

Short Notes on Periodic Table

Modern Periodic Table:

Earlier scientists assumed that the properties of elements are periodic functions of their atomic masses. On the basis of this assumption, Mendeleev placed 63 elements in a vertical column called groups and in horizontal rows called periods.

This method was rejected as it could not explain the position of certain elements, rare earth metals, and isotopes. A scientist named Henry Moseley removed these defects and put forward the modern periodic table with the modern periodic law.

Moseleys Periodic Law:

He stated that the properties of elements are periodic functions of their atomic number.

Modern Periodic Table:

A tabular arrangement of elements in groups and periods which highlights the regular trends in properties of elements is defined as the periodic table.

Group→	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓Period																		
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	* 71 Lu	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	* 103 Lr	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
			* 57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb		
			* 89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No		

Features of Modern Periodic Table

There are eighteen vertical columns known as groups in the modern periodic table which are arranged from left to right and seven horizontal rows which are known as periods.

Group number	Group name	Property
Group 1 or IA	Alkali metals	They form strong alkalis with water
Group 2 or IIA	Alkaline earth	They also form alkalis but weaker than group 1 elements

	metals	
Group 13 or IIIA	Boron family	Boron is the first member of this family
Group 14 or IVA	Carbon family	Carbon is the first member of this property
Group 15 or VA	Nitrogen family	This group has non-metals and metalloids
Group 16 or VIA	Oxygen family	They are also known as chalcogens
Group 17 or VIIA	Halogen family	The elements of this group form salts.
Group 18	Zero group	They are noble gases and under normal conditions they are inert.

Classifications of Elements in the Periodic Table

The elements of group 1, 2, 13, 14, 15, 16, and 17 are known as the main group elements or normal elements. The elements of groups 3, 4, 5, 6, 7, 8, 9, 11 and 12 are known as the transition elements. Group 18 is called **noble gases** or **inert gases**. Their outermost shell is completely filled. Due to this stable electronic configuration, they generally don't react with the other elements.

When we talk about the periods of a modern periodic table, one should keep in mind that the number of shells present in an atom determines its period number. The elements of period one will have only one shell, elements of period two will have two shells and so on. The first period of the modern periodic table is the shortest period as it contains only two elements. The period number two and three consists of eight elements each and is known as short groups. Period four and five have eighteen elements and are known as the long group. In the modern periodic table, group number 3 of period six contains the lanthanide series which are the rare earth elements. We have radioactive elements (actinides) present in group 3 of period seven.

Naming of Elements of Atomic Numbers Greater than 100

It is a generally accepted convention that the discoverer of an element has the honour of naming it. The inspiration often comes from origin, mythical characters, place, physical or chemical properties, and more recently to commemorate the names of eminent scientists. Of course, the suggestion has to be ratified by the International Union of Pure and Applied Chemistry (IUPAC). Newly discovered or undiscovered superheavy elements are often referred to in the scientific literature but until they have received permanent names and symbols from IUPAC, temporary designators are required. In 1978 IUPAC Commission on the Nomenclature of Inorganic Chemistry decided that it is necessary to have a systematic naming for the elements with atomic number greater than 100 ($Z > 100$), even for those which had not been discovered. The Commission decided that these elements would be best named systematically and that names should accord with the following rules:

The name is derived directly from the atomic number of the element using the following Latin numerical roots

Number	Root
0	nil
1	un
2	bi
3	tri
4	quad
5	pent
6	hex
7	sept
8	oct
9	enn

1. The roots are put together in the order of the digits which make up the atomic number and terminated by 'ium' to spell out the name. The final 'n' of 'enn' is elided when it occurs before 'nil', and the final 'i' of 'bi' and of 'tri' when it occurs before 'ium'.
2. The symbol of the element is composed of the initial letters of the numerical roots which make up the name.
3. The root 'un' is pronounced with a long 'u', to rhyme with 'moon'. In the element names each root is to be pronounced separately.

Here are a few examples of the names generated for elements with atomic numbers 101 to 900.

Atomic number	Name	Symbol
101	Unnilunium	Unu
102	Unnilbium	Unb
103	Unniltrium	Unt
104	Unnilquadium	Unq
105	Unnilpentium	Unp
106	Unnilhexium	Unh
107	Unnilseptium	Uns
108	Unniloctium	Uno
109	Unnilennium	Une
110	Ununnilium	Uun
111	Unununium	Uuu
112	Ununbium	Uub
113	Ununtrium	Uut
114	Ununquadium	Uuq
115	Ununpentium	Uup
116	Ununhexium	Uuh
117	Ununseptium	Uus
118	Ununoctium	Uuo
119	Ununennium	Uue
120	Unbinilium	Ubn
121	Unbiunium	Ubu
130	Untrinilium	Utn
140	Unquadnilium	Uqn
150	Unpentnilium	Upn
160	Unhexnilium	Uhn
170	Unseptnilium	Usn

180	Unoctnilium	Uon
190	Unennilium	Uen
200	Binilnilium	Bnn
201	Binilunium	Bnu
202	Binilbium	Bnb
300	Trinilnilium	Tnn
400	Quadnilnilium	Qnn
500	Pentnilnilium	Pnn
900	Ennilnilium	Enn

Shielding and Effective Nuclear Charge

For an atom or an ion with only a single electron, we can calculate the potential energy by considering only the electrostatic attraction between the positively charged nucleus and the negatively charged electron. When more than one electron is present, however, the total energy of the atom or the ion depends not only on attractive electron-nucleus interactions but also on repulsive electron-electron interactions. When there are two electrons, the repulsive interactions depend on the positions of *both* electrons at a given instant, but because we cannot specify the exact positions of the electrons, it is impossible to exactly calculate the repulsive interactions. Consequently, we must use approximate methods to deal with the effect of electron-electron repulsions on orbital energies.

Electron Shielding and Effective Nuclear Charge

If an electron is far from the nucleus (i.e., if the distance r between the nucleus and the electron is large), then at any given moment, many of the other electrons will be *between* that electron and the nucleus (Below Figure). Hence the electrons will cancel a portion of the positive charge of the nucleus and thereby decrease the attractive interaction between it and the electron farther away. As a result, the electron farther away experiences an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z . This effect is called electron shielding.

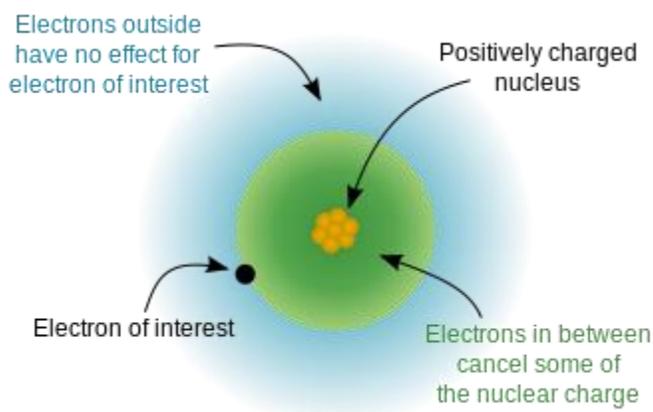


Figure: This image shows how inner electrons can shield outer electrons from the nuclear charge.

As the distance between an electron and the nucleus approaches infinity, Z_{eff} approaches a value of 1 because all the other $(Z-1)$ electrons in the neutral atom are, on the average, between it and the nucleus. If, on the other hand, an electron is very close to the nucleus, then at any given moment most of the other electrons are farther from the nucleus and do not shield the nuclear charge. At $r \approx 0$, the positive charge experienced by an electron is approximately the full nuclear charge, or $Z_{\text{eff}} \approx Z$. At intermediate values of r , the effective nuclear charge is somewhere between 1 and Z :

$$1 \leq Z_{\text{eff}} \leq Z.$$

Notice that $Z_{\text{eff}} = Z$ only for hydrogen and only for helium are Z_{eff} and Z comparable in magnitude

Shielding

Shielding refers to the core electrons repelling the outer electrons, which lowers the effective charge of the nucleus on the outer electrons. Hence, the nucleus has "less grip" on the outer electrons insofar as it is shielded from them.

Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$$Z_{\text{eff}} = Z - S$$

where Z is the atomic number (number of protons in nucleus) and S is the shielding constant. The value of Z_{eff} will provide information on how much of a charge an electron actually experiences.

