Intermediate Inorganic Chemistry
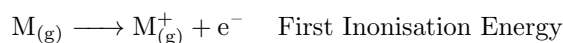
§1 P-BLOCK CHEMISTRY

§1.1 METALLOIDS

§1.2 ELECTRONEGATIVITY

§1.2.1 **Ionisation Energy (IE).** The energy required to remove completely an electrion from the gaseous atom or molecule in its 'ground state'.

$$M_{(g)} \longrightarrow M^+_{(g)} + e^- \quad \text{First Inonisation Energy}$$

$$M^{2+}_{(g)} \longrightarrow M^{3+}_{(g)} + e^- \quad \text{Second Inonisation Energy}$$

This process requries an input of energy (endothermic), so the ionisation energy will be positive.

Concerning the p (and s) blocks the inionisation energy increases from left to right (with some exceptions) and sharply decreases upon a new period. The higher (in number) the period the lower the ionisation energy. The most important factor is the distance between the nucleus and electron. With larger shells (e.g. p) the electrons are further away and so are not pulled on as heavily by the nucleus (lower effective nuclear charge). Notice on the graph where the ionisation energy does not increase across the period.

Values in kJmol⁻¹

H 1312									He 2372
Li 513	Be 899		B 801	C 1086	N 1402	O 1314	F 1681	Ne 2081	
Na 496	Mg 738		Al 578	Si 786	P 1012	S 1000	Cl 1251	Ar 1520	
K 419	Ca 590		Ga 579	Ge 762	As 947	Se 941	Br 1140	Kr 1351	
Rb 403	Sr 549		In 558	Sn 709	Sb 834	Te 869	I 1008	Xe 1170	
Cs 376	Ba 503		Tl 589	Pb 715	Bi 703	Po 812	At 930	Rn 1037	

☞ The ionisation energy of the metalloids are very similar (801–812), the increase in energy of going across the period is counteracted by moving down the table.

On descending groups the most irregular behaviour is seen in group 13. Ga and Ti are *higher* than expected. Ga is preceded by the first set of d orbitals and Ti is preceded by the first set of f orbitals. d and f orbitals provide very weak shielding in comparison to s and p orbitals, so we have a higher effective nuclear charge than expected. Pb breaks the trend down its group, this is because the atom is much larger than the others in its group, and so its electrons are moving much faster, these relativistic effects make it much harder to remove an electron.

The kink from Be to B comes from the Be having a full s shell, so removing an electron from Boron would be favourable to give it a full s-orbital. The kink from N to O comes from Oxygen
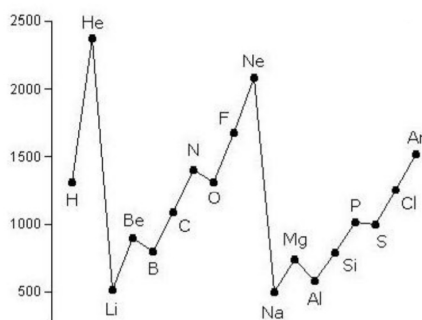
having a paired electron in its p-orbital, so they experience greater *Coulombic repulsion*. The removal of an electron relieves this repulsion.

§1.2.2 **Electron Affinity (EA).** The energy release when a gaseous atom, molecule or ion in its 'ground state' gains an electron.

$$\mathrm{X}_{(g)} + e^- \longrightarrow \mathrm{X}^-_{(g)} \qquad \text{First electron Affinity}$$

Since this process is favourable and energy will be given out (exothermic), this electron affinity will be negative.

Values in kJmol⁻¹							
H 73							He -48
Li 60	Be −18	B 23	C 122	N −7	O 141	F 328	Ne -116
Na 53	Mg −21	Al 44	Si 134	P 72	S 200	Cl 349	Ar -96
K 44	Ca −186	Ga 36	Ge 116	As 77	Se 195	Br 324	Kr -96
Rb 47	Sr −146	In 34	Sn 121	Sb 101	Te 190	I 295	Xe -77
Cs 45	Ba −46	Tl 30	Pb 35	Bi 101	Po 186	At 270	Rn -

☞ A positive value corresponds to energy being given out upon addition of an electron. Negative enthalpy.

