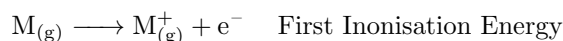# §1 P-block Chemistry

§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'.

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

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

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.

H 1312		**Values in kJmol⁻¹**					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.
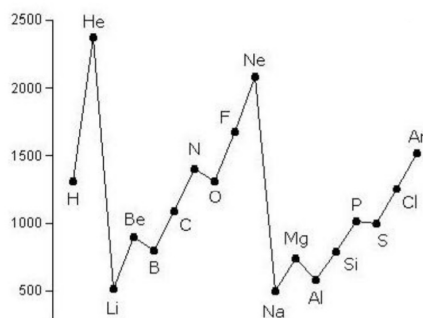
The kink from Be to B comes from the Be having a full s shell, so removing an electron from Boron would be favourable to give it a full s-orbital. The kink from N to O comes from Oxygen

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.

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

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.
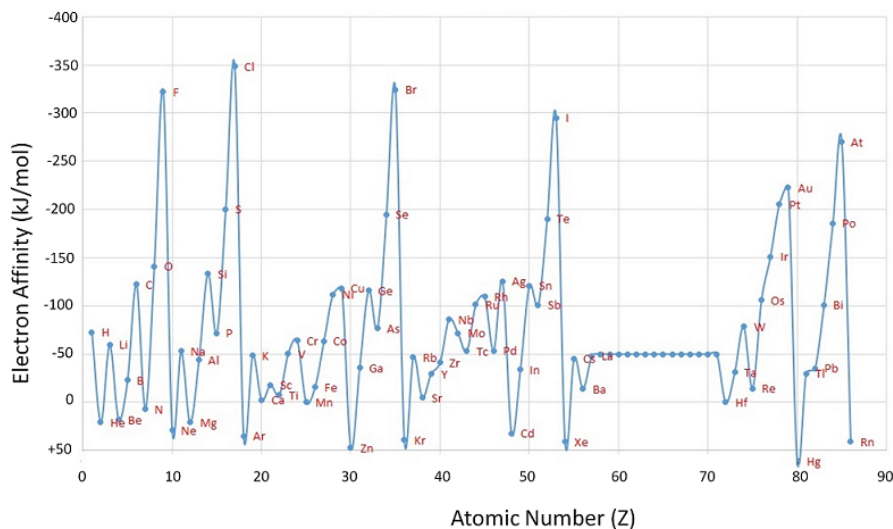
§1.2.3 **Electronegativity.** The ability of an atom to attract electron density towards itself in a molecule.

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.
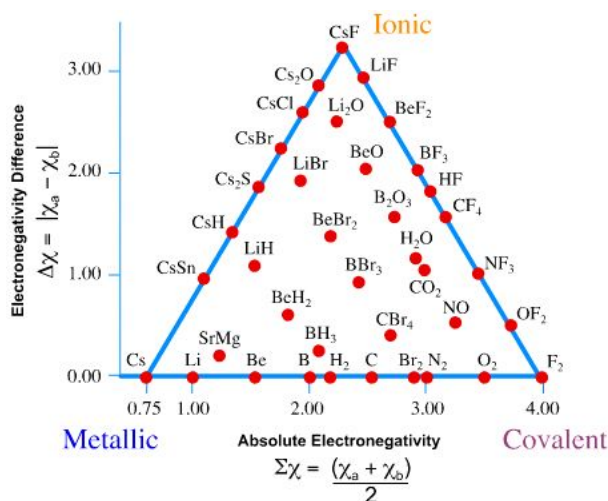
§1.2.4 **Summary.**

- 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 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.

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 electrins 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.

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

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.

