

Intermediate Inorganic Chemistry

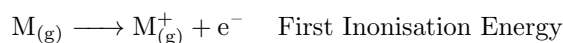
§1 P-BLOCK CHEMISTRY

§1.1 METALLOIDS

§1.2 ELECTRONEGATIVITY

28/10/20 — WEEK 1

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



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

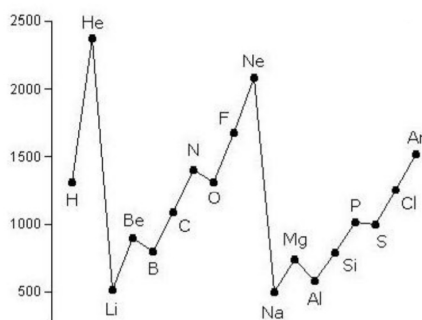
Concerning the p (and s) blocks the ionisation energy increases from left to right (with some exceptions) and sharply decreases upon a new period. The higher (in number) the period the lower the ionisation energy. The most important factor is the distance between the nucleus and electron. With larger 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.

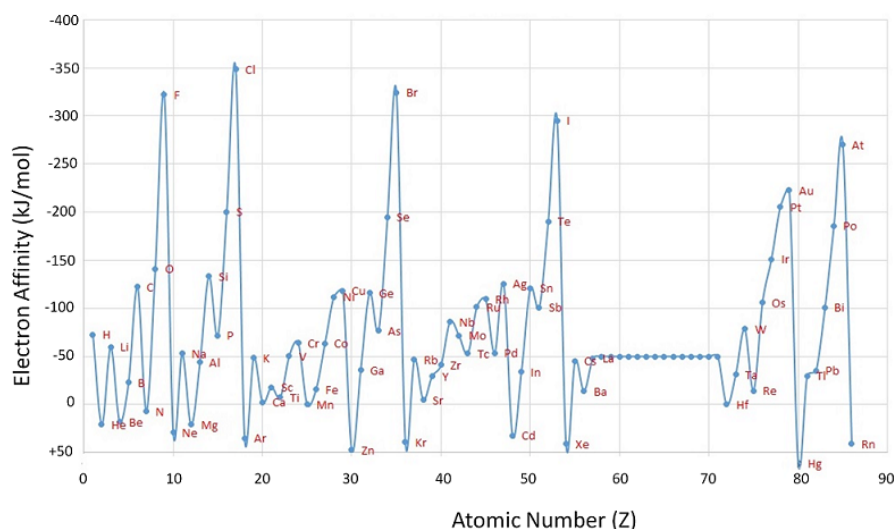


Since this process is favourable and energy will be given out (exothermic), this electron affinity will be negative.

| | | 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 fulfill 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 smaller than the first because 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. $\Delta \text{Bond energy} = XY_{\text{measured}} - XY_{\text{theoretical}}$

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

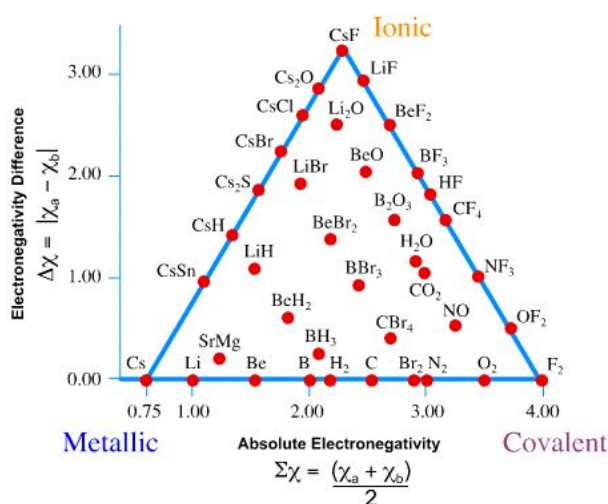
| | | | | | | | |
|------------|------------|------------|------------|------------|------------|-------------------|---------|
| | | H 2.20 | | | | | He - |
| Li 0.98 | Be 1.57 | B 2.04 | C 2.55 | N 3.04 | O 3.44 | F 3.98 | Ne - |
| Na 0.93 | Mg 1.31 | Al 1.61 | Si 1.90 | P 2.19 | S 2.58 | Cl 3.16 | 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 EFFECTIVE NUCLEAR CHARGE