We can see from the above equation that the effective nuclear charge of an atom increases as the number of protons in an atom increases. Therefore as we go from left to right on the periodic table the effective nuclear charge of an atom increases in strength and holds the outer electrons closer and tighter to the nucleus. As we will discuss later on in the chapter, this phenomenon can explain the decrease in atomic radii we see as we go across the periodic table as electrons are held closer to the nucleus due to increase in number of protons and increase in effective nuclear charge.

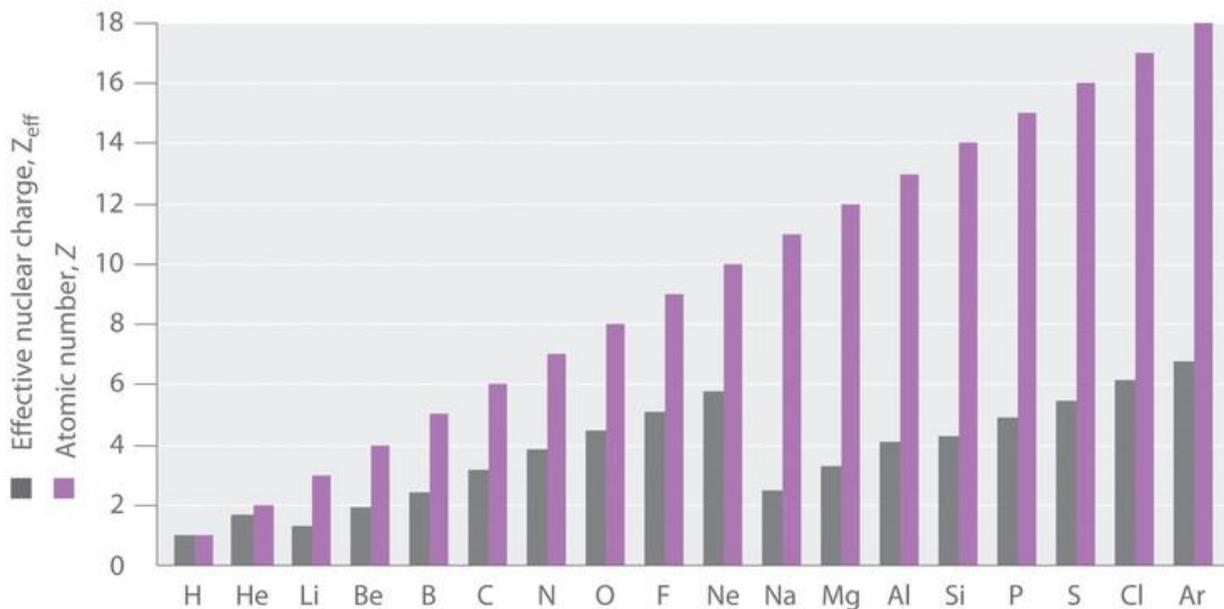


Figure : Relationship between the Effective Nuclear Charge Z_{eff} and the Atomic Number Z for the Outer Electrons of the Elements of the First Three Rows of the Periodic Table. Except for hydrogen, (Z_{eff} is always less than Z , and (Z_{eff} increases from left to right as you go across a row.

Electrons that are shielded from the full charge of the nucleus experience an *effective nuclear charge* (Z_{eff}) of the nucleus, which is some degree less than the full nuclear charge an electron would feel in a hydrogen atom or hydrogenlike ion.

Slater's Rules

We have previously described the concepts of electron shielding, orbital penetration and effective nuclear charge, but we did so in a qualitative manner. In this section, we explore one model for quantitatively estimating the impact of electron shielding, and then use that to calculate the effective nuclear charge experienced by an electron in an atom. The model we will use is known as Slater's Rules (J.C. Slater, *Phys Rev* **1930**, 36, 57).

Slater's Rules

The general principle behind Slater's Rule is that the actual charge felt by an electron is equal to what you'd expect the charge to be from a certain number of protons, but minus a certain amount of charge from other electrons. Slater's rules allow you to estimate the effective nuclear charge Z_{eff} from the real number of protons in the nucleus and the effective shielding of electrons in each orbital "shell" (e.g., to compare the effective nuclear charge and shielding 3d and 4s in transition metals). Slater's rules are fairly simple and produce fairly accurate predictions of things like the electron configurations and ionization energies.

SLATER'S RULES

- **Step 1:** Write the electron configuration of the atom in the following form:

(1s) (2s, 2p) (3s, 3p) (3d) (4s, 4p) (4d) (4f) (5s, 5p) . . .

- **Step 2:** Identify the electron of interest, and ignore all electrons in higher groups (to the right in the list from Step 1). These do not shield electrons in lower groups
- **Step 3:** Slater's Rules is now broken into two cases:
 - the shielding experienced by an s- or p- electron,
 - electrons within same group shield **0.35**, except the 1s which shield **0.30**
 - electrons within the n-1 group shield **0.85**
 - electrons within the n-2 or lower groups shield **1.00**
 - the shielding experienced by nd or nf valence electrons
 - electrons within same group shield **0.35**
 - electrons within the lower groups shield **1.00**

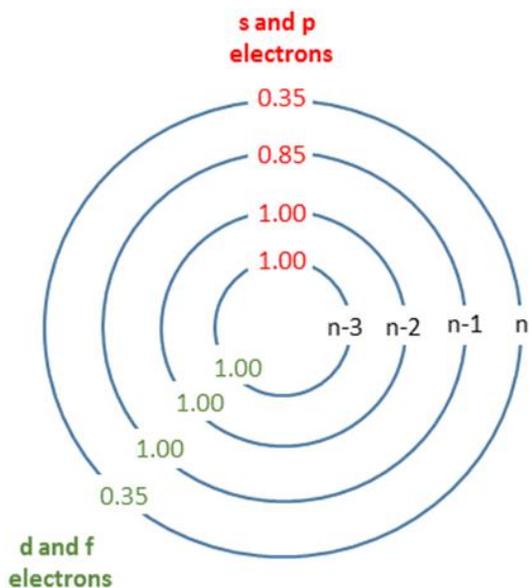


Figure: Graphical depiction of Slater's rules with shielding constants indicated.

Shielding happens when electrons in lower valence shells (or the same valence shell) provide a repulsive force to valence electrons, thereby "negating" some of the attractive force from the positive nucleus. Electrons really close to the atom ($n-2$ or lower) pretty much just look like protons, so they completely negate. As electrons get closer to the electron of interest, some more complex interactions happen that reduce this shielding.

EXAMPLE: The Shielding of 2p Electrons of Nitrogen Atoms

What is the shielding constant experienced by a 2p electron in the bromine atom?

Given: Nitrogen (N)

Asked for: S, the shielding constant, for a 2p electron

Strategy:

- Determine the electron configuration of nitrogen, then write it in the appropriate form.
- Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A N: $1s^2 2s^2 2p^3$

N: $(1s^2)(2s^2, 2p^3)$

Solution B

$$S[2p] = (0.85 \cdot 2) + (0.35 \cdot 4) = 3.10$$

- the 1s electrons shield the other 2p electron to 0.85 "charges".
- the 2s and 2p electrons shield the other 2p electron equally at 0.35 "charges".

EXAMPLE: The Shielding of 3d Electrons of Bromine Atoms

What is the shielding constant experienced by a $3d$ electron in the bromine atom?

Given: Bromine (Br)

Asked for: S , the shielding constant, for a $3d$ electron

Strategy:

Determine the electron configuration of bromine, then write it in the appropriate form.

Use the appropriate Slater Rule to calculate the shielding constant for the electron.

Solution A Br: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$

Br: $(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^{10})(4s^2, 4p^5)$

Ignore the group to the right of the $3d$ electrons. These do not contribute to the shielding constant.

Solution B $S[3d] = (1.00 \cdot 18) + (0.35 \cdot 9) = 21.15$

Calculating Z_{eff}

As discussed previously, Z_{eff} can be calculated by subtracting the magnitude of shielding from the total nuclear charge and the effective nuclear charge of an atom is given by the equation:

$$Z_{\text{eff}} = Z - S$$

EXAMPLE: What is the effective nuclear charge experienced by a valence p - electron in boron?

Given: Boron (B)

Asked for: Z_{eff} for a valence p - electron

Strategy:

- Determine the electron configuration of boron and identify the electron of interest.
- Use the appropriate Slater Rule to calculate the shielding constant for the electron.
- Use the Periodic Table to determine the actual nuclear charge for boron.
- Determine the effective nuclear constant.