It is very unfavourable for Neon to accept an electron and break its full p orbital, and very favourable for Fluorine to accept an electron and fufill its shell. It generally gets smaller as you move down a group due to more shielding. Nitrogen's value is negative because of the energy needed to overcome the electron- electron repulsion that occurs when two electrons occupy the same orbital (think back to IE). The same applies to all of group 15. Group 2 is also lower because it already has a full shell. The values of Group 13 (except for B) are all very similar due to the weak shielding provided by the preceding d and f orbitals. The 2nd period is is smaller than the first becuase of the small size, so it has a higher charge to radius ratio which gives higher repulsion.
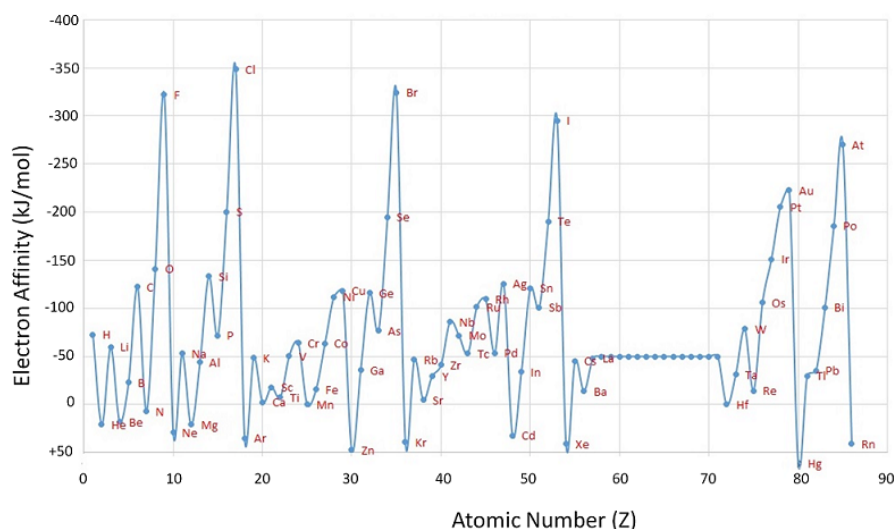
§1.2.3 **Electronegativity.** The ability of an atom to attract electron density towards itself in a molecule.

The calculation of electronegativity using the Pauling scale.

1. A hypothetical molecule XY

2. Compare the measured XY_{measured} bond energy with a theoretical bond energy $XY_{\text{theoretical}}$.

3. $XY_{\text{theoretical}} = \sqrt{XX^2 + YY^2}$

4. Δ Bond energy $= XY_{\text{measured}} - XY_{\text{theoretical}}$

A difference in bond energy implies a difference in electronegativity between the two atoms.

						H 2.20											He -
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne -
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar -
K 0.82	Ca 1.00											Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr -
Rb 0.82	Sr 0.95											In 1.78	Sn 1.96	Sb 2.05	Te 2.10	I 2.66	Xe -
Cs 0.79	Ba 0.89											Tl 2.04	Pb 2.33	Bi 2.02	Po 2.00	At 2.20	Rn -

The electronegativity across the p-block is relatively trendy, increasing across a period and down a group, once again all the metalloids have a similar electronegativity. The jump in periods 4 and 5 from 3 in groups 13 and 14 is from the d and f orbitals which provide weak shielding, giving them a higher effective nuclear charge. Electronegativity varies depending on the hybridisation, sp > sp^2 > sp^3. The van Arkel Ketelaar triangle is valid for simple sp compounds.

§1.2.4 **Summary.**

- Ionisation energies increase left to right and decrease top to bottom

- Electron affinities broadly increase left to right

- Electronegativity increases left to right and decreases top to bottom

Further reading: Inorganic Chemistry (M. Weller, T. Overton et al) (7th edition) sections 1.7 and 2.13
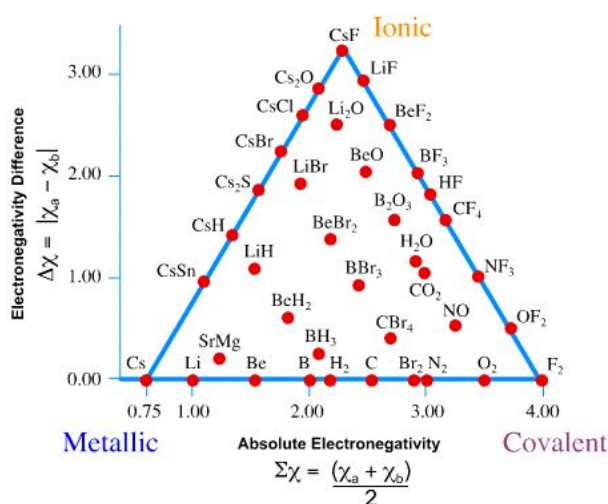
§1.3.1 **Slater's Rules.** There is a trendy decrease moving across each period and a trendy increase moving down each group.

H	Covalent radii in Å. Not all element radii are available.					He
0.30						-
Li	Be	B	C	N	O	F	Ne
1.23	0.89	0.88	0.77	0.70	0.66	0.64	-
Na	Mg	Al	Si	P	S	Cl	Ar
1.54	1.36	1.25	1.17	1.10	1.04	0.99	-
K	Ca	Ga	Ge	As	Se	Br	Kr
2.03	1.74	1.25	1.22	1.21	1.17	1.14	1.10
Rb	Sr	In	Sn	Sb	Te	I	Xe
2.10	1.92	1.50	1.40	1.41	1.37	1.33	1.30
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
2.35	1.98	1.55	1.54	1.52	1.53	-	-

Figure 1: Covalent radius

Slater's rule: the outermost electrons 'feel' a nuclear charge which is less than the actual charge because of shielding effects (s) from other electrons. $Z^* = Z - s$ (Z^* is sometimes called Z_{eff})

We can calculate the shielding constant (s) through simple calculations.