28/10/20 — WEEK 1

§1.3.1 Slater's Rules. There is a trendy decrease moving across each period and a trendy increase moving down each group.

| | | | | | | | |
|------------|------------|---|------------|------------|------------|------------|------------|
| 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 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.

- Write out the electronic configuration in the following way:
(1s), (2s, 2p), (3s, 3p), (3d), (4s, 4p), (4d), (4f), (5s, 5p) etc.
- 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
- 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) contributes 1.00 to s .

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

Figure 2: Effective nuclear charge

| | | Values in kJmol ⁻¹ | | | | | | | |
|-----------|-----------|-------------------------------|-----------|-----------|-----------|------------|------------|------------|--|
| H 1312 | | B 801 | C 1086 | N 1402 | O 1314 | F 1681 | Ne 2081 | He 2372 | |
| Li 513 | Be 899 | Al 578 | Si 786 | P 1012 | S 1000 | Cl 1251 | Ar 1520 | | |
| Na 496 | Mg 738 | Ga 579 | Ge 762 | As 947 | Se 941 | Br 1140 | Kr 1351 | | |
| K 419 | Ca 590 | In 558 | Sn 709 | Sb 834 | Te 869 | I 1008 | Xe 1170 | | |
| Rb 403 | Sr 549 | Tl 589 | Pb 715 | Bi 703 | Po 812 | At 930 | Rn 1037 | | |
| Cs 376 | Ba 503 | | | | | | | | |

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.

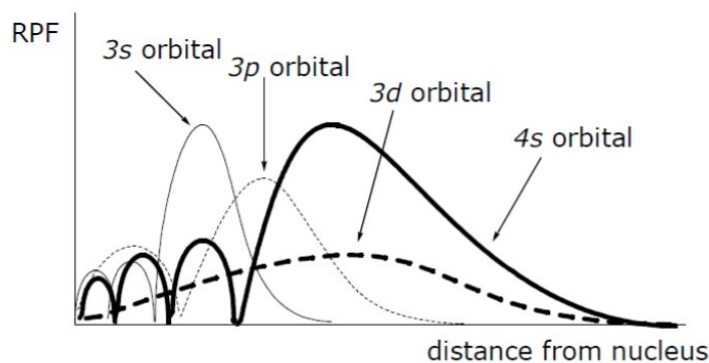


Figure 4: RPF is the probability of finding it there

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 decreasing 0.35 from one 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).

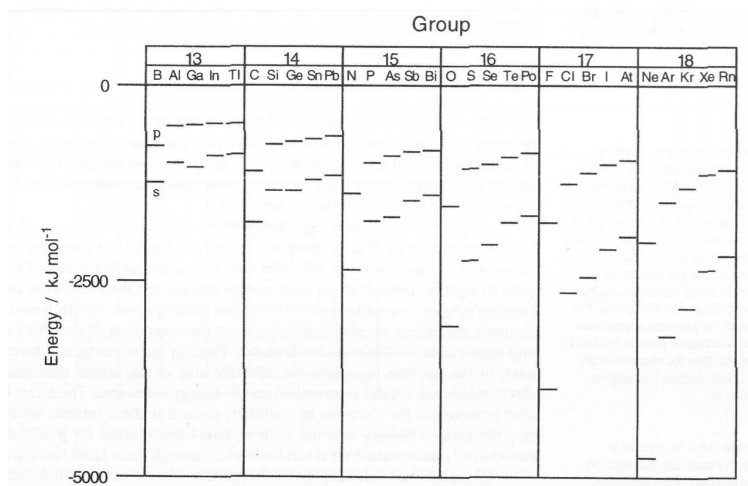


Figure 6: Highest occupied orbital energies

§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 \rightarrow 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).