Solution:

A B: $1s^2 2s^2 2p^1$. The valence p - electron in boron resides in the $2p$ subshell.

B: $(1s^2)(2s^2, 2p^1)$

B $S[2p] = 1.00(0) + 0.85(2) + 0.35(2) = 2.40$

C $Z = 5$

D $Z_{\text{eff}} = 2.60$

Atomic Radii

Atomic radii is useful for determining many aspects of chemistry such as various physical and chemical properties. The periodic table greatly assists in determining atomic radius and presents a number of trends.

Definition

Atomic radius is generally stated as being the total distance from an atom's nucleus to the outermost orbital of electron. In simpler terms, it can be defined as something similar to the radius of a circle, where the center of the circle is the nucleus and the outer edge of the circle is the outermost orbital of electron. As you begin to move across or down the periodic table, trends emerge that help explain how atomic radii change.

The effective nuclear charge (Z_{eff}) of an atom is the net positive charge felt by the valence electron. Some positive charge is shielded by the core electrons therefore the total positive charge is not felt by the valence electron. A detailed description of shielding and effective nuclear charge can be found here. Z_{eff} greatly affects the atomic size of an atom. So as the Z_{eff} decreases, the atomic radius will grow as a result because there is more screening of the electrons from the nucleus, which decreases the attraction between the nucleus and the electron. Since Z_{eff} decreases going down a group and right to left across the periodic table, the atomic radius will *increase* going down a group and right to left across the periodic table.

Types of Radius with Respect to Types of Bonds

Determining the atomic radii is rather difficult because there is an uncertainty in the position of the outermost electron – we do not know exactly where the electron is. This phenomenon can be explained by the Heisenberg Uncertainty Principle. To get a precise measurement of the radius, but still not an entirely correct measurement, we determine the radius based on the distance between the nuclei of two bonded atoms. The radii of atoms are therefore determined by the bonds they form. An atom will have different radii depending on the bond it forms; so there is no fixed radius of an atom.

Covalent Radius

When a covalent bond is present between two atoms, the covalent radius can be determined. When two atoms of the same element are covalently bonded, the radius of each atom will be half the distance between the two nuclei because they equally attract the electrons. The distance between two nuclei will give the diameter of an atom, but you want the radius which is half the diameter.

Covalent radii will increase in the same pattern as atomic radii. The reason for this trend is that the bigger the radii, the further the distance between the two nuclei. See explanation for Z_{eff} for more details.

The covalent radius depicted below in Figure will be the same for both atoms because they are of the same element as shown by X.

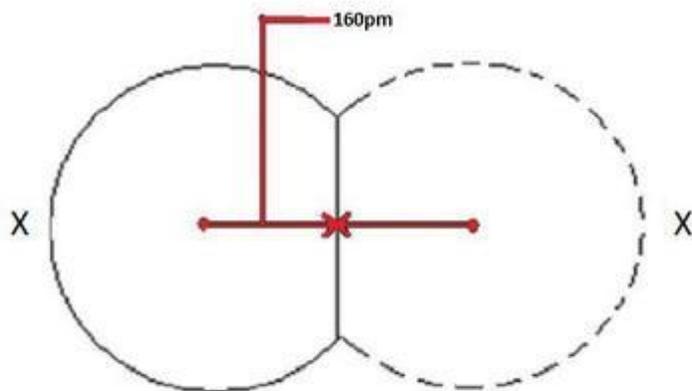


Figure: *Covalent radii*

Ionic Radius

The ionic radius is the radius of an atom forming ionic bond or an ion. The radius of each atom in an ionic bond will be different than that in a covalent bond. This is an important concept. The reason for the variability in radius is due to the fact that the atoms in an ionic bond are of greatly different size. One of the atoms is a cation, which is smaller in size, and the other atom is an anion which is a lot larger in size. So in order to account for this difference, one must get the total distance between the two nuclei and divide the distance according to atomic size. The bigger the atomic size, the larger radius it will have. This is depicted in Figure 2 as shown below where the cation is displayed on the left as X^+ , and clearly has a smaller radius than the anion, which is depicted as Y^- on the right.

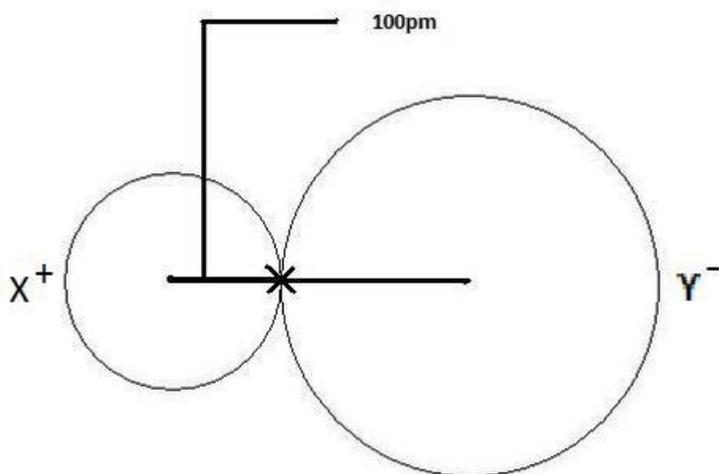


Figure: *Ionic radii*

Metallic Radius

The metallic radius is the radius of an atom joined by metallic bond. The metallic radius is half of the total distance between the nuclei of two adjacent atoms in a metallic cluster. Since a metal will be a group of atoms of the same element, the distance of each atom will be the same.

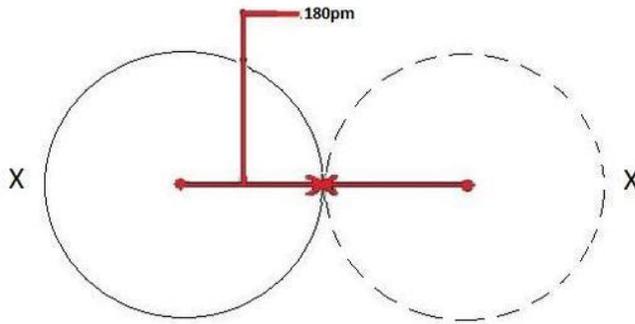
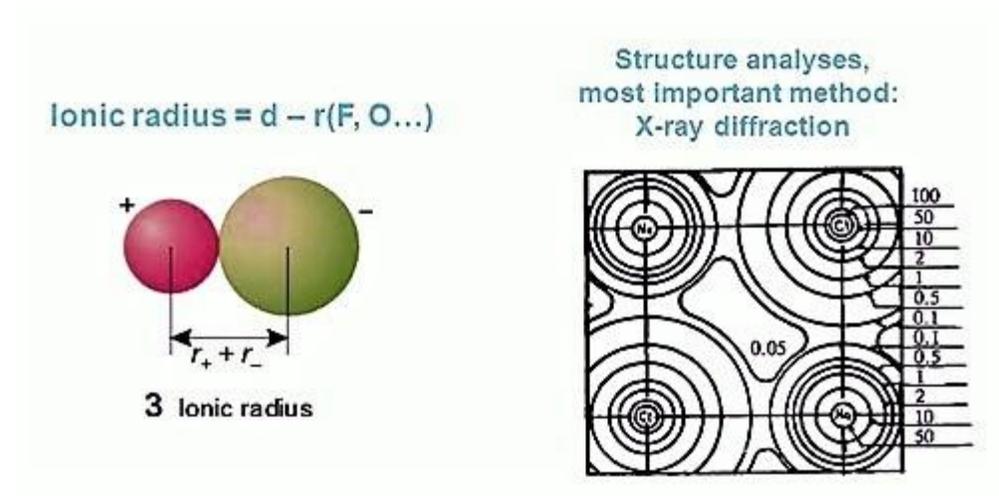


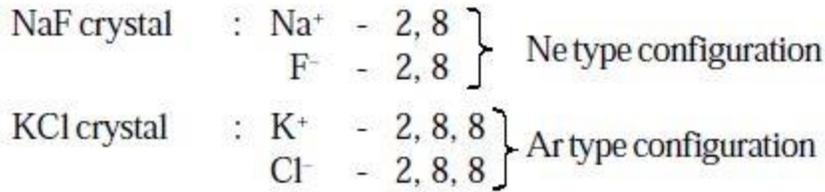
Figure: Metallic radii from metallic bonding

Calculation of Ionic Radii in Pauling's Method



The radius of an isolated ion is complicated to define. Theoretically, the radius of an ion extends to infinity. So the absolute radius of an ion is not doable to determine. The radius is evaluated from the experimental space between two nearest neighbors.

