

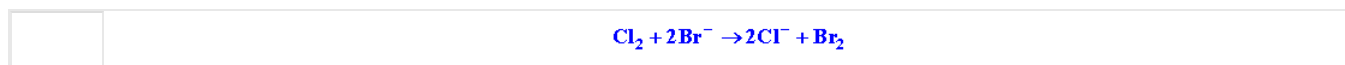
5.4: Some Chemical Implications

A detailed study of the chemical implications of the orbital theory of electronic structure must await our discussion of the chemical bond. However, we can at this point correlate the gross chemical behaviour of the elements with the general results of the orbital theory.

The effective nuclear charge is a minimum for the group I elements in any given row of the periodic table. Therefore, it requires less energy to remove an outer electron from one of these elements than from any other element in the periodic table. The strong reducing ability of these elements is readily accounted for. The variation in the relative reducing power of the elements across a given period or within a given group will be determined by the variation in the effective nuclear charge. The ability of the elements in a given row of the periodic table to act as reducing agents should undergo a continuous decrease from group I to group VII, since the effective nuclear charge increases across a given row. Similarly, the reducing ability should increase down a given column (group) in the table since the effective nuclear charge decreases as the principal quantum number is increased. Anticipating the fact that electrons can be transferred from one atom (the reducing agent) to another (the oxidizing agent) during a chemical reaction, we expect the elements to the left of the periodic table to exhibit a strong tendency to form positively charged ions.

The ability of the elements to act as oxidizing agents should parallel directly the variations in the effective nuclear charge. Thus the oxidizing ability should increase across a given row (from group I to group VII) and decrease down a given family. These trends are, of course, just the opposite of those noted for the reducing ability. We can also relate the chemical terms "reducing ability" and "oxidizing ability" to the experimentally determined energy quantities, "ionization potential" and "electron affinity." The reducing ability should vary inversely with the ionization potential, and the oxidizing ability should vary directly with the electron affinity. The elements in groups VI and VII should exhibit a strong tendency for accepting electrons in chemical reactions to form negatively charged ions. Francium, which possesses a single outer electron in the 7s orbital, should be the strongest chemical reducing agent and fluorine, with an orbital vacancy in the 2p subshell, should be the strongest oxidizing agent. ([Click here for note.](#))

A great deal of chemistry can now be directly related to the electronic structure of the elements. For example, the reaction



is explained chemically by stating that Cl_2 is a stronger oxidizing agent than Br_2 . The electronic interpretation is that the orbital vacancy in Cl is in a 3p orbital and closer to the nucleus than the 4p orbital vacancy in Br. Thus the effective nuclear charge which attracts the extra electron is larger for the Cl atom than for the Br atom. We could of course interpret this same reaction by stating that the Br^- ion is a stronger reducing agent than is the Cl^- ion. In other words the extra electron in the Br^- ion is less tightly held than is the extra electron in the Cl^- ion. The explanation in terms of the relative effective nuclear charges is the same as that given above.

The decrease in the effective nuclear charge down the halogen family of elements leads to some interesting differences in their chemistry. For example, hydrogen chloride may be prepared from sodium chloride and sulphuric acid:



However, the same method cannot be employed in the preparation of hydrogen bromide or hydrogen iodide. In the preparation of hydrogen bromide from sodium bromide,



some of the HBr reacts further,



and the HBr is thus contaminated. In preparation of hydrogen iodide a further reaction again occurs:



Reactions (3) and (4) are clearly redox reactions in which the halide ions reduce the sulphur in the SO_4^{2-} anion to a lower oxidation state. Since Cl has the highest effective nuclear charge, the Cl^- ion should be the weakest reducing agent of the three halide ions. Indeed, the Cl^- ion is not a strong enough reducing agent to change the oxidation state of S in SO_4^{2-} . The Br^- ion possesses an intermediate value for the effective nuclear charge and thus it is a stronger reducing agent than the Cl^- ion. The Br^- ion reduces the oxidation number of sulphur from (+6) to (+4). Since the I^- ion binds the extra electron least of all (the electron is in an $n = 5$ orbital and the effective nuclear charge of iodine is the smallest of the three), it should be the strongest reducing agent of the three halide ions. The I^- ion in fact reduces the sulphur from (+6) to (-2).