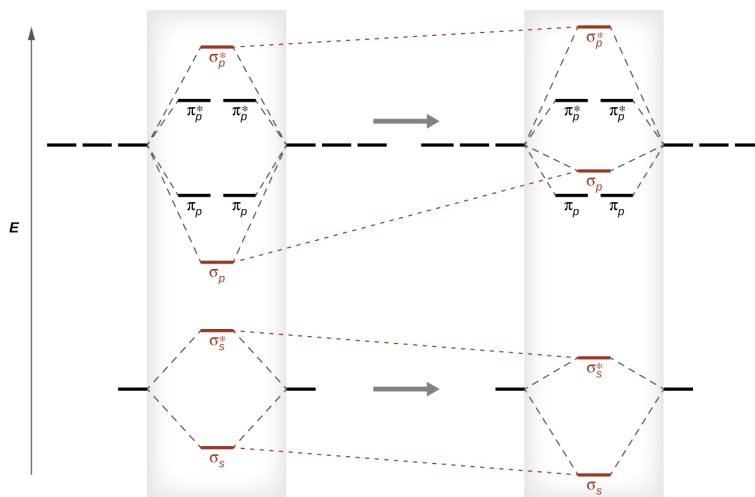


Figure 7: MO shape of Oxygen(left) and Nitrogen(right)

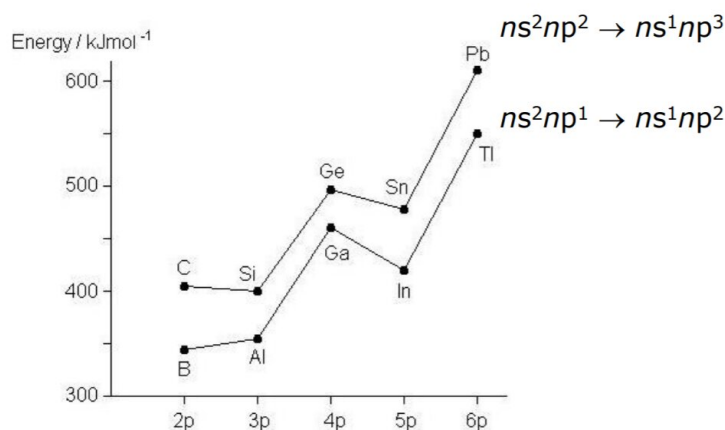


Figure 8: Reorganisation energies of groups 13 and 14

As we go down a group the energy to promote an s electron to a p-orbital increases, with the sharp exception 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 boundary 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 | | | | | | • FLUORIDES | | | | | |
|------------------------------------|-----|-----|----|----|----|------------------------------------|-----|-----|----|----|----|
| B | C | N | O | F | Ne | B | C | N | O | F | Ne |
| Al | Si | P | S | Cl | Ar | Al | Si | P | S | Cl | Ar |
| Ga | Ge | As | Se | Br | Kr | Ga | Ge | As | Se | Br | Kr |
| In | Sn | Sb | Te | I | Xe | In | Sn | Sb | Te | I | Xe |
| Tl | Pb* | Bi* | Po | At | Rn | Tl | Pb* | Bi* | Po | At | Rn |
| Discrete covalent molecules | | | | | | Discrete covalent molecules | | | | | |
| Covalent network structure | | | | | | Covalent network structure | | | | | |
| Ionic with some covalent character | | | | | | 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 prefer lower oxidation states.

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

The inert pair effect 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 $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$ 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 results in the bond enthalpy not offsetting the rehybridisation energy cost. (i.e. it costs more energy to form an sp^3 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.

