Chem Factsheet

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Periodic Table: Anomalies of first member of group

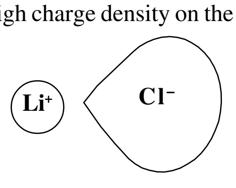
Before working through this Factsheet you should:
- Be familiar with the general trends across periods and down groups in the periodic table;
- Be familiar with general properties of Groups 1, 2 and 7.

After working through this Factsheet you will:
- Understand why period 2 elements generally display noticeably different properties to the other elements in the same group;
- Be familiar with examples of the atypical properties of lithium, beryllium and fluorine;
- Understand what is meant by the "diagonal relationship" in the Periodic Table.

Why are period 2 elements different?
- The atoms are very small in size;
- The elements are very electronegative;
- They have no d-orbitals.

Consequences of small size
- Lower than expected electron affinity.
  We might have expected high electron affinity for these elements - the new electron will be very close to the nucleus. However, because of their small size, the extra electron is being put into a region that is already crowded with electrons - producing a significant amount of repulsion.
  For example, although the general trend is for electron affinity to decrease down a group, fluorine has a lower electron affinity than chlorine, and oxygen has a lower electron affinity than sulphur.

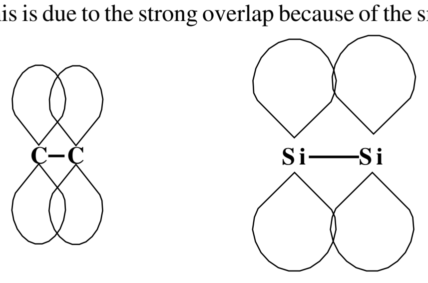
- Increased covalent character for small cations.
  This is due to high charge density on the cations - bonds are polarised.



For example lithium chloride dissolves in alcohols, unlike the remainder of group 1 chlorides; beryllium chloride dissolves in diethyl ether, unlike the remainder of group 2 chlorides.

> ***Remember:*** *ionic compounds generally dissolve in polar solvents and covalent compounds in non-polar solvents.*

- π-bonds are more efficient between 2p orbitals than 3p (or higher).
  This is due to the strong overlap because of the small size of the atoms.



For example carbon forms very many compounds with double or triple carbon-carbon bonds, whilst silicon does not. Nitrogen and oxygen exist as diatomic molecules (involving multiple bonds), whilst phosphorus and sulphur exist as P_4 and S_8 respectively, with no multiple bonds.

Consequences of high electronegativity
- Coupled with small size, high electronegativity accentuates nonmetallic behaviour.
  This means that the metallic elements form compounds with appreciable covalent character, as described above. Some oxides - eg beryllium - are amphoteric.

- Nitrogen, oxygen and fluorine can be involved in **hydrogen bonds.**
  As a consequence, the boiling points of NH_3, H_2O and HF are **higher** than those of PH_3, H_2S and HCl, although the general group trend is for boiling points of hydrides to increase down the group.

Consequences of lack of d-orbitals
- Form a maximum of four bonds.
  For example, nitrogen exhibits a maximum valency of 3 (eg ammonia NH_3) but phosphorus can form PCl_5. Similarly, sulphur forms SF_6, but no equivalent compound is formed by oxygen.

- Some reactions which occur for other members of the group cannot occur for the first member.
  This is because some reactions progress via a transition state involving an additional bond; the lack of availability of d-orbitals in the second energy level means that a mechanism that works for the rest of the group will not work for the first member.
  For example, carbon tetrachloride (CCl_4) is resistant to hydrolysis, but the other tetravalent group 4 chlorides will hydrolyse.

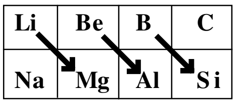
Anomalies of lithium
- Thermal decomposition of carbonates, nitrates and hydroxides to give the oxide.
  This is due to the high charge density of the lithium ion - combination with the high charge density oxide ion is favoured.
- Does not form peroxides and superoxides readily due to small size of the ion.
- Some compounds show a degree of covalent character due to polarising power of the small Li^+ ion.
- Relatively low solubility of carbonate, fluoride, hydroxide and phosphate due to the high lattice enthalpy.

Anomalies of beryllium
- Compounds show appreciable covalent character - eg dissolving in organic solvents, low melting points, hydrolysed by water. This is due to its much larger ionisation energy and the much smaller size of its ions.
- Amphoteric hydroxide.
- Does not form oxide in air at room temperature.
- Will not react with water and dilute acids.

Anomalies of fluorine
- Hydrofluoric acid is a weak acid (due to the high H-F bond strength).
- Hydrogen fluoride has a high boiling point (hydrogen bonding).
- The F-F bond strength is very low, because the small size of the atom brings the lone pairs close together.
- Forms compounds with all elements except helium, neon and argon.
- Does not form oxy-acids as it is more electronegative than oxygen.
- Only exhibits oxidation state of -1, as it is the most electronegative element.
- Is such a strong oxidising agent that it must be prepared by electrolysis, rather than chemically.
- Because of its small size, more fluorine atoms can be packed around a central atom - eg AlF_6^{3-} is formed, but only $AlCl_4^-$.