1. Write out the electronic configuration in the following way:

   (1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p) etc.

2. When considering a particular electron in an ns or np orbital:

   Each electron with the same principal quantum number i.e. (ns, np), (nd) contributes 0.35
   Each electron in the (n-1) shell contributes 0.85
   Each electron in the (n-2) or lower shells contribute 1.00

3. When considering a particular electron in an nd or nf orbital:

   Each of the other electrons in the (nd, nf) group contributes 0.35
   Each of the electrons in a lower group than the one being considered contributes 1.00

☞ Do **NOT** include the electron that you are considering when calculating s, it cannot shield the nucleus from itself.

The effective nuclear charge increases across a period and down a group. The values begin to flatten out at the bottom periods, this is because (n-2) contribtues 1.00 to s.

Li	Be	B	C	N	O	F	Ne
1.30	1.95	2.60	3.25	3.90	4.55	5.20	5.85
Na	Mg	Al	Si	P	S	Cl	Ar
2.20	2.85	3.50	4.15	4.80	5.45	6.10	6.75
K	Ca	Ga	Ge	As	Se	Br	Kr
2.20	2.85	5.00	5.65	6.30	6.95	7.60	8.25
Rb	Sr	In	Sn	Sb	Te	I	Xe
2.20	2.85	5.00	5.65	6.30	6.95	7.60	8.25
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
2.20	2.85	5.00	5.65	6.30	6.95	7.60	8.25

Figure 2: Effective nuclear charge

Values in kJmol^{-1}

H							He
1312							2372
Li	Be	B	C	N	O	F	Ne
513	899	801	1086	1402	1314	1681	2081
Na	Mg	Al	Si	P	S	Cl	Ar
496	738	578	786	1012	1000	1251	1520
K	Ca	Ga	Ge	As	Se	Br	Kr
419	590	579	762	947	941	1140	1351
Rb	Sr	In	Sn	Sb	Te	I	Xe
403	549	558	709	834	869	1008	1170
Cs	Ba	Tl	Pb	Bi	Po	At	Rn
376	503	589	715	703	812	930	1037

Figure 3: Ionisation energy

Despite this flattening off the ionisation energy decreases down the groups (except for 13), this is because the radius is also an important factor for determining ionisation energy.
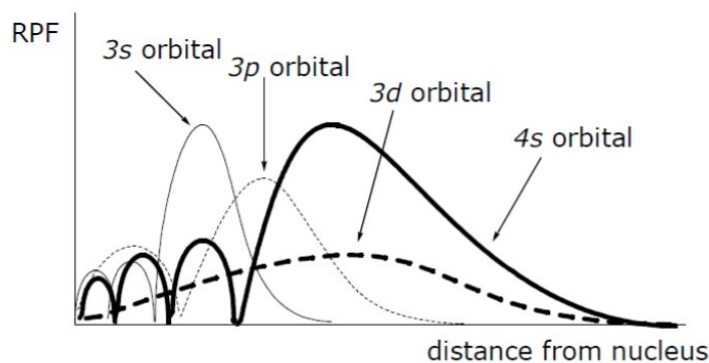
Figure 4: RPF is the probability of finding it there

Slater's rules are very simplistic and can only explain the increase across period in ionisation energy, it cannot explain the reduction in ionisation energy down a group. This is because it does not take into account the penetration of higher principal quantum number electrons. When a 4s electron is closer to the nucleus it will feel more charge.

§1.3.2 **Covalent and Ionic Radii.** A covalent radius is defined as half the length of a symmetrical homonuclear element bond (X-X)

H 0.30	Covalent radii in Å. Not all element radii are available.					He -
Li 1.23	Be 0.89	B 0.88	C 0.77	N 0.70	O 0.66	F 0.64	Ne -
Na 1.54	Mg 1.36	Al 1.25	Si 1.17	P 1.10	S 1.04	Cl 0.99	Ar -
K 2.03	Ca 1.74	Ga 1.25	Ge 1.22	As 1.21	Se 1.17	Br 1.14	Kr 1.10
Rb 2.10	Sr 1.92	In 1.50	Sn 1.40	Sb 1.41	Te 1.37	I 1.33	Xe 1.30
Cs 2.35	Ba 1.98	Tl 1.55	Pb 1.54	Bi 1.52	Po 1.53	At -	Rn -

Figure 5: Covalent radius

☞ Bonds will shorten if ionic character is present, so we must account for electronegativity differences.