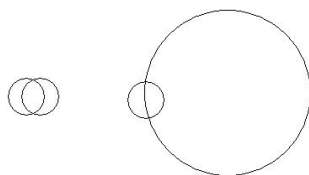


Figure 9: overlap of atoms helps to determine bond strength

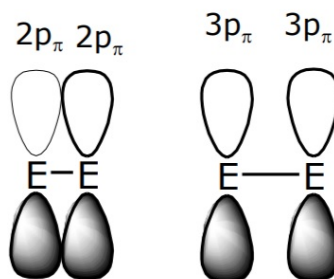
In Bi the 1s electron reaches 60% c, thus $m = 1.26$ (relativistic effects), so the 1s orbital contracts by 20% thus lowering its energy. This is called direct relativistic orbital contraction.

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

d and f orbitals experience indirect relativistic orbital expansion (destabilised). Their poor penetration and the contraction of the s and p electrons leaves them more shielded and less affected by Z^* .

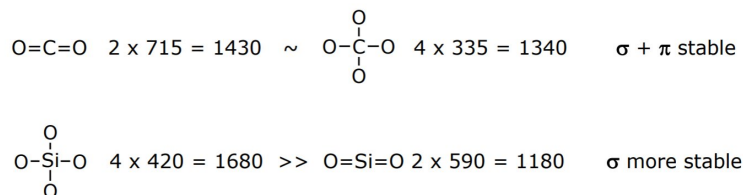
§1.5 MULTIPLE BONDING Generally as we go down the groups the bonds become weaker, the orbitals are more diffuse and the bonds are longer.

In the first row the $2p_\pi$ orbitals are used 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.

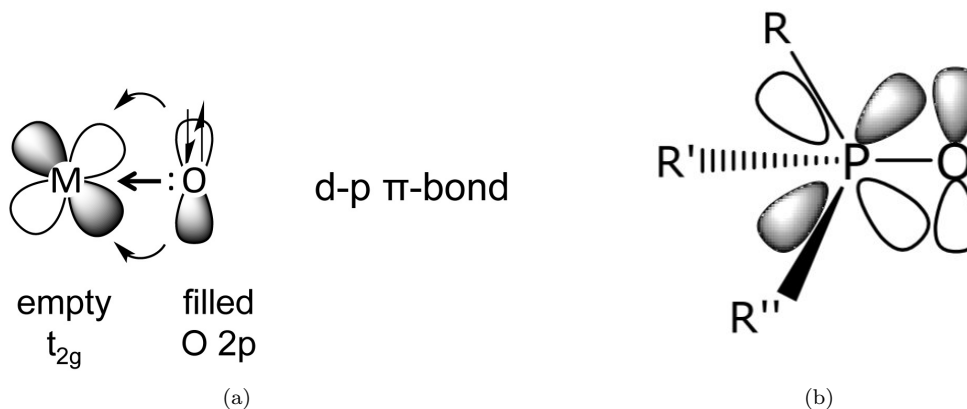


| | | |
|-----|------|--------------------------|
| C=O | C-O | $\Delta\pi$ |
| 715 | 335 | 380 kJ mol ⁻¹ |
| S=O | Si-O | $\Delta\pi$ |
| 590 | 420 | 170 kJ mol ⁻¹ |

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.



§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 bond, the O back bonds to the vacant d-orbital on the P atom, giving a double bond from the π bond formed.



| | CCl ₄ | SiCl ₄ | GeCl ₄ | SnCl ₄ | PbCl ₄ |
|--|------------------|-------------------|-------------------|-------------------|-------------------|
| ΔH°_f kJmol ⁻¹ | -107 | -628 | -510 | -493 | -284 |
| M-Cl kJmol ⁻¹ | 326 | 402 | 339 | 314 | — |

ΔH°_f of Si is greater than C because of the ionic contribution to the Si-Cl bond (Si is less elec-

tronegative). Then as the orbitals become bigger and overlap becomes poorer ΔH°_f falls, as does the M-Cl bond energy.