Pauling has calculated the radii of the ions on the basis of the observed internuclear distances in four crystals namely NaF, KCl, RbBr, and CsI; this calculation named Pauling's Method. In each ionic crystal, the cations and anions are isoelectronic with inert gas configuration.



Further the following two assumptions are made to assign the ionic radii.

(i) The cations and anions of an ionic crystal are assumed to be in contact with each other and hence the sum of their radii will be equal to the inter nuclear distance between them.

$$r(\text{C}^+) + r(\text{A}^-) = d(\text{C}^+ - \text{A}^-) \dots \dots \dots (1)$$

where,

$r(\text{C}^+)$ – radius of cation, C^+

$r(\text{A}^-)$ – radius of anion, A^-

$d(\text{C}^+ - \text{A}^-)$ – internuclear distance between C^+ and A^- ions in $\text{C}^+ \text{A}^-$ ionic crystal

(ii) For a given noble gas configuration, the radius of an ion is inversely proportional to its effective nuclear charge. i.e.

$$r(\text{C}^+) \propto 1/Z^*(\text{C}^+) \dots \dots \dots (2)$$

$$r(\text{A}^-) \propto 1/Z^*(\text{A}^-) \dots \dots \dots (3)$$

where, $Z^*(\text{C}^+)$ & $Z^*(\text{A}^-)$ are the effective nuclear charges of cation (C^+) and anion (A^-) respectively. On combining (2) & (3)

$$r(\text{C}^+)/r(\text{A}^-) = Z^*(\text{A}^-)/Z^*(\text{C}^+) \dots \dots \dots (4)$$

Hence the above two equations (1) & (4) can be used to evaluate the values of $r(\text{C}^+)$ and $r(\text{A}^-)$ provided that the values of $d(\text{C}^+ - \text{A}^-)$, $Z^*(\text{C}^+)$ and $Z^*(\text{A}^-)$ are known.

When a neutral atom gains an electron to become an anion (-ve ion), its radius increases. This is projected due to the increase in the number of electrons which the similar nuclear charge has to hold. The force of attraction on the electrons decreases and so the radius increases.

Li ⁺ 0.60	Be ²⁺ 0.31	B ³⁺ 0.20	C ⁴⁺ 0.15	O ²⁻ 1.40	F ⁻ 1.36
Na ⁺ 0.95	Mg ²⁺ 0.65	Al ³⁺ 0.50	Si ⁴⁺ 0.41	S ²⁻ 1.84	Cl ⁻ 1.81
K ⁺ 1.33	Ca ²⁺ 0.99			Se ²⁻ 1.98	Br ⁻ 1.95
Rb ⁺ 1.48	Sr ²⁺ 1.33	Zn ²⁺ 0.74		Te ²⁻ 2.21	I ⁻ 2.16
Cs ⁺ 1.69	Ba ²⁺ 1.35				

Table: Pauling set of ionic radii

Linus Pauling was the original scientist to explain the phenomena of electronegativity. The best method to explain his method is to look at an imaginary molecule that we will call XY. By comparing the considered X-Y bond energy with the theoretical X-Y bond energy (computed as the average of the X-X bond energy and the Y-Y bond energy), we can explain the comparative affinities of these two atoms with deference to each other.

$$\Delta \text{ Bond Energies} = (X-Y)_{\text{measured}} - (X-Y)_{\text{expected}}$$

If the electronegativities of X and y are similar, then we would imagine the calculated bond energy to equal the theoretical (expected) bond energy and consequently, the Δ bond energies would be zero. If the electronegativities of these atoms are not similar, we would see a polar molecule where one atom would start to pull electron density toward itself, causing it to become moderately negative.

The number of positive charges in the nucleus resolves both the number of electrons that enclose an atom and the number of electrons that can be misplaced or gained to form ions. Thus as the charge on the ion becomes more positive, there will be fewer electrons and the ion will have a lesser radius.

As the charge on the ion becomes more negative, there will be more electrons and the ion will have a bigger radius. As the atomic figure increases in any given feature of the Periodic Table, the number of protons and electrons increases and thus the size of the atom or ion increases.

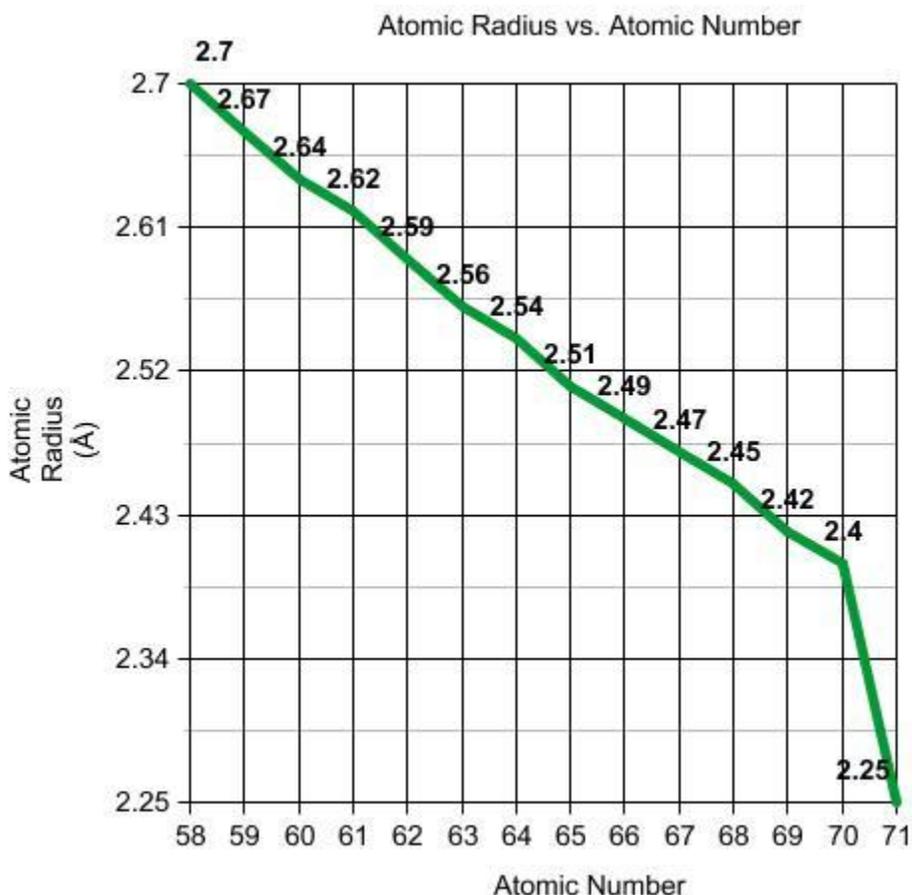
Lanthanide Contraction

The Lanthanide Contraction describes the atomic radius trend that the Lanthanide series exhibit. Another important feature of the The Lanthanide Contraction refers to the fact that the 5s and 5p orbitals penetrate the 4f sub-shell so the 4f orbital is not shielded from the increasing nuclear change, which causes the atomic radius of the atom to decrease. This decrease in size continues throughout the series.

Introduction

The Lanthanide Contraction applies to all 14 elements included in the Lanthanide series. This series includes Cerium(Ce), Praseodymium(Pr), Neodymium(Nd), Promethium(Pm), Samarium(Sm), Europium(Eu), Gadolinium(Gd), Terbium(Tb), Dysprosium(Dy), Holmium(Ho), Erbium(Er), Thulium(Tm), Ytterbium(Yb), and Lutetium(Lu). The atomic radius, as according to the Lanthanide Contraction, of these elements decreases as the

atomic number increases. We can compare the elements Ce and Nd by looking at a periodic table. Ce has an atomic number of 58 and Nd has an atomic number of 60. Which one will have a smaller atomic radius? Nd will because of its larger atomic number.