Make this itemized. There is a decrease across a period as effective nuclear charge increases, the nuclear charge increases by 1 whilst only decreaseing 0.35 from ony more p-electron. Radii increases down a group as the valence electrons are in the next principal quantum shell so they're further from the nucleus (Slater's rules cannot account for this). Obviously anions are large because of more inter-electron repulsion and cations are smaller because of a less repulsion. Thusly a higher oxidation state means a higher effective nuclear charge. Radii will also vary depending on the coordination number (ligands giving electron density).
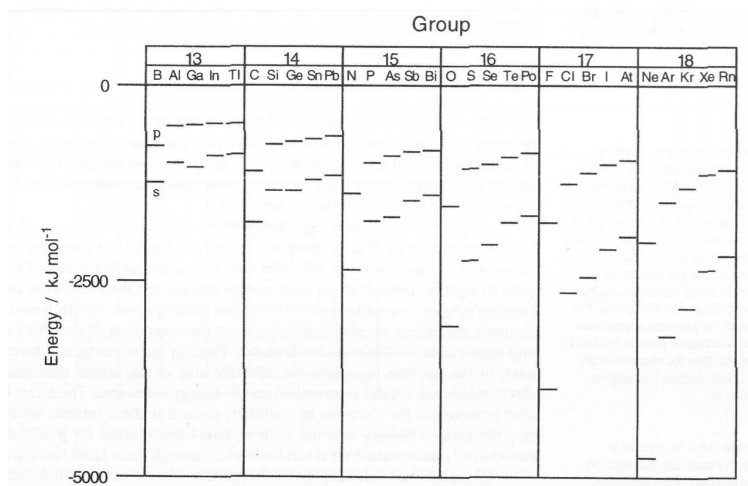
Figure 6: Highest occupied orbital energies

§1.3.3 **s-p energies.** Down a group the s & p orbitals increase (less negative) in energy and the s-p energy separation decreases. The higher principal quantum shell electrons are further away from the nucleus and so the pull is less and the s cannot penetrate as far inside, making s & p closer together and giving a less negative energy for both (it's easier for the electron to leave). Ga and Ge deviate from this trend, once again this is from the 3d orbital preceding them, thus decreasing the energy of the s orbitals as they can penetrate further into the 3d orbital, making the s orbital more evenly distributed. (I don't if this is right, he said something about an s orbital being more evenly distributed? **Check this out later.**) The 4s orbital for As, Se, Br and Kr are lower than expected. This is because of the increased Z^* from their higher proton count having a strong effect on the 4s electrons which allow it to penetrate further into the core.

The distance between s & p increases and the energy decreases as we go across a period. Due to a better Z^* and more penetration for s. This is why the σ and π levels swap around from N_2 to O_2 due to s-p mixing: For Li $\longrightarrow$ N (three or fewer electrons in the p orbitals) the s-p orbitals are close together and so can mix, mathematically the σ_s and σ_p wavefunctions combine (influence each other) with the result that the σ_s orbital becomes more stable and the σ_p becomes less stable, similarly their antibonding orbitals also follow the same trend. This causes the σ_p to switch places with the degenerate(same energy levels) π_p molecular orbitals. (Molecular Orbitals from 1st year).
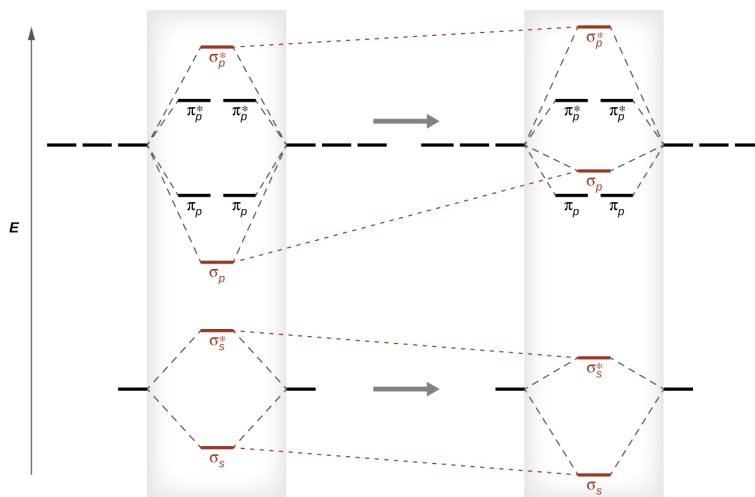
Figure 7: MO shape of Oxygen(left) and Nitrogen(right)
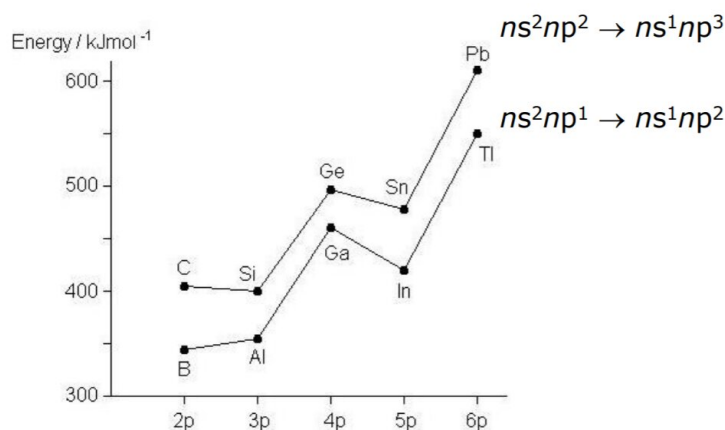
Figure 8: Reorganisation energies of groups 13 and 14

As we go down a group the energy to promote an s electron to a p-orbital increases, with the sharp execption of Ge and Ga, as the 4s orbital is preceded by a 3d row, so the energy of the 4s orbital is lower (more stable). Unexpectedly Ti and Pb have the highest promotion energy, this has substantial implications on hybridisation energies. Remember when an electron moves the others do not stay static, their energies change due to electron correlation.