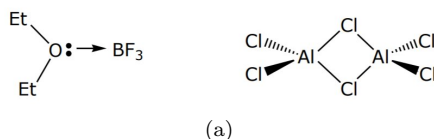
CCl₂ and SiCl₂ do not exist, because it is more energetically favourable to hybridise and form their trichlorides instead. But GeCl₂ does exist, due to the 3d shielding effect on the 4s which allows it to bond like that, GeCl₄ also exists. PbCl₂ is more stable than PbCl₄ because of relativistic effects and the inert pair effect.

§1.6 THE TRIELS

WEEK 3

Consisting of Group 13. They have the general config of ns²np¹. So their chemistry is dominated by electron deficiency, they have fewer valence electrons than the number of valence orbitals (two completely empty p orbitals). They form Lewis acids.

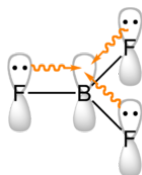
EX₃ e.g. BF₃ has 6 valence electrons, so it accepts an electron from a Lewis base. AlCl₃ is useful for Friedel Crafts reactions, it actually forms a dimer as the lone pair of electrons on the Cl forms a dative bond with the other aluminium atom. However in reality the bonds are delocalised around the ring.



- 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 disproportionate: $3MX \longrightarrow 2M + MX_3$
- The +1 oxidation state becomes more stable as the group descends.

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

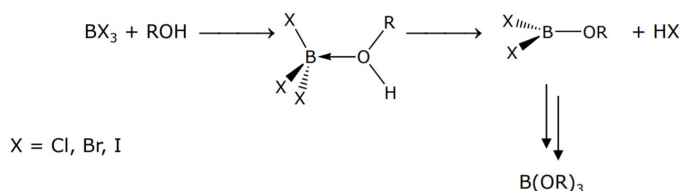
§1.6.1 Boron Chemistry. BX_3 exists for all Halogens. BF_3 can participate in π bonding. The B-F bond is very short so there is some overlap between the vacant p-orbital in Boron and the spare electron pair in Fluoride, so there is some π bonding character in BF_3 . Although the bond is not strong because of the large electronegativity difference, it still has influence on the properties of BF_3 .



Lewis acid strength: $\text{BI}_3 > \text{BBr}_3 > \text{BCl}_3 > \text{BF}_3$. 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.

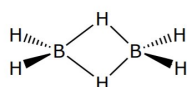
BX_3 undergo exchange reactions.



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:

$\text{MF}_3\text{L} > \text{MCl}_3\text{L} > \text{MBr}_3\text{L} > \text{MI}_3\text{L}$. This is the opposite for B. This is because of the longer bonds and so no π back bonding. MF_3 is a stronger Lewis acid as fluoride is very electronegative and so that makes the vacant p-orbital on the triel more electronegative making it easier to accept a pair of electrons.



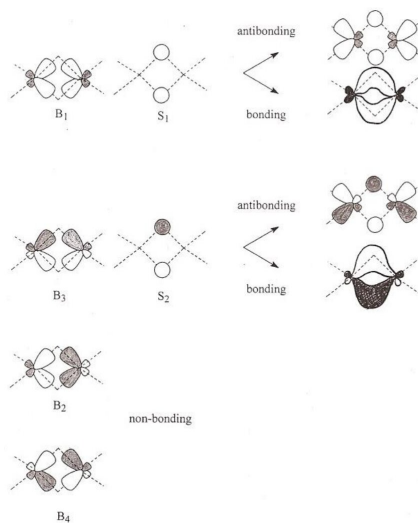
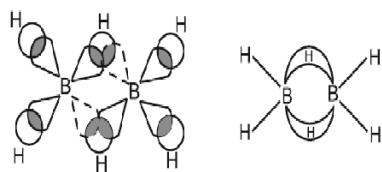
| | |
|-------|---------------------------|
| B-H | 2 centre-2 electron bonds |
| B-H-B | 3 centre-2 electron bonds |

Boron Hydrides (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 orbital 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.

Hydrides become less stable 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 hydrides and borohydrides are very good at reducing.

