The Periodic Properties of Atoms

The Periodic Table: In the 1870's, the Russian chemist Mendeleev developed the periodic table, based upon the relationship between the atomic weights of the elements and their chemical properties. As one ascends from lightest to heaviest elements, there is a periodic recurrence of chemical properties. For example, the elements with atomic numbers 2, 10, 18, 36, 54, and 86 all are chemically inert (the noble gases), while those with atomic numbers one greater 3, 11, 19, 37, 55, and 87 are all extremely reactive metals (the alkali metals).



Rare Earth Metals

The rows or **periods** of the periodic table contain the elements with the same principle quantum number (n) for their outermost electrons. That is, until the fourth period, which contains the first row of transition metals, where the electrons of highest energy exist in d orbitals, which follow in the building-up order s orbitals of a higher shell, being grouped in the same period with elements of higher principle quantum number (n).

The columns or **groups** in the periodic table contain elements with the same electron configuration in the outermost shell. For example, the outermost shell of a noble gas is completely filled, while the outermost shell of an alkali metal contains only one electron.

Examine the periodic table at right showing which subshell contains the highest energy electrons in the ground state of each element. Compare to the table above to understand how the periodic nature of chemical properties corresponds to the configuration of outer-shell electrons. Notice that the blocks into which the table above is subdivided correspond to the type of subshell, s, p, d, or f and therefore to the momentum quantum number (l).



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Periodic Properties

As one reads across the periodic table from left to right in a given period, the pull exerted upon the outer-shell electrons by the positively charged nucleus *increases* with atomic number. There are more protons in the nucleus and therefore more positive charge. As one reads down the periodic table from top to bottom in a given group, however, the pull of the nucleus upon the outer-shell electrons *decreases* due to the *shielding* of the nuclear charge by electrons in the lower energy shells, which are between the nucleus and the outermost electrons. In other words, the outer-most electrons on the right side of the table in a given period are bound more tightly than those on the left, and the outer-most electrons of atoms on the bottom of a given row are bound less tightly than those on the top. For the most part, these two general trends account for the **periodic properties**.

Atomic Radius: The first periodic property we will discuss is atomic radius (AR), which is the distance from the center of the nucleus to the outer edge of the electron cloud. We are therefore discussing the relative sizes of atoms.



atomic radius decreases



Lithium

To illustrate the variation of atomic radius across or down the periodic table, we have three stylized illustrations of the elements, lithium, fluorine, and chlorine. In the first group of the second period is the alkali metal lithium. To the right in the same period, in the seventh group, is the halide fluorine. Because of the increased nuclear charge in fluorine, which has nine protons, the electrons in the *L* shell are bound more closely than in lithium, which has only three. A lithium atom is therefore larger than a fluorine atom, even though it contains less mass.

One below fluorine in the same group is another halide, chlorine. An atom of chlorine is larger than an atom of fluorine because of the addition of a new shell, M.



Fluorine



Ionization Energy: The energy required to remove an electron from a gaseous atom in its ground state, ionization energy (IE) reflects how closely bound the electrons are by the nuclear charge. The process may be represented by an equation such as:

 $\text{Li}(g) \xrightarrow{\text{IE}} \text{Li}^+ + e^-$

The relative ionization energy of atoms within a group or period closely parallels the trend in atomic radius. Across a period, for example, the smaller the atom, the greater the ion-ization energy.

ionization energy increases

Groups VIIIA н^е Ň. IIIA IVA ٧A VIA 10 Ne B 3 3 7 N 3 D F ĽI Be ionization TT/ CI 10 Ar ገደ Mg 18 Al ዤ P ิ Na ୀମ SI 10 S IIIB 1VB ٧B VIB VILB VILLB IB IIВ energy 32 Ge 33 As ED Kr ገር K ହ୍ର Ca ସା ସଥ Sc Ti ଥା Ga ଞ୍ଚ Se 28 21 27 20 27 V Cr Mn Fe Co छ Br 23 NI ଙ୍କ Cu ⊡ Zn decreases 30 30 32 38 31 59 50 97 Zr Nb Mo Tc Ru Rh Pd Ag ≌7 Rb ∷ Sr SD Y Cd In ⊡ Sn ଆ Sb .22 Te 3 ਤੀ Xe 122 120 121 123 123 123 124 Hf Ta W Re Os II 124 124 123 123 124 124 ଅ Cs ⊠ ਤ7/ Ba La* 73 Pt 闷 Au ∷0 Hg 30 TI Bi Pb Po At Ř'n 37 Fr Ba Ac*** Unq Unp Unh 30 30 32 39 31 Nd Pm Sm Eu Gd ٩ Tb Ho Dy Ēr Tm Υb Ľu *Actinide series 20 21 22 23 21 25 25 27 Th Pa U Np Pu Am Cm Bk Fm Md No Cf Es

Electron Affinity: Electron affinity is the energy released or absorbed when an electron is added to a neutral, gaseous atom. The formula for this process is as follows:

 $F(g) + e^- \longrightarrow F^- + EA$

While the process of removing an electron from a neutral atom is always endothermic (requiring the input of ionization energy), the addition of an electron is can be either endothermic or exothermic, meaning that the electron affinity may be either positive or negative.

Like the ionization energy, the general tendency for electron affinity parallels the periodic tendencies of atomic radius. In general, the reaction is more exothermic towards the right side of the periodic table, where the new electron is bound more tightly (into a lower energy state), and less exothermic as you move down the table within a group.

There are some exceptions to these general tendencies however. The reaction with the nonmetals in the second period is less exothermic than with their congeners below. This is probably due to crowding of electrons in the smaller 2p orbitals. This is especially pronounced with nitrogen, for which the reaction is actually endothermic. The three outer shell electrons of nitrogen in their ground state occupy their p orbitals singly. Due to electron-electron repulsion, the addition of the new electron produces a state that is less stable (of higher energy).

Electronegativity: This is a dimensionless scale which reflects the relative attraction of the nucleus of a particular atom for the electrons in a chemical bond. It depends upon the values for ionization energy and electron affinity. The tighter an atom holds its electrons, the more electronegative it is.



On the scale fluorine has the highest electronegativity with a value of 4. (The noble gases, because they don't react to form bonds are not included) Oxygen has the value 3.5, nitrogen 3.0, and carbon 2.5. Below oxygen in the same group, sulfur has the value 2.5. On the other end of the periodic table, lithium has the electronegativity 1.0 and sodium, below it in group IA, has the value 0.9.

Metallic character: The properties that distinguish metals, which include their high conductivity of heat and electricity, depend upon the high mobility of electrons. Metallic elements, therefore, possess low ionization energy and low electron affinity. The elements with the highest metallic character are in the lower left corner of the periodic table, those with the least metallic character, the upper right.