ANOMALOUS BEHAVIOUR OF THE 2ND ROW ELEMENTS

Li, Be, B, C, N, O, F

For the elements in the 2nd row, as the atomic number **increases**, the atomic radius of the elements **decreases**, the electronegativity **increases**, and the ionization energy **increases**.

The 2nd row has two metals (lithium and beryllium), making it the least metallic period and it has the most nonmetals, with four. The elements in the 2nd row often have the most extreme properties in their respective groups; for example, fluorine is the most reactive halogen, neon is the most inert noble gas, and lithium is the least reactive alkali metal.

These differences in properties with the subsequent rows are a result of:

- the smaller size of the atoms
- an outer shell with a maximum of 8 electrons (2s and 2p) and an underlying shell with just 2 electrons
- no acessible d-orbitals - energy too high for use in bonding

Apart from the 2nd row (ignoring H/He 1st row) the later rows all end with inert gases but these do not have completed quantum levels. The 2nd row elements in general can only use the 2s and 2p electrons for bonding restricting the total number of bonds to 4.

So N is not expected to have more than 4 bonds and 3 is common, while for P 5 and 6 bonded species are quite common.

Reactivity of metals and metalloids
For **Lithium**, compared to other alkali metals

Reaction with water:
Li reacts slowly with water at 25 °C
Na reacts violently and K in flames

$2M(s) + 2H_2O(l) \rightarrow 2M^+(aq) + 2OH^- + H_2(g)$

In general Li, Be, B, C, N, O, F are less reactive towards water than their heavier congeners.

Reaction with oxygen:

In conditions of excess oxygen, only Li forms a simple oxide, Li_2O. Other metals form peroxides and superoxides

Reaction with nitrogen:
Li reacts directly with N_2 to form Li_3N

$6Li(s) + N_2 (g) \rightarrow 2Li_3N(s)$.

No other alkali metal reacts with N_2

Solubility:

LiF, LiOH and Li_2CO_3 are less soluble than the corresponding Na and K compounds

For **Beryllium** compared to the other alkaline earth metals:

With water:

All Group 2 metals except Be, react with water

$M(s) + 2H_2O(l) \rightarrow M^{2+}(aq) + 2OH^-(aq) + H_2 (g)$

With oxygen (air):
Be only reacts with air above 600 °C if it is finely powdered. The BeO that is formed is amphoteric (other Group 2 oxides are basic).

Of the Group 2 elements only Be reacts with NaOH or KOH to liberate H_2 and form $[Be(OH)_4]^{2-}$.

Li and Be are metals but are less conducting than the higher members of Group 1 and 2 elements due to their high IEs (electrons are close to nucleus).

Ionization of **Boron** to B^{3+} requires a large input of energy and B adopts a covalent polymeric structure with semi-metallic properties.

The other elements of Group 14 become increasingly metallic as the group is descended due to the decrease in ionization energies.

Crystalline Boron is chemically inert - unaffected by boiling HCl and only slowly oxidized by hot concentrated HNO_3 when finely powdered.

Covalent character

Li^+ and Be^{2+} are small and have strong polarizing abilities. Their compounds are more covalent than those of the heavier elements in their groups.

$BeCl_2$ is covalent while MCl_2 (M = Mg-Ba) are ionic. The conductivity of fused beryllium chloride is only 1/1000 that of sodium chloride under similar conditions.

Catenation

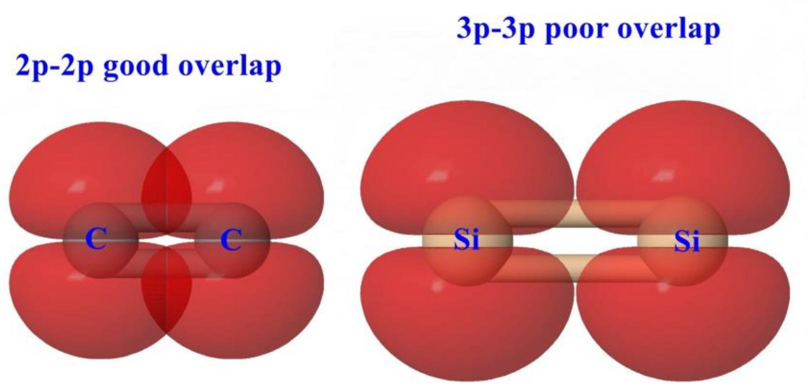
Catenation is the linkage of atoms of the same element into longer chains. Catenation occurs most readily in carbon, which forms covalent bonds with other carbon atoms to form longer chains and structures. This is the reason for the presence of the vast number of organic compounds in nature.

The ability of an element to catenate is primarily based on the bond energy of the element to itself, which decreases with more diffuse orbitals (those with higher azimuthal quantum number) overlapping to form the bond. Hence, carbon, with the least diffuse valence shell 2p orbital is capable of forming longer p-p sigma bonded chains of atoms than heavier elements which bond via higher valence shell orbitals.

Hetero-catenation is quite common in Inorganic Chemistry. Phosphates and silicates with P-O-P-O and Si-O-Si-O linkages are examples of this.

Multiple Bonds

C, N and O are able to form multiple bonds (double and/or triple). In Group 14, C=C double bonds are stable (134 pm) but Si=Si double bonds (227 pm) are uncommon. The diagram below shows how multiple bonds are formed involving π overlap of 2p orbitals. By comparison the 3p orbitals of the corresponding third row elements Si, P, and S are more diffuse and the longer bond distances expected for these larger atoms would result in poor π overlap.



C=C bond length = 134 pm and Si=Si bond length = 227 pm

Oxidizing ability of oxygen and fluorine

Due to the high electron affinities and electronegativities of oxygen and fluorine, they tend to form strong ionic bonds with other elements. They even react with noble gases to form compounds such as XeO_3, XeO_4, XeF_4 and XeF_6.

In 1962 Neil Bartlett at the University of British Columbia reacted platinum hexafluoride and xenon, in an experiment that demonstrated the chemical reactivity of the noble gases. He discovered the mustard yellow compound, xenon hexafluoroplatinate, which is perhaps now best formulated as a mixture of species, $[XeF^+][PtF_5]^-$, $[XeF^+][Pt_2F_{11}]^-$, and $[Xe_2F_3]^+[PtF_6]^-$.

A few hundred compounds of other noble gases have subsequently been discovered: in 1962 for radon, radon difluoride (RnF_2), and in 1963 for krypton, krypton difluoride (KrF_2). The first stable compound of argon was reported in 2000 when argon fluorohydride (HArF) was formed at a temperature of 40 K (-233.2 °C). Neutral compounds in which helium and neon are involved in chemical bonds have still not been formed.

Noble gas compounds have already made an impact on our daily lives. XeF_2 is a strong fluorinating agent and has been used to convert uracil to 5-fluorouracil, one of the first anti-tumor agents.

Source :
http://wwwchem.uwimona.edu.jm:1104/courses/CHEM1902/IC10K_MG_Fajans.html