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Inorganic Chemistry

Department of Chemistry

L.S COLLEGE MUZAFFARPUR
B. R. A. BIHAR UNIVERSITY
Dr. Priyanka

TOPIC:- General group Trends(Group 16)

General group Trends

The size of the Group 16 elements increases down the group as extra shells of electrons are added. The ionization enthalpy decreases as the size of the atom increases. The ionization enthalpies of the Group16 elements are strikingly less than these of the corresponding Group 15 elements. This is attributed to the fact that Group15 elements have ns^2 np^3 configuration, the p orbitals are half filled conferring extra stability and consequently removal of an electron is difficult. The electronegativities decrease with increasing atomic number. Thus in view of the fall in electronegativity, metallic character within the group increases with increase in atomic size.

The large difference in melting and boiling points between oxygen and sulphur can be explained on the basis of their structure. Oxygen exists as diatomic molecules and the bond energy of O=O is very high (498 KJ mol^{-1}). The molecules are held by weak van der Waal's forces. Sulphur exists as S_8, the S-S bond energy (264 KJ mol^{-1}) is greater than O-O bond energy (142 KJ mol^{-1}). Thus sulphur has greater catenation power than oxygen and higher melting and boiling points.

Oxidation states and Bond type

The elements have outermost electronic configuration of ns^2 np^4 and can achieve noble gas configuration by gaining two electrons forming M^{2-} ion or by acquiring a share in two electrons by forming two covalent bonds. The M^{2-} ion is known for oxygen (which is highly electronegative) and to a lesser extent for sulphur. Sulphur, selenium and tellurium show +2, +4 and +6 oxidation states. The +4 and +6 oxidation states are realized by utilizing vacant d orbitals. Oxygen always displays -2 oxidation state in metallic and non-metallic oxides except in OF_2 where it shows +2 oxidation state. This is because fluorine is more electronegative than oxygen.

Oxygen, and to a lesser extent, sulphur differ from other members in their ability to catenate and form peroxides H-O-O-H and polysulphides, H_2S_n (n=2 to 8) respectively.

The tendency to form multiple bonds decreases down the group. Carbon dioxide (O=C=O) is very stable, carbon disulphide is moderately stable, the corresponding selenium compound is less stable whereas the tellurium compound is not known.

The bond between sulphur and oxygen are shorter than a single bond. In addition to the σ - bond between the elements, a π-bond is formed by overlap of filled 2p orbitals of oxygen with a vacant 3d-orbital of sulphur. This is called a $p\pi$ -$d\pi$ bond. The sizes and energies of the 2p orbital of oxygen and 3d orbital of sulphur are comparable allowing effective overlap.