§1.7 WADE'S RULES

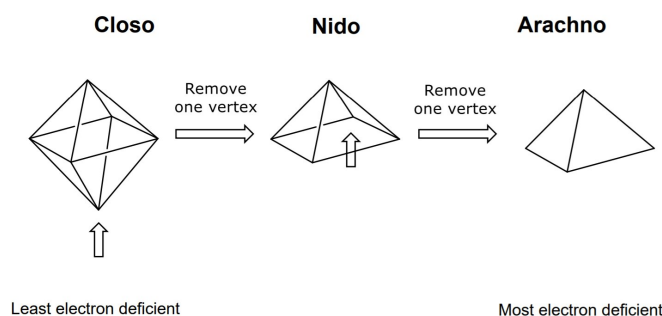
WEEK 3

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 structure 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.

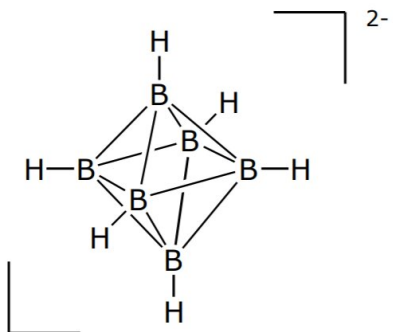
Wade's Rules can also apply for different atoms by treating them as BH groups

| | |
|---------------|-----------------|
| C, Si, Ge, Sn | BH |
| N, P, As | BH ₂ |
| S, Se | BH ₃ |



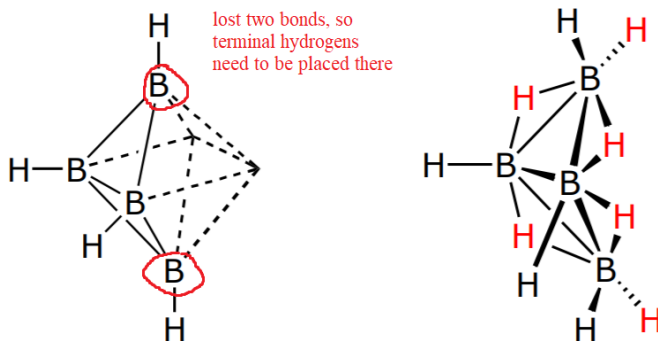
Learn from an example. $B_6H_6^{2-}$

- $B_6H_6^{2-} = (BH)_6^{2-}$ = six B-H units, six pairs of electrons
- Number of electrons available for cluster bonding = $14 = 6 \times 2$ (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 = $14 = 4 \times 2 + 6$.
- 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.



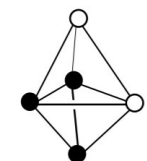
§1.7.1 **Carboranes.** Wade's rules also apply to carboranes, molecules where one or more of the Boron atoms have been replaced with a Carbon atom. The B-H and C-H⁺ fragments are said to be isolobal, meaning:

- 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

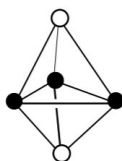
This means that the B-H and C-H units are interchangeable in clusters and so we can use Wade's rules for them too.

Example C₂B₃H₅

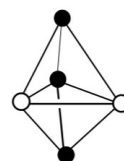
- C₂B₃H₅ = (CH)₂(BH)₃ = (CH⁺)₂(BH)₃²⁻ Since the C-H⁺ is positive we need a 2⁻ charge to be distributed across the rest of the B-H units.
- Number of electrons, 6 (BH) + 4 (CH) + 2(BH negative charge) = 12 = 6 pairs, so n = 6
- n-1 = 5, 5 vertices so we have a trigonal bipyramid.
- CH + BH = 5 = n-1 so 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 repel, so distance is stability.
- This means the most stable is the 1,5- structure



1,2-C₂B₃H₅



1,5-C₂B₃H₅



2,3-C₂B₃H₅

§1.8 THE TETRELS

WEEK 4

Group 14 elements, Carbon, Silicon, Germanium, Tin and Lead.