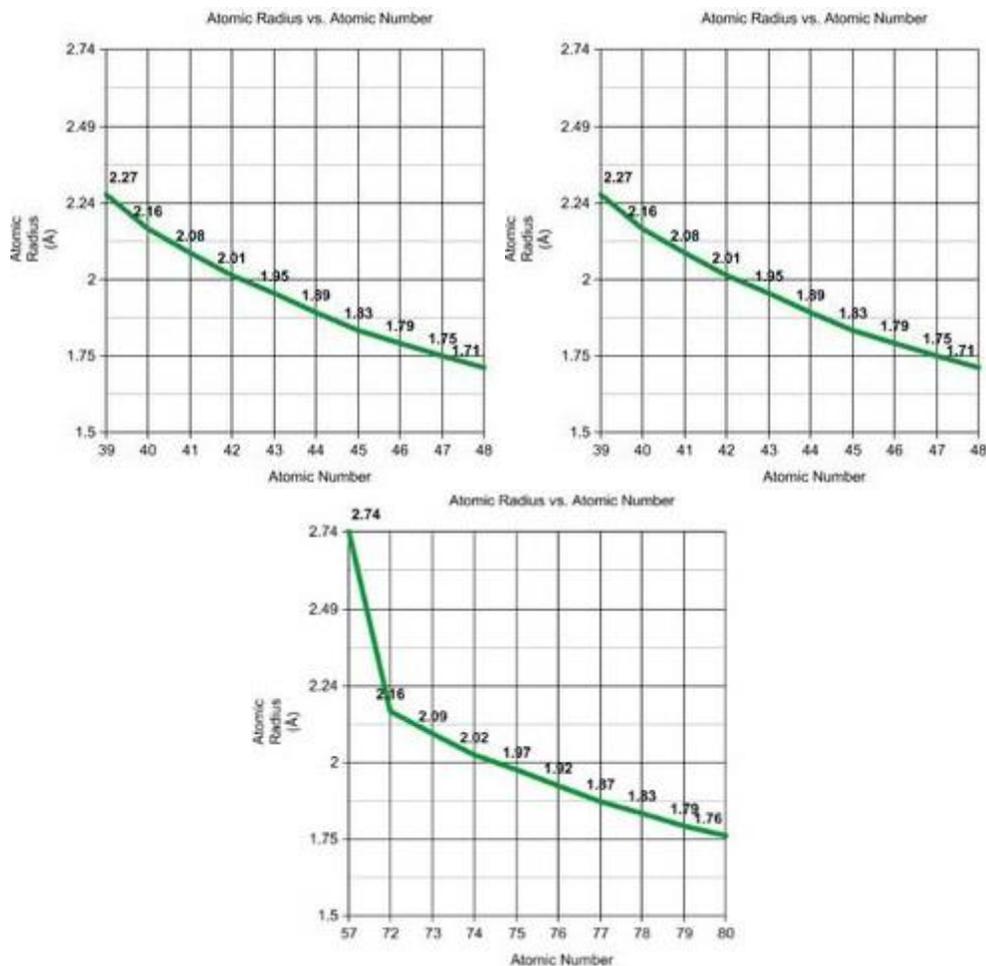


The graph shows the atomic radius decreasing as the atomic number is increasing, Lanthanide Contraction.

Shielding and its Effects on Atomic Radius

The Lanthanide Contraction is the result of a poor shielding effect of the 4f electrons. The shielding effect is described as the phenomenon by which the inner-shell electrons shield the outer-shell electrons so they are not effected by nuclear charge. So when the shielding is not as good, this would mean that the positively charged nucleus has a greater attraction to the electrons, thus decreasing the atomic radius as the atomic number increases. The s orbital has the greatest shielding while f has the least and p and d in between the two with p being greater than d.

The Lanthanide Contraction can be seen by comparing the elements with f electrons and those without f electrons in the d block orbital. Pd and Pt are such elements. Pd has 4d electrons while Pt has 5d and 4f electrons. These 2 elements have roughly the same atomic radius. This is due to Lanthanide Contraction and shielding. While we would expect Pt to have a significantly larger radius because more electrons and protons are added, it does not because the 4f electrons are poor at shielding. When the shielding is not good there will be a greater nuclear charge, thus pulling the electrons in closer, resulting in a smaller than expected radius.



Row 1 of Periodic Table D block Row 2 Row 3

The graphs depict the atomic radii of the first three rows of transition metals. We can apply the same principle as applied with the elements Pd and Pt to whole rows and columns. As we can see by comparing Row 1 with Row 2, the atomic radii differ greatly between the elements, but if we compare Row 2 with Row 3, the atomic radii do not have much difference. Elements with atomic number 23 and 41 lie in the same column of the periodic table and have a significantly large difference in atomic radii (atomic radii increases from Row 1 to Row 2), but elements 41 and 73, also in the same column, only differ slightly. This is the cause of introducing 4f electrons in Row 3. In Row 3, we would expect the elements to carry on the same trend as was witnessed between Rows 1 and 2 (large increase in atomic radii) but we do not. This is because the 4f orbitals are not doing a great job of shielding.

D Block Contraction (Scandide Contraction)

The d block contraction, also known as the Scandide Contraction, describes the atomic radius trend that the d block elements (Transition metals) experience. Normally the trend for atomic radius, moving across the periodic table is that the atomic radius decreases significantly. In the transition metals with D electrons as we move from left to right across the periodic table, the element's atomic radius only decreases slightly. This is because they have the same amount of s electrons, but are only differing in d electrons. These d electrons are in an inner shell (penultimate shell) and electrons are getting added to this shell, another shell is not created. The d electrons are not good at shielding the nuclear charge, so the atomic radius does not change much as electrons are added. Almost like disregarding the D electrons being added.

Effects on Ionization Energy and Properties

As the proton number increases and the atomic radius decreases, the ionization energy increases. This is due to a more positively charged nucleus and a greater pull on the electrons by the nucleus. A greater pull is the result of an increased effective nuclear charge. Effective nuclear charge is caused by the nucleus having a more positive charge than the negative charge on the electron (net positive charge). The density, melting point, and hardness increase from left to right throughout the Lanthanide Series. The Lanthanide Contraction makes chemical separation of the Lanthanides easier. The Lanthanide Contraction, while making the chemical separation of Lanthanides easier, it makes the separation of elements following the series a bit more difficult.

Relativistic Effect

Relativistic effects are important for fast-moving particles. Because the average speeds of valence electrons are low, it was originally thought [in fact by Dirac (1) himself] that relativity then was unimportant. It has now been known for a while that relativistic effects can strongly influence many chemical properties of the heavier elements. Well-confirmed examples include the yellow color, nobility, and trivalency of gold and the large effects on the bond lengths. A probable, but not explicitly demonstrated, consequence is the liquidity of mercury at room temperature.

In a broad sense, the differences between the sixth period (Cs through Rn) and the preceding fifth period (Rb through Xe) largely result from relativistic effects and the lanthanide contraction (the traditional explanation). This information has been noted in chemistry textbooks for a couple of decades now.

The inner electrons move fast in heavy elements. For the innermost, 1s shell, the average radial velocity is for a nonrelativistic, hydrogenlike approximation

$$[v_r]_{1s} = Z \quad (1)$$

$$= 80 \text{ for Hg} \quad (2)$$

in atomic units, where the speed of light, c , is $137.035999679(94)$ (year 2008 standard value). This leads to a mass increase,

$$m = \gamma m_0 \quad (3)$$

$$\text{where } \gamma = \frac{1}{\sqrt{1 - (v/c)^2}} \quad (4)$$

The increased mass gives a smaller Bohr radius

$$a_0 = \hbar^2/m_e^2. \quad (5)$$

This yields a relativistic contraction and stabilization of all s and most p orbitals of many-electron atoms. The non-relativistic binding energy is $E_n = -Z^2/2n^2$ and the first relativistic correction to it will be of order $E_n^{\text{rel}} = -Z^4/2n^3 c^2$.

For hydrogenlike atoms, an exact solution of the Dirac equation shows that the higher s and p states are percentally as strongly relativistic as their inner counterparts. Moreover, because of the stronger screening of the nuclear attraction by the contracted s and p shells, one obtains in many-electron atoms a relativistic expansion and

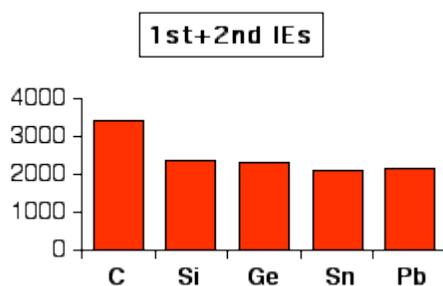
destabilization of d and f shells. These effects are large enough to substantially contribute to the chemical differences between periods 5 (Rb through Xe) and 6 (Cs through Rn) of the periodic table.