§1.4   INERT PAIR EFFECT We can see that when we change the electronegativity of the bonded atom (from Oxygen to Fluorine) it changes the boundry of when we have a discrete covalent molecule and when we have a network structure, like in the van Ketelaar triangle. We can see that with the more electronegative Fluoride it favours covalent bonds more.

• OXIDES

B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb*	Bi*	Po	At	Rn

	Discrete covalent molecules
	Covalent network structure
	Ionic with some covalent character

• FLUORIDES

B	C	N	O	F	Ne
Al	Si	P	S	Cl	Ar
Ga	Ge	As	Se	Br	Kr
In	Sn	Sb	Te	I	Xe
Tl	Pb*	Bi*	Po	At	Rn

	Discrete covalent molecules
	Covalent network structure
	Ionic with some covalent character

*	Pb(II)	Bi(III)

☞   Covalent network structures are like diamonds.

These trends are governed by electronegativity differences, Indium has a much lower negativity than Xenon, and so has less oxidation states. This is generally more trendy higher up on the periodic table, whereas elements in the lower periods may perfer lower oxidation states.

• OXIDES

• HALIDES

B	C	N	O	F	Ne
+3	+2 +4	+1 +2 +3 +4 +5		-1	
+3	+4	+1 +2 +3	+2 +1 -2	-1	
Al	**Si**	**P**	**S**	**Cl**	**Ar**
+3	+4	+3 +5	+4 +6	+1 +4 +6 +7	
+3	+4	+3 +5	+1 +4 +6	+1 +3 +5	
Ga	**Ge**	**As**	**Se**	**Br**	**Kr**
+3	+2 +4	+3 +5	+4 +6	+4	
+1 +3	+2 +4	+3 +5	+4 +6	+1 +3 +5	+2
In	**Sn**	**Sb**	**Te**	**I**	**Xe**
+3	+2 +4	+3	+4 +6	+5	+6 +8
+1 +3	+2 +4	+3 +5	+4 +6	+1 +3 +5 +7	+2 +4 +6
Tl	**Pb**	**Bi**	**Po**	**At**	**Rn**
+3	+2 +4	+3	+4		
+1 +3	+2 +4	+3 +5			

The inert pair effet is the tendency of electrons in the outermost s orbital to remain unionised or unshared in the compounds of group 13-16 elements.

The most common oxidation state for group 13 is +3, however +1 is common for Tl (at the bottom of group 13). The stability for group 13 is Al < Ga < In < Ti going down the group. Why is this? No one knows. We can guess and say that the relativistic effects are stabilising the 6s orbital of Tl. More importantly the strength of the covalent bonds also decrease down a group due to poor orbital overlap. This resulsts in the bond enthalpy not offsetting the rehybridisation energy cost. (i.e. it costs more energy to form an sp3 orbital for Pb than would be in the Pb-C bond and so is not energetically favourable.)

Look at the figure below, as you can see with two small atoms the overlap of their s orbitals is very effective, both have large amounts of electron density overlapped. However with the small-big case, the big one has a very tiny amount of electron density in the small region, so the overlap is poor.
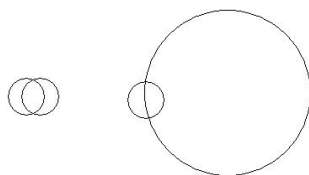
Figure 9: overlap of atoms helps to determine bond strength

In Bi the 1s electron reaches 60% c, thus m = 1.26 (relativistic effects), so the 1s orbital contracts by 20% thus lowering its energy. This is called direct relativistic orbital contraction.

The s orbitals penetrate most and so are more stabilised (less available for bonding). p orbitals contract much less due to poorer penertration and so are more available for bonding.

d and f orbitals experience indirect relativist orbital expansion (destabilised). Their poor penertration and the contraction of the s and p electrons leaves them more shielded and less affectedby Z*.

§1.5 MULTIPLE BONDING Generally as we go down the groups the bonds become weaker, the orbitals are more diffuse and the bonds are longer.

In the first row the $2p_\pi$ orbitals are use in multiple bonding, they have a good overlap due to a short bond length, despite having a smaller covalent overlap. In the second row and beyond the larger covalent radius is cancelled out by the much larger bond length, so there is no common multiple bonding.
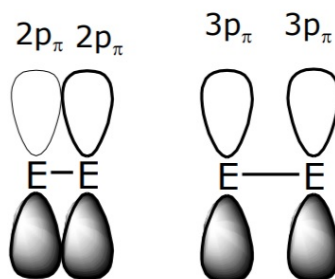
C=O	C-O	$\Delta\pi$
715	335	380 kJ mol^{-1}
S=O	Si-O	$\Delta\pi$
590	420	170 kJ mol^{-1}

So we can see that Si which is down a period from C has half of the stabilisation energy from a double bond. Thus the single bonded Silicone Oxide is more stable, unlike Carbon, where the p_π-p_π overlap stabilises the bond.