H 1312			Values in kJmol⁻¹					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

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.
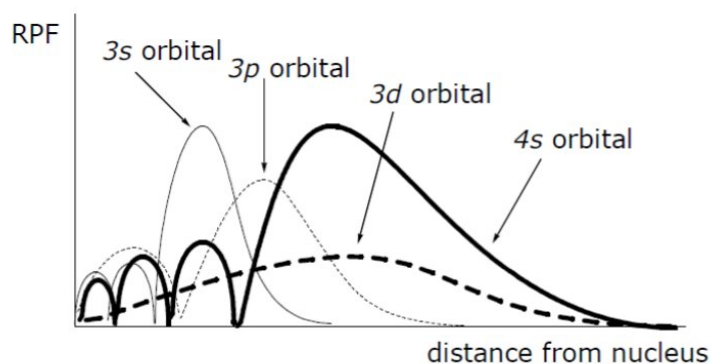

Figure 4: RPF is the probability of finding it there

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)

Covalent radii in Å. Not all element radii are available.

H 0.30							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).
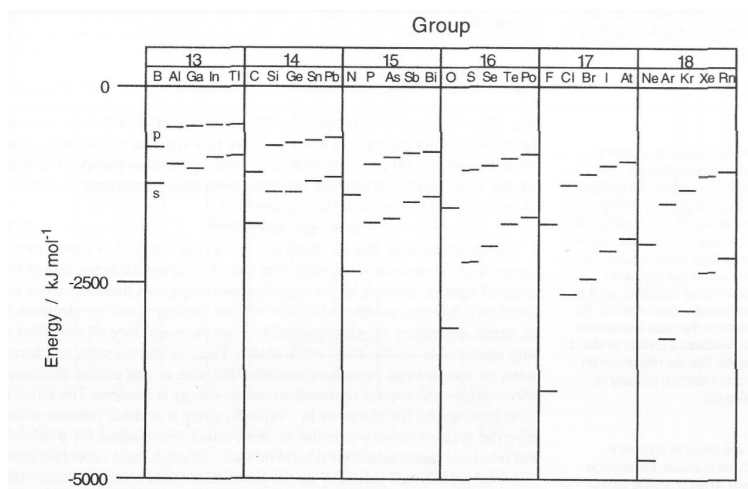

Figure 6: Highest occupied orbital energies

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, giving a less negative energy (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 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 (Molecular Orbitals from 1st year). 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.
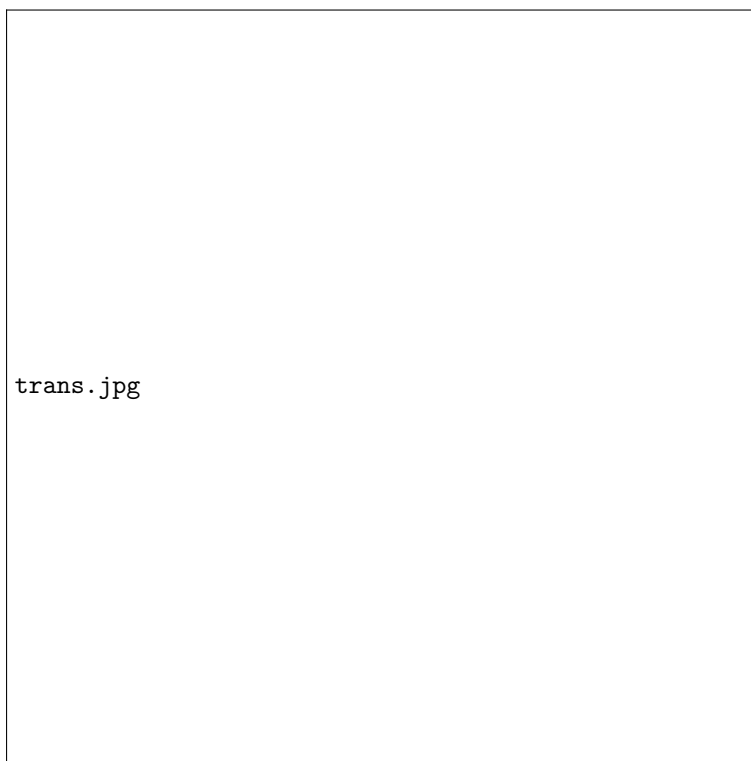

Figure 7: Reorganisation energies of groups 13 and 14

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 4p orbital is preceded by a 3d row, so the energy of the 4p 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.