Inert pair effect:

The relativistic contraction of the s orbitals increases with the increase of atomic number and consequently, the stability of the s electrons increases towards the heavier elements. Consequently, Hg ($6s^2$) is less reactive than Zn ($4s^2$) or Cd($5s^2$).

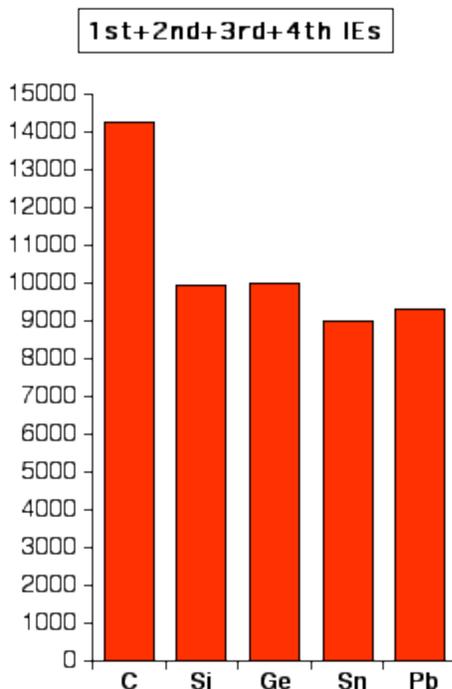
It also explains the increasing stability of +2 oxidation state of Pb($6s^26p^2$) than Sn($5s^25p^2$) or Ge($4s^24p^2$). If the elements in Group 4 form 2+ ions, they lose their p electrons, leaving the s^2 pair unused. For example, to form a lead(II) ion, lead loses its two 6p electrons, but the 6s electrons are left unchanged, an "inert pair".

Ionization energies usually decrease down a group as electrons get further from the nucleus. This is not the case in Group 14. This first chart shows how the total ionization energy needed to form a 2+ ion varies down the group. Values are given in kJ mol^{-1}



Notice the slight increase between tin and lead. This indicates that it is more difficult to remove the p electrons from lead than from tin.

However, examining the pattern for the loss of all four electrons in the chart below, this discrepancy between tin and lead is much more apparent. The relatively large increase between tin and lead is due to the greater difficulty in removing the $6s^2$ pair in lead than the corresponding $5s^2$ pair in tin.



(Again, the values are all in kJ mol⁻¹, and the two charts are on approximately the same scale.)

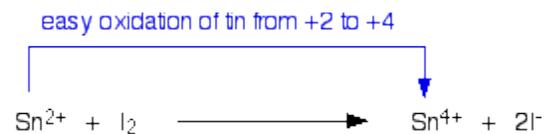
These effects are due to the Theory of Relativity. Heavier elements such as lead experience a relativistic contraction of the electrons that draws the electrons closer to the nucleus than expected. Because they are closer, they are more difficult to remove. The heavier the element, the greater this effect becomes. This affects s electrons to a greater degree than p electrons.

In lead, the relativistic contraction makes it energetically more difficult to remove the 6s electrons than expected. The energy releasing terms when ions are formed (like lattice enthalpy or hydration enthalpy) cannot compensate for this extra energy. Therefore, it makes no energetic sense for lead to form 4+ ions.

Examples from tin chemistry

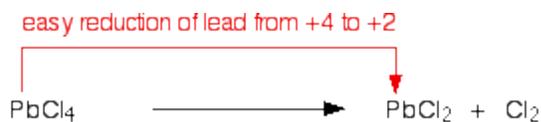
For tin and below, the +2 state is increasingly common, and there is a variety of both tin(II) and tin(IV) compounds. However, tin(IV) is the more stable oxidation state; it is therefore fairly easy to convert tin(II) compounds into tin(IV) compounds. This is best illustrated in that Sn²⁺ ions in solution are strong reducing agents.

A solution containing tin(II) ions (solvated tin(II) chloride, for example) reduces iodine to iodide ions. In the process, the tin(II) ions are oxidized to tin(IV) ions.



Examples from lead chemistry

With lead, the situation is reversed. The lead(II) oxidation state is the more stable; there is a strong tendency for lead(IV) compounds to react, forming lead(II) compounds. Lead(IV) chloride, for example, decomposes at room temperature to give lead(II) chloride and chlorine gas:



For Zn, Cd, Hg, the Ionization potential values should decrease in moving down in a group. The 3rd Ionization potential involving the d electrons decreases from Zn to Cd and drops even more sharply from Cd to Hg. The 1st and 2nd ionization potentials involving the s electrons decrease from Zn to Cd and again increase from Cd to Hg. It is due to more relativistic contraction of the s orbitals compared to the d and f orbitals.

It also explains the sequence of IP values between Au(5d¹⁰6s¹) and Ag(4d¹⁰5s¹). The relativistic effect predicts that the s electrons are more tightly bound and the d electrons are more loosely bound. The first IP involving the s electrons runs as Au(9.22eV) > Ag(7.57eV) while the 2nd IP involving the d electron follows the opposite sequence, Ag(21.5eV) > Au(20.5eV). The more tightly bound ns orbital in Au also explains the higher electron affinity (2.3 eV) of Au than that of either Ag(1.2 eV) or Cu(1.22eV).

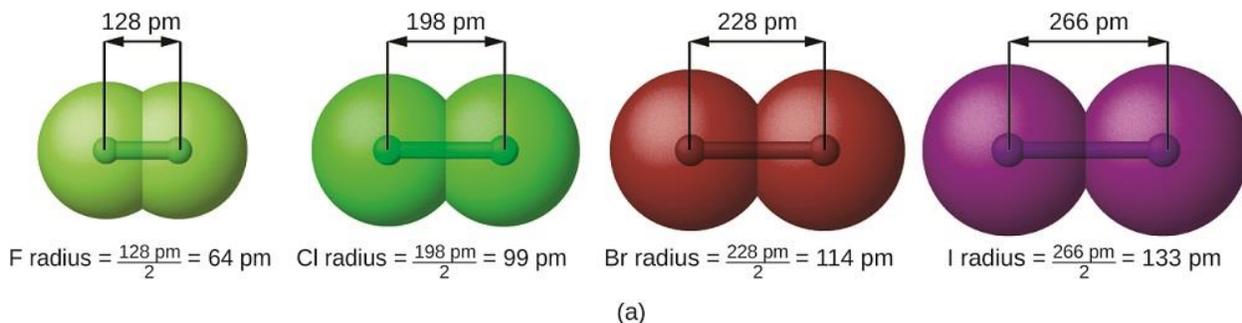
In addition to the effect of lanthanide contraction, the relativistic effects on 6s orbital are also partly responsible for the similarity between the respective congeners (e.g. Zr, Hf, Nb, Ta etc.) of 4d and 5d series.

Stability of the dimeric species, Hg₂²⁺, Au₂ : Due to relativistic contraction, the 6s orbitals of Au and Hg⁺ are very much tightly bound and it explains the high dissociation energy of Au-Au (2.34 eV) compared to Ag-Ag(1.65eV) or Cu-Cu(1.95 eV). Hg⁺ is isoelectronic with Au and the relativistic effect can explain the remarkable stability of Hg₂²⁺ compared to Cd₂²⁺ or Zn₂²⁺.

Stability of higher oxidation states of the 5d series: Due to relativistic effects on the 5d series, the contracted 6s orbital shields the d and f orbitals more effectively from the nuclear charge, so that the d and f electrons got loosely bound. Because of the fact, the 5d electrons can participate more fully for bonding purposes compared to the 4d electrons of the 4d series for which the relativistic effects are less. It explains the higher stabilities of the higher oxidation states of the 5d series.

Periodic Variation in Covalent Radius

The quantum mechanical picture makes it difficult to establish a definite size of an atom. However, there are several practical ways to define the radius of atoms and, thus, to determine their relative sizes that give roughly similar values. We will use the covalent radius, which is defined as one-half the distance between the nuclei of two identical atoms when they are joined by a covalent bond (this measurement is possible because atoms within molecules still retain much of their atomic identity).