O=C=O   2 x 715 = 1430   ~   O-C-O   4 x 335 = 1340   σ + π stable

O-Si-O   4 x 420 = 1680   >>   O=Si=O 2 x 590 = 1180   σ more stable
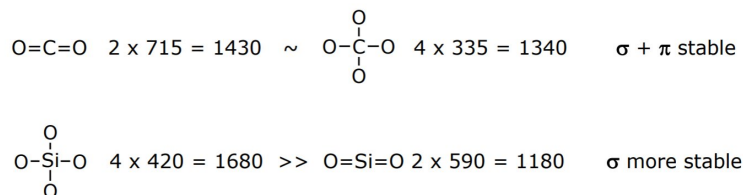
§1.5.1 **p_π-d_π overlap.** A filled p-orbital can donate to a vacant d-orbital that is pointing in its directions. More dispersed so can reach over the longer bond, this is called d-p π back bonding or p_π-d_π bonding (very confusing, I know). One example of this is the P=O beond, the O back bonds to the vacant d-orbital on the P atom, giving a double bond from the π bond formed.

d-p π-bond

| | empty t_{2g} | filled O 2p | |
(a)

(b)
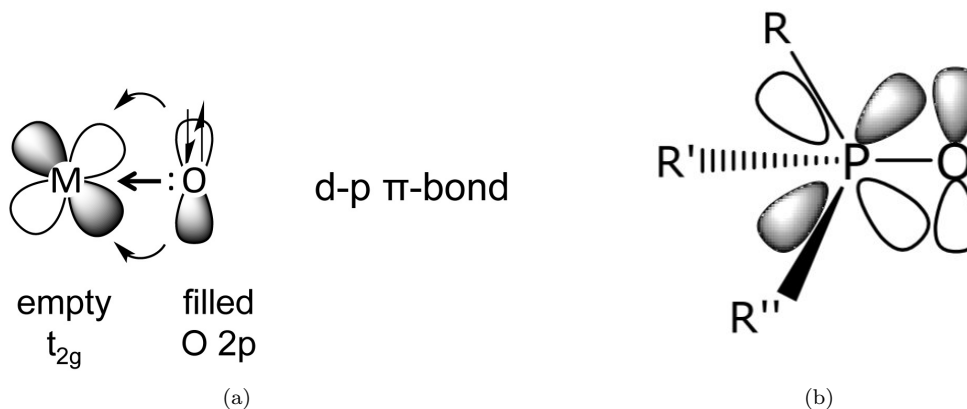
	CCl_4	$SiCl_4$	$GeCl_4$	$SnCl_4$	$PbCl_4$
$\Delta H^\circ{}_f$ kJmol^{-1}	-107	-628	-510	-493	-284
M-Cl kJmol^{-1}	326	402	339	314	—

$\Delta H^\circ{}_f$ of Si is greater than C because of the ionic contribution to the Si-Cl bond (Si is less electronegative). Then as the orbitals become bigger and overlap becomes poorer $\Delta H^\circ{}_f$ falls, as does the M-Cl bond energy.

CCl_2 and $SiCl_2$ do not exist, because it is more energetically favourable to hybridise and form their trichlorides instead. But $GeCl_2$ does exist, due to the 3d shielding effect on the 4s which allows it to bond like that, $GeCl_4$ also exists. $PbCl_2$ is more stable than $PbCl_4$ because of relativistic effects and the inert pair effect.

§1.6 THE TRIELS

Consisting of Group 13. They have the general config of ns^{2}np^1. So their chemistry is dominated by electron deficiency, they have fewer valence electrons than the number of vaence orbitals (two completely empty p orbitals). They form Lewis acids.

EX_3 e.g. BF_3 has 6 valence electrons, so it accepts an electron from a Lewis base. $AlCl_3$ is useful for Fieldel Crafts reactions, it actually forms a dimer as the lone pair of electrons on the Cl forms a dative bond with the other aluminium atom. However in reality the bonds are delocalised around the ring.

(a)
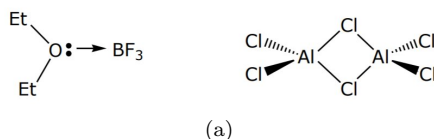
- EX has 4 valence electrons is most stable for Tl (but not when X = H).

- Boron clusters also form EX, (X = H, Cl)

- For AlX and GaX they diproportionate: $3\,MX \longrightarrow 2\,M + MX_3$

- The +1 oxidation state becoems more stable as the group descends.

This descending trend is because of the inert pair effect, the tendency of electrons in the outmermost s orbital to remain unionised or unshared in compounds of group 13-16.

