was made by Bartlett in 1962. Prior to that they had been thought to be inert.)

Elements of the First Short Period (Li - F)

They are poor representatives of their groups. (The second short period elements are much better for this.) The reason is connected to their small size and lack of (empty) d-orbitals which limits their coordination number to 4 in the absence of multicentre bonding.

- To achieve their normal valencies, Be, B and C "use" a valence state where one of the 1s electrons is promoted to the p-subshell.
- "Electron deficient" Li, Be and B compounds are Lewis acids. This involves a change in hybridization. The extent to which the coordination number can be increased is limited by negative charge build-up on the acceptor.
- Li, Be and B also tend to be involved in molecules featuring 3-centre, 2 e\(^-\) bonding as a way to reduce their electron deficiency.
- N, O and (perhaps) F compounds can be Lewis bases because of the available electron pairs on these atoms. The sharing of more than one pair is opposed by positive charge build-up on the donor atom, and sometimes steric factors.
- Li\(^+\) exists in rather few compounds because of its small size. Covalent and multicenter bonding is common e.g. the lithium alkyls.
- Be\(^{2+}\) would be even more polarizing than Li\(^+\) so no compounds containing it exist. Covalency is the norm e.g. BeF\(_2\) and [Be(H\(_2\)O)\(_4\)]\(^{2+}\), which hydrolys extensively to BeOH containing species.
- for Li, Be and B there is a marked similarity to the diagonally related Mg, Al and C. Although the valencies differ, the chemical behaviour such as covalency of halides or coordination chemistry tends to be somewhat similar. For example, there are close parallels between the lithium alkyls and the magnesium alkyls or between beryllium halides and the aluminium halides.
- For B, C and N, there are no (long-lived) compounds in which the elements are cationic. Covalency dominates the chemistry of these elements.
- There are compounds containing anions e.g. C\(_2\)\(^2-\) (acetylide) and N\(^3-\), which is a major product when Mg burns in air.
- The chemistry of O and F is dominated by anion formation and covalency. Remember, O\(^2-\) is too strong a base to exist in water though solid compounds are known. Fluoride, F\(^-\) is only a weak base and so known in solids and aqueous solution.
- C, N and O commonly participate in multiple bonding by the use of p-orbitals. N\(_2\) is a rather unreactive molecule because of the great strength of the triple bond. O\(_2\) is much more reactive, partly because it is a bi-radical. F\(_2\) is very reactive because the filled p-orbitals perpendicular to the bond repel each other.
Covalent Bonds

Covered as part of the previous section.

Elements of the Second Short Period (Na to Ar)

These elements are much more representative of the chemistry of the elements below them in their groups. This specially true for the non-metalic elements:

- The elements of this period and those below it do not tend to use their p-orbitals for p-bonding. Rather the empty d-orbitals are used if p-bonding occurs.

  For example, aside from special sterically encumbered cases, there are few compounds containing Si=Si, P=P or S=S bonds. An example of an exception is (CH₃)₃C-P=P-C(CH₃). pp-pp-bonding is not stable with respect to addition reactions: a kinetic effect.

- Multiple bonding that does occur usually involves a first short period element such as oxygen or nitrogen. Examples include Cl₃PO, SO₂ or ClO₂. Such molecules may contain pp-dp-bonding, and the octet rule is often violated. On the other hand, there is no analogue in silicon chemistry of O=C=O. SiO₂ is a network solid although the Si-O-Si groupings are linear which does hint and p-interactions.

- The d-obital can be invoked to explain valence states where the coordination number exceeds 4 (and the octet is exceeded also.) Examples include PCl₅, SF₆ and IF₇. The possibility of higher coordination numbers lead also to different reactivity, e.g. CCl₄ which is inert to hydrolysis and SiCl₄.

- The metals differ from the first memeber of their group, e.g. sodium does not form covalent compounds, aluminum is a cation-forming metal quite unlike boron, and the coordination numbers are often 6 rather than 4 for these second row elements.

The Remainder of the Non-Transition Elements

This section contains a group-by-group summary of the properties characterizing each group and indicating, again, how the top member of each group differs. The following is list of key properties appropriate for comparisions:

1. Metallic character.
2. Properties of the oxides:
   1. Ionic vs covalent
   2. Acidic vs basic
3. Properties of the halides:
   1. Ionic vs molecular
   2. Ease of hydrolysis
5. Trends in structure:
   1. Coordination numbers for discrete species
   2. Aggregation in the solid state to increase coordination number
7. Tendency to catenate.
8. The relative importance of $pp$ vs $pp$-$dp$ vs $dp$-$dp$ bonding.
9. The general strength of covalent bonding.
10. The relative importance of the lower valent states vs the higher valent states.

---

**Group IA or 1**

See text Table 8.1. The elements have chemistry dominated by the ionic 1+ state. The behaviour going down a group is well-behaved. The following decrease down a group:

1. Melting points and heats of sublimation.
2. Lattice energies (mostly).
3. Effective hydrated radii and hydration energies.
4. Ionization Enthalpies.

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**Group IIA or 2 and IIB or 12**

See text Table 8.2. For group IIA (Mg, Ca, Sr, Ba and Ra) which all form the 2+ ionic state there are again well-behaved trends including those mentioned for group IA and adding:

1. Solubility of the sulphates and carbonates.
2. Thermal instability of the carbonates and nitrates.

which decrease going down the group. Group IIB metals (Zn, Cd and Hg) have two s-electrons outside filled d-subshells. In Zn and Cd the d-electrons do a somewhat poorer screening job than the closed shells of the group IIA so that the 2+ ions (which are more polarizing) are more inclined to form complex ions with $NH_3$, halides and $CN^-$.