Periodic Table of the Elements

Period	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6	Group 7	Group 8	Group 9	Group 10	Group 11	Group 12	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	H																	He
2	Li	Be											B	C	N	O	F	Ne
3	Na	Mg											Al	Si	P	S	Cl	Ar
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn	Uut	Fl	Uup	Lv	Uus	Uuo

(b)

Figure : (a) The radius of an atom is defined as one-half the distance between the nuclei in a molecule consisting of two identical atoms joined by a covalent bond. The atomic radius for the halogens increases down the group as n increases. (b) Covalent radii of the elements are shown to scale. The general trend is that radii increase down a group and decrease across a period.

We know that as we scan down a group, the principal quantum number, n , increases by one for each element. Thus, the electrons are being added to a region of space that is increasingly distant from the nucleus. Consequently, the size of the atom (and its covalent radius) must increase as we increase the distance of the outermost electrons from the nucleus. The trends for the entire periodic table can be seen in Figure.

as we move across a period from left to right, we generally find that each element has a smaller covalent radius than the element preceding it. This might seem counterintuitive because it implies that atoms with more electrons have a smaller atomic radius. This can be explained with the concept of effective nuclear charge, Z_{eff} . This is the pull exerted on a specific electron by the nucleus, taking into account any electron–electron repulsions. For hydrogen, there is only one electron and so the nuclear charge (Z) and the effective nuclear charge (Z_{eff}) are equal. For all other atoms, the inner electrons partially *shield* the outer electrons from the pull of the nucleus, and thus:

$$Z_{\text{eff}} = Z - \text{shielding}$$

Shielding is determined by the probability of another electron being between the electron of interest and the nucleus, as well as by the electron–electron repulsions the electron of interest encounters. Core electrons are adept at shielding, while electrons in the same valence shell do not block the nuclear attraction experienced by each other as efficiently. Thus, each time we move from one element to the next across a period, Z increases by one, but the

shielding increases only slightly. Thus, Z_{eff} increases as we move from left to right across a period. The stronger pull (higher effective nuclear charge) experienced by electrons on the right side of the periodic table draws them closer to the nucleus, making the covalent radii smaller.

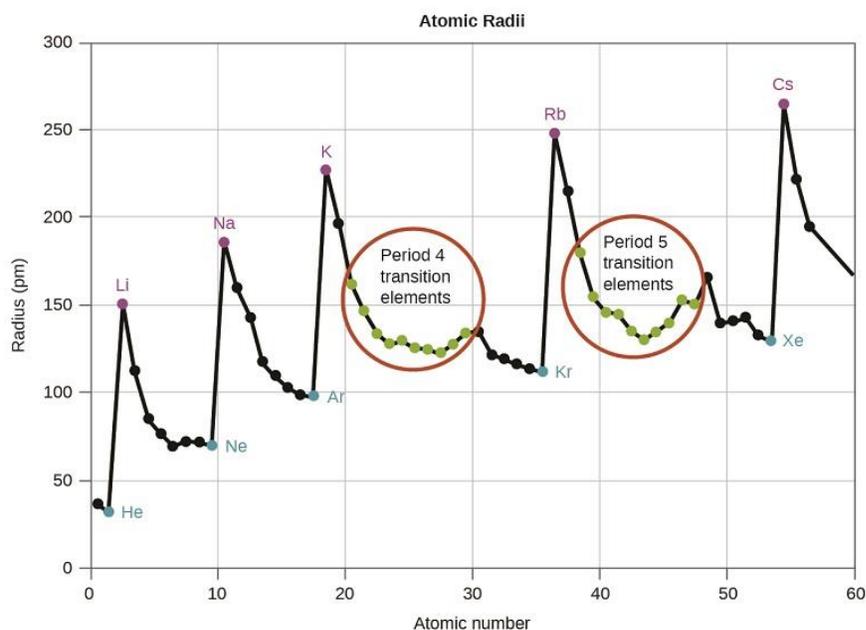


Figure 6: Within each period, the trend in atomic radius decreases as Z increases; for example, from K to Kr. Within each group (e.g., the alkali metals shown in purple), the trend is that atomic radius increases as Z increases.

Thus, as we would expect, the outermost or valence electrons are easiest to remove because they have the highest energies, are shielded more, and are farthest from the nucleus. As a general rule, when the representative elements form cations, they do so by the loss of the ns or np electrons that were added last in the Aufbau process. The transition elements, on the other hand, lose the ns electrons before they begin to lose the $(n - 1)d$ electrons, even though the ns electrons are added first, according to the Aufbau principle.

Variation in Ionic Radii

Ionic radius is the measure used to describe the size of an ion. A cation always has fewer electrons and the same number of protons as the parent atom; it is smaller than the atom from which it is derived (Figure 6.5.36.5.3). For example, the covalent radius of an aluminum atom ($1s^2 2s^2 2p^6 3s^2 3p^1$) is 118 pm, whereas the ionic radius of an Al^{3+} ($1s^2 2s^2 2p^6$) is 68 pm. As electrons are removed from the outer valence shell, the remaining core electrons occupying smaller shells experience a greater effective nuclear charge Z_{eff} (as discussed) and are drawn even closer to the nucleus.



Figure : The radius for a cation is smaller than the parent atom (Al), due to the lost electrons; the radius for an anion is larger than the parent (S), due to the gained electrons.

Cations with larger charges are smaller than cations with smaller charges (e.g., V^{2+} has an ionic radius of 79 pm, while that of V^{3+} is 64 pm). Proceeding down the groups of the periodic table, we find that cations of successive elements with the same charge generally have larger radii, corresponding to an increase in the principal quantum number, n .

An anion (negative ion) is formed by the addition of one or more electrons to the valence shell of an atom. This results in a greater repulsion among the electrons and a decrease in Z_{eff} per electron. Both effects (the increased number of electrons and the decreased Z_{eff}) cause the radius of an anion to be larger than that of the parent atom. For example, a sulfur atom ($[\text{Ne}]3s^23p^4$) has a covalent radius of 104 pm, whereas the ionic radius of the sulfide anion ($[\text{Ne}]3s^23p^6$) is 170 pm. For consecutive elements proceeding down any group, anions have larger principal quantum numbers and, thus, larger radii.

Atoms and ions that have the same electron configuration are said to be isoelectronic. Examples of isoelectronic species are N^{3-} , O^{2-} , F^- , Ne, Na^+ , Mg^{2+} , and Al^{3+} ($1s^22s^22p^6$). Another isoelectronic series is P^{3-} , S^{2-} , Cl^- , Ar, K^+ , Ca^{2+} , and Sc^{3+} ($[\text{Ne}]3s^23p^6$). For atoms or ions that are isoelectronic, the number of protons determines the size. The greater the nuclear charge, the smaller the radius in a series of isoelectronic ions and atoms.

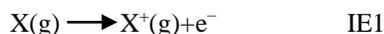
Secondary Periodicity:

Discuss the trend in atomic size: Si, Ge, Sn

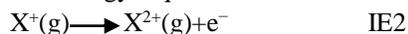
Comparing the size of Si, Ge, Sn it is evident from the electronic configuration there occurs an increase in principal quantum no which should lead to increase in atomic size. Also, from the electronic configuration of Ge, it has 10 3d electrons. Poor screening effect leading to increase in effective nuclear charge which leads to decrease in atomic size. Here, the effect of d contraction predominates over the increase in principal quantum no. Thus, the size of Ge is lesser than Si. As we move from Ge to Sn, it is evident from electronic configuration the only factor is the increase of principal quantum no. which accounts for increase in atomic size.

Variation in Ionization Energies

The amount of energy required to remove the most loosely bound electron from a gaseous atom in its ground state is called its first ionization energy (IE_1). The first ionization energy for an element, X, is the energy required to form a cation with +1 charge:



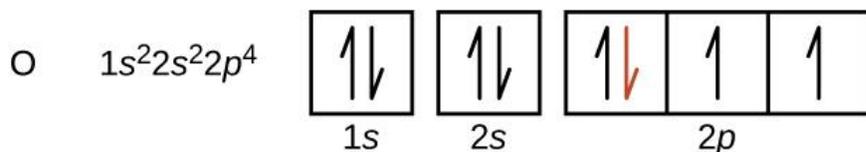
The energy required to remove the second most loosely bound electron is called the second ionization energy (IE_2).