§1.6.1 **Boron Chemistry.** BX_3 exists for all Halogens. BF_3 can participate in π bonding. The B-F bond is very short so there is some overlap between the vacant p-orbital in Boron and the spare electron pair in Fluoride, so there is some π bonding characterists in BF_3. Although the bond is not strong because of the large electronegativity difference, it still has influence on the properties of BF_3
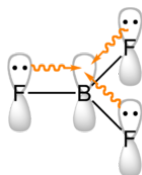
Lewis acid strength: $BI_3 > BBr_3 > BCl_3 > BF_3$. This is due to longer bonds, and so the overlap between the p-orbitals is lesser. Thus the vacant Boron p-orbital can better accept a lone pair of electrons.

We know that the non-Fluoride halides for the other triels dimerise e.g. $AlCl_3$ to Al_2Cl_6. This is due to a poor overlap of Cl and Al due to the large orbitals, so dimerisation is preferable to π bonding.

BX_3 undergo exchange reactions.
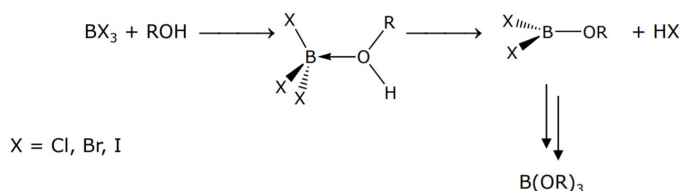
This does not happen to BF_3 because the B-F bonds are too strong, instead it acts as a catalyst. Low acidity but high stability.

If we compare the stability of the acid-base(**L**) complex for of Al, Ga, In we see:

$MF_3\textbf{L} > MCl_3\textbf{L} > MBr_3\textbf{L} > MI_3\textbf{L}$. This is the opposite for B. This is becaue of the longer bonds and so no π back bonding. MF_3 is a stronger lewis acid as fluride is very electrowidthdrawing and so that makes the vacant p-orbital on the triel more electronegative making it easier to accept a pair of electrions.
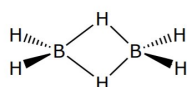

Boron Hydries (Boranes), BH_3 cannot π bond with H as it has no lone pairs, so it forms an electron deficient dimer. Valence bond theory cannot account for this structure as there are not enough valence electrons.

The B sp^3 hybridises but with an empty electron instead. There is then overlap between the empty sp^3 B orbital, a filled sp^3 orbital and the 1s electron, this forms a banana bond

The different colours represent the different *phases* of the electrons. They all need to be of the same phase to form a bond together. They need to have the same *symmetry*. You need to go over MO again, idiot.

Hydries become less stables as the group descends, Gallane was only discovered in 1989. In_3 and Tl_3 are too unstable to exist unless they are coordinated with a Lewis base.
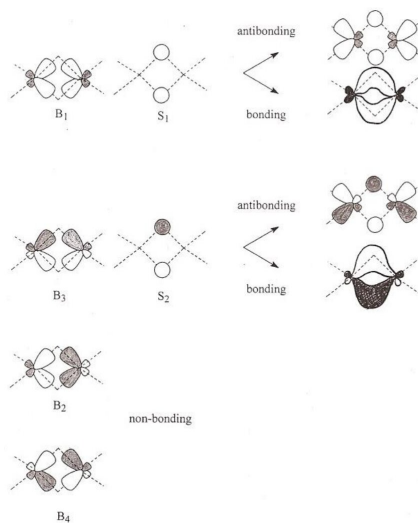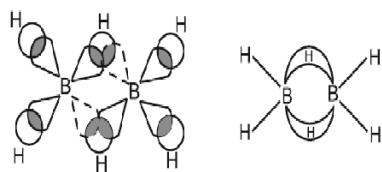
Aluminum compounds are more stable when substituted with alkyls e.g. AlR_2H, they form stable dimers.

Aluminum hyrides and borohydrides are very good at reducing.

Rules to predict the structure of Boron hydrides (B_nH_m or anions of that $B_nH_m{}^{x-}$) by counting the number of electron pairs for cluster bonding.

1. Each B-H unit donates two electrons (one pair) to cluster bonding.

2. Any additional hydrogen atoms i.e. not bonded to Boron, donates one electron to cluster bonding.

3. Add the overall charge of the molecule e.g. 2 extra electrons for a 2^- charge

4. Add up the total number of electrons, should be even, so there are 2n in total, meaning n pairs of electrons involved in cluster bonding.

5. If we have n pairs then the structure is based around a polyhedron with n-1 vertices. e.g. 7 pairs means a 6 vertexed polyhedron which is an octahedron.

6. Count the number of B-H units.

   - If B-H = number of vertices (n-1) then place one B-H unit at each vertex, this structure is described as **CLOSO**, CLOSED, there is no open face.

   - If B-H is one fewer than the number of vertices, B-H - 1 = n-1, then places B-H units at all but one of the vertices, this structure is described as **NIDO**, NEST.

   - If the number of B-H units is two fewer than the number of vertices, B-H - 2 = n-1, then fill all but two of the vertices (these two vertices must be adjacent), the structue is described as **ARACHNO**, COBWEB.