Mercuric ion, $Hg^{2+}$, where the f-subshell also has been filled, is quite different in that it is even more inclined to form complexes. The oxidation potential for mercury is positive, whereas the others are all negative, which means that mercury metal is rather easily produced in its reactions. It also readily forms the mercurous ion, $Hg^{2+}$.

---

**Group IIIA or 3 and IIB or 13**

See text Table 8.3. The text includes the group IIIA elements and the rest of the lanthanides among the non-transition metals because of the relative simplicity of their chemistry. They all behave as quite electropositive elements and form the 3+ ion. Scandium behaves as if it falls somewhere between aluminum and gallium in terms of its covalency. The lanthanides are so similar to each another that separation is difficult. (Cation exchange chromatography is used.)

All the group IIB elements form compounds containing the 3+ ion, but there is a marked tendency towards covalency especially for aluminum e.g. its alkyls are volatile liquids and its chloride sublimes.
Group IIIB is the first group to clearly demonstrate the "inert pair effect". On descending the group, there is a tendency for the $1^+$ ions to become more and more stable. $\text{Tl}^{1+}$ is more stable than $\text{Tl}^{3+}$ and its chemistry is complicated by its redox behaviour.

(The unusual stability of $\text{Hg}^0$ could also be ascribed to the inert pair effect.)

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**Group IVB or 14**

See text Table 8.4. This is the group in which the property differences between the first member, carbon, and the rest is perhaps most marked. Knowing the chemistry of carbon is almost useless for predicting the chemistry of the remaining elements! The chemistry of carbon is dominated by its extraordinary ability to catenate. While silicon can form analogues to the hydrocarbons, multiple bonding is not viable, and the Si-O bond is the important bond in silicon chemistry.

The chemistry of the group IVB elements in their IV oxidation state is predominantly covalent: $\text{SiCl}_4$ is a liquid as is $\text{Pb(C}_2\text{H}_5)_4$, the infamous anti-knock gasoline additive.

The covalent bonds generally weaken on descending the group.

The divalent state of carbon (in carbenes) is very reactive and it comes in both singlet and triplet forms. Silicon has virtually no chemistry in this state.

For the rest of the group, the II state becomes successively more stable going down the group. The "inert pair" is usually stereoactive in both molecular and solid state aggregated compounds. The $\text{M(II)}$ compounds can never be considered truly ionic. The trend is probably associated with decreasing covalent bond strengths compared to the energy needed to obtain the valence state because the ionization potential differences are small:

\[
\text{GeCl}_2 + \text{Cl}_2 \rightarrow \text{GeCl}_4 \text{ (Rapid at 25 °C)}
\]

\[
\text{SnCl}_2 + \text{Cl}_2 \rightarrow \text{SnCl}_4 \text{ (Slow at 25 °C)}
\]

\[
\text{PbCl}_2 + \text{Cl}_2 \rightarrow \text{PbCl}_4 \text{ (Does not go except at higher temperature and pressure)}
\]

$\text{PbBr}_4$ and $\text{PbI}_4$ cannot be made.
Group VB or 15

See text Table 8.5. The oxidation states V and III are normal for this group. Phosphorus compounds are all covalent, but the tendency towards ionic behaviour increases down the group especially for the III state, but, the only species that can be considered as predominantly cations are SbO\(^+\) and BiO\(^+\) and Bi\(^{3+}\) in its fluoride.

Group VIB or 16

See text Table 8.6. This group is relatively well-behaved so that its features can be tabulated:

1. The 2- ions exist in salts with electropositive elements.
2. There are also anions containing one covalent bond e.g. RS\(^-\) or HS\(^-\).
3. There are covalent compounds of type (for example) R\(_2\)E or X\(_2\)E (R is organic, X is a halogen and E is the group VIB element).
4. There are monocations of type R\(_3\)E\(^+\)
5. There are anionic oompounds where the group VI element is in the IV or VI state, and with coordination numbers 4, 5 and 6 e.g. SCl\(_4\), SeF\(_5\), TeF\(_6\). There are stereoactive lone pairs to worry about!
6. The hydrides, H\(_2\)E decrease in stability down the group.
7. The elements themselves become gradually more metallic.
8. The tendency to form anionic complexes increases e.g. SeBr\(_6\)\(^{2-}\), TeBr\(_6\)\(^{2-}\) and even PoI\(_6\)\(^{2-}\).

Group VIIB or 17

See text Table 8.7. With the elements of group IA, this group is the most well-behaved. The properties progress nicely down the group:

1. The elements all form th X\(^-\) ion and compounds with one covalent bond e.g. RX or HX.
2. Interhalogens e.g. CIF have properties somewhat intermediate between the parent dihalogens, but they are polar in the expected sense.
3. The higher oxidation states are II, V and VII.
4. There are no simple cationic ions X\(^+\) but Br\(_2\)\(^+\), I\(_2\)\(^+\), Cl\(_3\)\(^+\), Br\(_3\)\(^+\) and several larger iodine cations have been prepared.

The Transition Elements of the d and f-Blocks