- Melting point lessens down the period
- Density greatens down the period
- Atomic radius greatens down the period
- Ionisation energy obviously lessens down the period
- Most common oxidation state is +4 except for Lead where it's +2
- Electronegativity lessens down the period
- Oxides formed are normally MO₂ except for Lead which is most commonly PbO and Carbon which can take both
- Carbon and silicone oxides are acidic (as expected from smaller more localised bonds) whilst the other oxides are amphoteric
- As expected when reacted with a Halogen you get MX₄ except for Lead which is MX₂

§1.8.1 **Hydrides.** MH_4 is only formed up until Tin. We can see that the bond lengths get much larger down the period

| | |
|------|--------|
| C-H | 1.09 Å |
| Si-H | 1.48 Å |
| Ge-H | 1.53 Å |
| Sn-H | 1.70 Å |

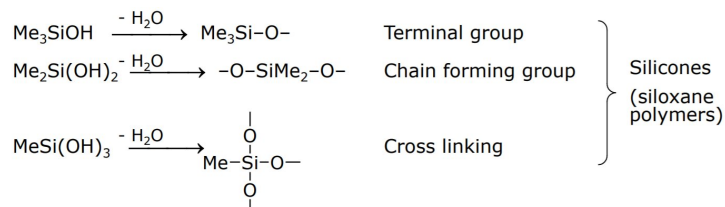
The M-H bonds get weaker down the group, a larger and more diffuse orbital, the bonds are a lot more polar and making it open to attack. Low lying LUMOS (easier for HOMO to be promoted?) also make it weaker. Because of this stability trend PbH_4 is so unstable no bond length has actually been measured.

§1.8.2 **Halides.** CX_4 is very stable, however the rest of the tetrels are volatile and very susceptible to hydrolysis. $\text{SiCl}_4 + 2\text{H}_2\text{O} \longrightarrow \text{SiO}_2 + 4\text{HCl}$

For Ge \longrightarrow Pb MX_2 is also formed due to a more polar bond, lower lying LUMOs and a more electrophilic metalloid.

§1.8.3 **Silicone.** Named after the apparent (but not actual) resemblance of Ph_2SiO to the Ketone Ph_2CO . They are nothing alike, Ph_2SiO is a polymer and they are not made the same.

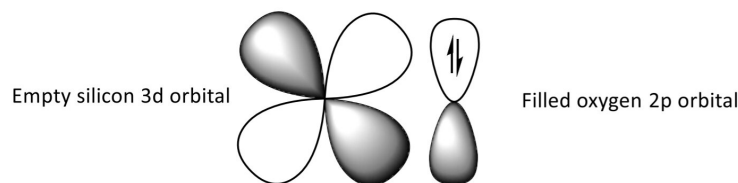
- Hydrolysis of organohalides
- $\text{Me}_3\text{SiCl} + \text{H}_2\text{O} \longrightarrow \text{Me}_3\text{SiOH} + \text{HCl}$ This forms Silanol and HCl
- Under the presence of acid Silanol condenses
- $2\text{Me}_3\text{SiOH} \xrightarrow{-\text{H}_2\text{O}} \text{Me}_3\text{Si}-\text{O}-\text{SiMe}_3$ siloxane, this does not happen with R_3COH
- To form polymeric siloxanes we need three types of monomers, the proportions of which will determine the properties of the siloxane polymer (silicone)



The thermal and chemical stability comes from the strength of the Si-C bonds and the Si-O-Si bridges.

| | | | | | | |
|------------------------------------|-------|-----|------|-----|-------|-----|
| Bond strengths kJmol^{-1} | C-C | 346 | C-O | 357 | C-Si | 318 |
| | Si-Si | 222 | Si-O | 452 | Si-Cl | 381 |

Very inert but will react with fluorinating agents, Si-F is very strong, also with concentrated OH solutions. The Si-O bond is very strong because of the back bonding from oxygen to empty silicon.



It's easy to make double and triple bonds with first row elements because of the good orbital overlap, whilst it is possible to make π bonds with the heavier group 14 elements σ bonds will always be preferred.