A word about oxidation numbers and electron density distributions is appropriate at this point. An oxidation number does not, in general, represent the formal charge present on a species. Thus S is not S^{+6} in the SO_4^{2-} ion, nor is it S^{-2} in the H_2S molecule. However, the average electron density in the direct vicinity of the sulphur atom does increase on passing from SO_4^{2-} to H_2S . From their relative positions in the periodic table it is clear that oxygen will have a greater affinity for electrons than sulphur. Thus when sulphur is chemically bonded to oxygen the electron density in the vicinity of the sulphur atom is decreased over what it was in the free atom and increased in the region of each oxygen atom. Again it is clear from the relative positions of H and S in the periodic table that sulphur has a greater affinity for electrons than does hydrogen. Thus in the molecule H_2S , the electron density in the vicinity of the sulphur atom is increased over that found in the free atom. In changing the immediate chemical environment of the sulphur atom from that of four oxygen atoms to two hydrogen atoms, the electron density (i.e., the average number of electrons) in the vicinity of the sulphur atom has increased. The assignment of actual oxidation numbers is simply a bookkeeping device to keep track of the number of electrons, but the sign of the oxidation number does indicate the direction of the flow of electron density. Thus sulphur has a positive oxidation number when combined with oxygen (the sulphur atom has lost electron density) and a negative one when combined with hydrogen (the electron density around sulphur is now greater than in the sulphur atom).

The above are only a few examples of how a knowledge of the electronic structure of atoms may be used to understand and correlate a large amount of chemical information. It should be remembered, however, that chemistry is a study of very complex interactions and the few simple concepts advanced here cannot begin to account for the incredible variety of phenomena actually observed. Our discussion has been based solely on energy, and energy alone never determines completely the course of a reaction on a macroscopic level, i.e., when many molecules undergo the reaction. There are statistical factors, determined by the changes in the number of molecules and in the molecular dimensions, which must also be considered. Even so, the energy effect can often be overriding.

In the long form of the periodic table, families are labelled by both a number and by the letter A or B. Thus there is a IA family and a IB family. It will be noted that the elements in a B family all occur in the series of transition elements in which the *d* orbitals are being filled. In the A families, however, the *d* orbitals are either absent or are present as closed inner shells. For example, consider the electronic configurations of K (IA) and Cu (IB):

K [Ar]4s ¹	Cu [Ar]3d ¹⁰ 4s ¹
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Note that the most stable configuration for Cu is not [Ar] 3d⁹4s² as expected. By transferring one of the 4s electrons to the 3d vacancy, the *d* subshell is filled and the electronic energy is lowered. The electron density distribution of the Cu atom is therefore a spherical one. Both K and Cu have one outer electron with a spherical charge distribution. They should have some properties in common, such as a tendency to lose one electron and form a positive ion. For this reason both families are labelled I. However, the shell underlying the outer electron in the K atom possesses a rare gas configuration, while in the Cu atom it is a set of filled *d* orbitals. This difference in electronic structure is sufficient to cause considerable differences in their chemistry, hence the further labels A and B.

A rare gas configuration is always one of great stability, particularly when it occurs in a positive ion. (Recall that $I_2 = 47.3$ eV for sodium.) The species K^{+2} is never observed in solution chemistry, and could be produced in the gas phase only by an expenditure of energy far in excess of that observed in ordinary chemical reactions. The Cu^+ ion, on the other hand, very readily loses a second electron to form the Cu^{+2} ion. Indeed, Cu^{+2} is the more common ionic form of copper. Thus the d^{10} closed shell structure is more easily broken than a rare gas configuration, giving to Cu a variable valency of one or two.

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