7. Place any remaning hydrogens as bridging Hs around the open face. If there are any left then place them on the electron deficient boron atoms around the open face, they are the ones that have 'lost' the most bonds from the original **CLOSO** structure.
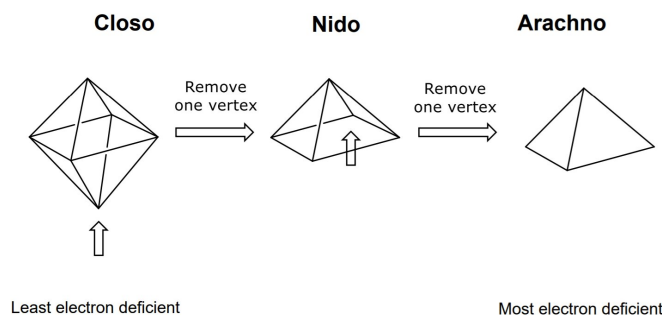

Learn from an example. $B_6H_6{}^{2-}$

- $B_6H_6{}^{2-} = (BH)_6{}^{2-}$ = six B-H units, six pairs of electrons

- Number of electrons available for cluster bonding = 14 = 6*2 (from B-H units) + 2 (from the 2 minus charge)

- 14 electrons in total so n = 7 pairs.

- n-1 = 6, meaning 6 vertices which gives us an octahedron.

- Count the number of B-H units, six, this is the same as n-1, which means we have a **CLOSO** structure, and one B-H fragment at each vertex.

- We have no extra hydrogens so the structure is complete.
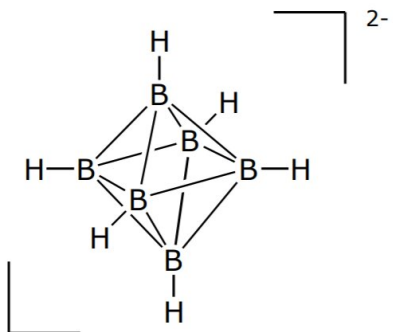
A second example. B_4H_{10}

- $B_4H_{10} = (BH)_4H_6 =$ four B-H units and six hydrogens.

- Number of electrons available for cluster bonding $= 14 = 4*2 + 6$.

- 14 electrons in total so n $= 7$

- n-1 $= 6$, 6 vertices so we have an octahedron

- 4 B-H units, two less than the number of vertices (n-1), so we have an **ARACHNO** structure. Do not fill two adjacent vertices with B-H fragments.

- We have 6 extra electrons, four of these will be bridging hydrogens around the open face, in the positions of symmetry for that structure, bridge each boron with a hydrogen.

- The two that are left will go to the most electron deficient boron atoms, which at the ends of the structure, they have 'lost' two bonds (from the **CLOSO** structure), and so hydrogens are placed there.
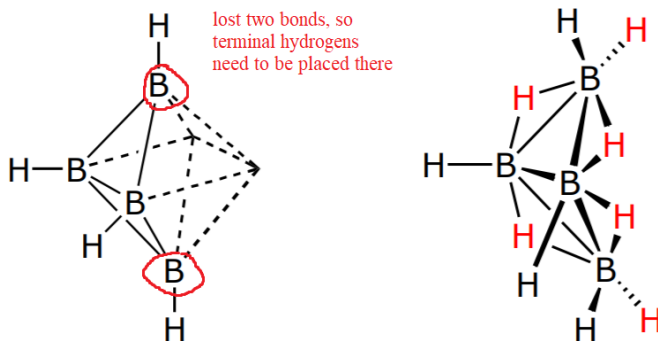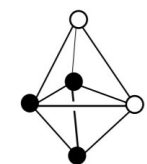
§1.7.1 **Carboranes.** Wade's rules also apply to carboranes, molecules where one or more of the Boron atoms have been replaces with a Carbon atom. The B-H and C-H$^+$ fragments are said to be isolobal, meaning:

- They have the same number of electrons - isoelectronic.

- Their frontier orbitals (the HOMO and LUMO orbitals) have the same symmetries

- Their frontier orbitals are of similar energy

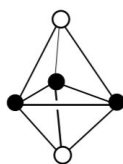- Their frontier orbitals are of the same shape

This means that the B-H and C-H units are interchangable in clusters and so we can use Wade's rules for them too.
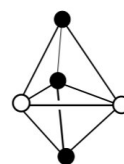
Example $C_2B_3H_5$

- $C_2B_3H_5 = (CH)_2(BH)_3 = (CH^+)_2(BH)_3$ $^{2-}$ Since the C-H$^+$ is positive we need a 2^- charge to be ditributed across the rest of the B-H units.

- Number of electrons, 6 (BH) + 4 (CH) + 2(BH negative charge) = 12 = 6 pairs, so n = 6

- n-1 = 5, 5 vertices so we have a trigonal bipyramid.

- CH + BH = 5 = n-1 so we have **CLOSO**

- However we have 3 different ways of arranging our CH units.

- The most stable form is having the two CH units be as far apart as possible, since they have CH$^+$ units they will repell, so distance is stability.

- This means the most stable is the 1,5- structure

$1,2\text{-}C_2B_3H_5$ $\qquad$ $1,5\text{-}C_2B_3H_5$ $\qquad$ $2,3\text{-}C_2B_3H_5$