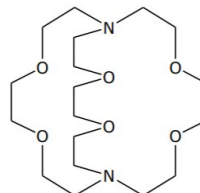
§1.8.4 **Zintl ions (with Wade's Rules).** The reductions of Lead with Sodium formed these ions.

$\text{Pb} \xrightarrow[\text{NH}_3]{\text{Na}} 4\text{Na}^+ + [\text{Pb}_9]^{4-}$ The use of cryptand ligands enables the crystallisation of these compounds

$[\text{Pb}_9]^{4-} + \text{Pb} \xrightarrow[\text{NH}_3]{\text{crypt-222}} 2[\text{Pb}_5]^{2-}$

Zintl ions can contain group 1 and 2 metals along with the post transition group 12 metals, or metalloids from 13 to 16

crypt-222 = 2.2.2-cryptand =
4,7,13,16,21,24-hexaoxa-1,10-
diazabicyclo[8.8.8]hexacosane



The Sodium ion is bound inside this compound, meaning it can't pair with the lead cluster

§1.9 THE Pnictogens Assessing trends down group 15

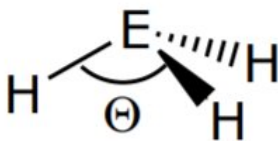
- Ionisation energy goes down
- Electron affinity goes up
- Electronegativity goes down
- Nitrogen takes oxidation states -3, +1 to +5, P and As +3 and +5, and Sb and Bi only take +3
- Atomic radius goes up

Nitrogen triple bond is the most stable bond possible so the forming of it is very favourable, this makes N_2 a common end product in explosives. The N^{3-} ion does exist. $6\text{Li} + \text{N}_2 \longrightarrow 2\text{Li}_3\text{N}$, Li^+ is very small and so the lattice energy is very high. There is very little catenation (joining of atoms, like in benzene) due to a weak N-N bond.

Phosphorous has many allotropes because of catenation. White, black and red phosphorous. Red phosphorous has a layered structure, similar to those that As, Sb and Bi form. The elements become more metallic down the group.

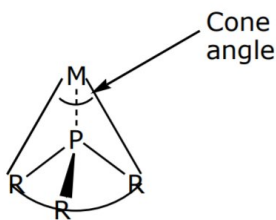
Phosphorous forms P(III) and P(V) oxides, P_4O_6 and P_4O_{10} . Whilst Nitrogen forms 7 oxides, all of which are less stable than N_2 and O_2

They all form Hydrides of EH_3 , the bond energy decreases down the group and so the stability decreases.



| N | P | As | Sb |
|-------|------|------|------|
| 106.7 | 93.6 | 92.1 | 91.6 |

NH_3 has a relatively high boiling point (-33°C), high polarity and H bonding. NH_3 (ammonia) is basic. PH_3 is not basic, as the P-H bonds are $p\sigma-s\sigma$ and the 3s orbital in P contributes little to the bonding, it is the lone pair.



When bonding to a metal, PR_3 is a good ligand, the cone angle increases for bigger R groups, this affects other ligands which are attached to the metal.

For the MX_3 halides all of them are formed, but for MX_5 this is not the case

| | F | Cl | Br | I |
|----|---|----|----|---|
| P | Y | Y | Y | Y |
| As | Y | Y | N | N |
| Sb | Y | Y | N | N |
| Bi | Y | N | N | N |

NF_3 has a boiling point of -129 , bond angle of 102 , which is less than NH_3 which is 107 . In PF_3 the electronegativity of F lowers the energy of the P 3d orbitals and so it has good π backbonding. In the solid state PCl_5 exists as tetrahedral $[\text{PCl}_4]^+$ and Octahedral $[\text{PCl}_6]^-$, but in the gaseous phase it's just regular trigonal bipyramidal. In PBr_5 a Br^- anion dissociates and so it takes the form $[\text{PBr}_4]^+\text{Br}^-$.