Diagonal Relationships

This refers to the similarities exhibited between the first element of some groups and the second element of the next group to the right.

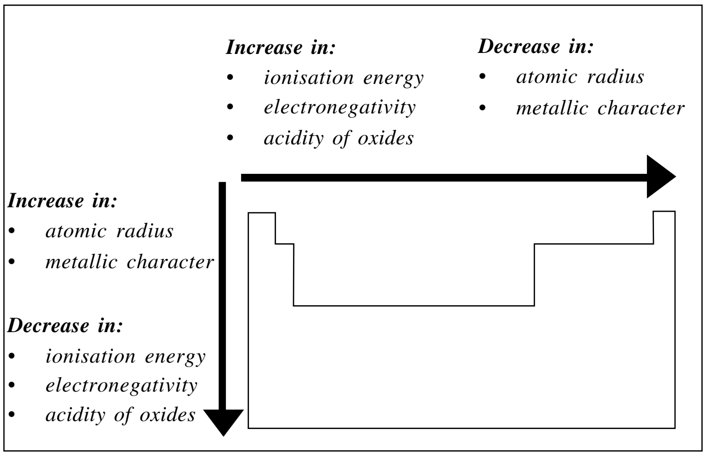


Note: this relationship does **not** hold for all the groups; the only significant relationships are the ones illustrated above.

Why is there a relationship?

Diagonal relationships occur because of the trends in properties down groups and across periods.The trend in properties across a period is usually opposite to the trend down a group - for example, ionisation energy increases across a period but decreases down a group, while atomic radius decreases across a period but increases down a group (Fig 1).

Fig 1. Trends in the periodic table



So, for example, atomic radius decreases from lithium to beryllium, but increases from beryllium to magnesium. The result is that the atomic radii of lithium and magnesium are similar (1.55×10^{-10}m and 1.6×10^{-10} m respectively).

In particular, the **polarising power** of the corresponding ions is similar. This is because the increase in size from one period to the next is offset by the increased charge.

Similarities between lithium and magnesium include:

- on reaction with air, forms oxide, not peroxide or superoxide
- carbonates thermally decompose, giving the oxide and carbon dioxide
- nitrates thermally decompose, giving the oxide, nitrogen dioxide and oxygen

Similarities between beryllium and aluminium include

- appreciable covalent character of compounds (eg the chlorides are largely covalent)
- formation of electron-deficient covalent chlorides, which tend to dimerize or polymerize
- amphoteric oxides
- hydrolysis of salts

Note that lithium and beryllium differ from the remainder of the elements in their groups with regard to these properties, as discussed above.

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Practice Questions

1. (a) Explain why the boiling points of hydrogen fluoride and hydrogen bromide are both higher than that of hydrogen choride

   (b) Explain why hydrofluoric acid is a weak acid

2. Lithium chloride dissolves in alcohols; sodium chloride does not.

   (a) Explain the significance of these observations

   (b) Account for these observations

3. (a) Explain why some chemical similarities between beryllium and aluminium are to be expected

   (b) State **two** such similarites

4. Explain why alkenes are common, but the corresponding silicon compounds, silenes, are very rare.

5. Suggest why lithium fluoride is insoluble

6. Explain why PCl_5 exists, but not NCl_5

Answers

1. (a) The boiling point of hydrogen fluoride is higher than that of hydrogen chloride because of the strong hydrogen bonding present in HF, which is not present in HCl. The boiling point of hydrogen bromide is higher than that of hydrogen bromide because of the increasing strength of the Van der Waals forces, due to increasing molecular size

   (b) The greater the degree of ionisation in water, the stronger the acid. Since the H-F bond is very strong, hydrogen fluoride does not ionize fully in water

2. (a) Alcohol is an organic solvent. Covalent substances would be expected to dissolve in it, but not ionic ones. This suggests that lithiumchloride has appreciable covalent character.

   (b) The lithium cation is very small with a very high charge density. The ionic bond becomes polarised, giving rise to some covalent character.

3. (a) This is an example of the diagonal relationship. Trends across the period are in the opposite direction to trends down the group, leading to similarites between an element and the element diagonally below it to the right. These similarites include ionisation energy, electronegativity, atomic radius and polarising power of cations.

   (b) Any two of: appreciable covalent character of compounds; amphoteric oxides; hydrolysis of salts; electron-deficient chlorides which dimerize/polymerize (*other acceptable answers are possible- they should refer to properties shared by beryllium and aluminium, but not shared with the remainder of group 2)*

4. The small size of carbon atoms allows a high degree of overlap between neighbouring 2p-orbitals. The larger size of silicon atoms means there is very little overlap between the 3p-orbitals

5. Extremely high lattice enthalp due to both anion and cation being small.

6. Nitrogen has no d-orbitals available, and so cannot form more than four bonds.