The energy required to remove the third electron is the third ionization energy, and so on. Energy is always required to remove electrons from atoms or ions, so ionization processes are endothermic and IE values are always positive. For larger atoms, the most loosely bound electron is located farther from the nucleus and so is easier to remove. Thus, as size (atomic radius) increases, the ionization energy should decrease. Relating this logic to what we have just learned about radii, we would expect first ionization energies to decrease down a group and to increase across a period.

Figure: This version of the periodic table shows the first ionization energy of (IE_1), in kJ/mol, of selected elements.

Another deviation occurs as orbitals become more than one-half filled. The first ionization energy for oxygen is slightly less than that for nitrogen, despite the trend in increasing IE_1 values across a period. Looking at the orbital diagram of oxygen, we can see that removing one electron will eliminate the electron–electron repulsion caused by pairing the electrons in the $2p$ orbital and will result in a half-filled orbital (which is energetically favorable). Analogous changes occur in succeeding periods (note the dip for sulfur after phosphorus in Figure)



Removing an electron from a cation is more difficult than removing an electron from a neutral atom because of the greater electrostatic attraction to the cation. Likewise, removing an electron from a cation with a higher positive charge is more difficult than removing an electron from an ion with a lower charge. Thus, successive ionization energies for one element always increase. As seen in Table , there is a large increase in the ionization energies (color change) for each element. This jump corresponds to removal of the core electrons, which are harder to remove than the valence electrons. For example, Sc and Ga both have three valence electrons, so the rapid increase in ionization energy occurs after the third ionization.

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
K	418.8	3051.8	4419.6	5876.9	7975.5	9590.6	11343
Ca	589.8	1145.4	4912.4	6490.6	8153.0	10495.7	12272.9
Sc	633.1	1235.0	2388.7	7090.6	8842.9	10679.0	13315.0
Ga	578.8	1979.4	2964.6	6180	8298.7	10873.9	13594.8
Ge	762.2	1537.5	3302.1	4410.6	9021.4	Not available	Not available
As	944.5	1793.6	2735.5	4836.8	6042.9	12311.5	Not available

Table : Successive Ionization Energies for Selected Elements (kJ/mol)

Variation in Electron Affinities

The electron affinity [EA] is the energy change for the process of adding an electron to a gaseous atom to form an anion (negative ion).



This process can be either endothermic or exothermic, depending on the element. The EA of some of the elements is given in Figure . You can see that many of these elements have negative values of EA, which means that energy is released when the gaseous atom accepts an electron. However, for some elements, energy is required for the atom to become negatively charged and the value of their EA is positive. Just as with ionization energy, subsequent EA values are associated with forming ions with more charge. The second EA is the energy associated with adding an electron to an anion to form a -2 ion, and so on.

Electron Affinity Values for Selected Elements (kJ/mol)

Period	Group 1	Group 2	Group 13	Group 14	Group 15	Group 16	Group 17	Group 18
1	H -72							He +20*
2	Li -60	Be +240*	B -23	C -123	N 0	O -141	F -322	Ne -30
3	Na -53	Mg +230*	Al -44	Si -120	P -74	S -20	Cl -348	Ar +35*
4	K -48	Ca +150*						
5	Rb -46	Sr +160*						
6	Cs -45	Ba +50*						
7	Fr -45	Ra +50*						

* Calculated value

Figure: This version of the periodic table displays the electron affinity values (in kJ/mol) for selected elements.:

As we might predict, it becomes easier to add an electron across a series of atoms as the effective nuclear charge of the atoms increases. We find, as we go from left to right across a period, EAs tend to become more negative. The exceptions found among the elements of group 2 (2A), group 15 (5A), and group 18 (8A) can be understood based on the electronic structure of these groups. The noble gases, group 18 (8A), have a completely filled shell and the incoming electron must be added to a higher n level, which is more difficult to do. Group 2 (2A) has a filled ns subshell, and so the next electron added goes into the higher energy np , so, again, the observed EA value is not as the trend would predict. Finally, group 15 (5A) has a half-filled np subshell and the next electron must be paired with an existing np electron. In all of these cases, the initial relative stability of the electron configuration disrupts the trend in EA.

We also might expect the atom at the top of each group to have the largest EA; their first ionization potentials suggest that these atoms have the largest effective nuclear charges. However, as we move down a group, we see that the second element in the group most often has the greatest EA. The reduction of the EA of the first member can be attributed to the small size of the $n = 2$ shell and the resulting large electron–electron repulsions. For example, chlorine, with an EA value of -348 kJ/mol, has the highest value of any element in the periodic table. The EA of fluorine is -322 kJ/mol. When we add an electron to a fluorine atom to form a fluoride anion (F^-), we add an electron to the $n = 2$ shell. The electron is attracted to the nucleus, but there is also significant repulsion from the other electrons already present in this small valence shell. The chlorine atom has the same electron configuration in the valence shell, but because the entering electron is going into the $n = 3$ shell, it occupies a considerably larger region of space and the electron–electron repulsions are reduced. The entering electron does not experience as much repulsion and the chlorine atom accepts an additional electron more readily.

The properties discussed in this section (size of atoms and ions, effective nuclear charge, ionization energies, and electron affinities) are central to understanding chemical reactivity. For example, because fluorine has an energetically favorable EA and a large energy barrier to ionization (IE), it is much easier to form fluorine anions than cations. Metallic properties including conductivity and malleability (the ability to be formed into sheets) depend on having electrons that can be removed easily. Thus, metallic character increases as we move down a group and decreases across a period in the same trend observed for atomic size because it is easier to remove an electron that is farther away from the nucleus.

Electronegativity

Valence electrons of both atoms are always involved when those two atoms come together to form a chemical bond. Chemical bonds are the basis for how elements combine with one another to form compounds. When these chemical bonds form, atoms of some elements have a greater ability to attract the valence electrons involved in the bond than other elements.

Electronegativity is a measure of the ability of an atom to attract the electrons when the atom is part of a compound. Electronegativity differs from electron affinity because electron affinity is the actual energy released when an atom gains an electron. Electronegativity is not measured in energy units, but is rather a relative scale. All elements are compared to one another, with the most electronegative element, fluorine, being assigned an electronegativity value of 3.98. Fluorine attracts electrons better than any other element. The table below shows the electronegativity values for the elements.

PAULING ELECTRONEGATIVITY VALUES																										
1																	7	B	8	C	9	N	10	O	11	F
2	Li	Be															13	Al	14	Si	15	P	16	S	17	Cl
3	Na	Mg															31	Ga	32	Ge	33	As	34	Se	35	Br
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	39	In	40	Sn	41	Sb	42	Te	43	I				
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	49	Hg	50	Tl	51	Pb	52	Bi	53	Po	54	At		
6	Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	81	Hg	82	Tl	83	Pb	84	Bi	85	Po	86	At			
7	Fr	Ra																								

Figure: The electronegativity scale was developed by Nobel Prize winning American chemist Linus Pauling. The largest electronegativity (3.98) is assigned to fluorine and all other electronegativity measurements are on a relative scale.

Since metals have few valence electrons, they tend to increase their stability by losing electrons to become cations. Consequently, the electronegativities of metals are generally low. Nonmetals have more valence electrons and increase their stability by gaining electrons to become anions. The electronegativities of nonmetals are generally high.

Trends

Electronegativities generally increase from left to right across a period. This is due to an increase in nuclear charge. Alkali metals have the lowest electronegativities, while halogens have the highest. Because most noble gases do not form compounds, they do not have electronegativities. Note that there is little variation among the transition metals. Electronegativities generally decrease from top to bottom within a group due to the larger atomic size.

Of the main group elements, fluorine has the highest electronegativity (EN = 4.0) and cesium the lowest (EN = 0.79). This indicates that fluorine has a high tendency to gain electrons from other elements with lower electronegativities. We can use these values to predict what happens when certain elements combine.

When the difference between electronegativities is greater than ~1.7, then a complete exchange of electrons occurs. Typically this exchange is between a metal and a nonmetal. For instance, sodium and chlorine will typically combine to form a new compound and each ion becomes isoelectronic with its nearest noble gas. When we compare the EN values, we see that the electronegativity for Na is 0.93 and the value for Cl is 3.2. The absolute difference between ENs is $|0.93 - 3.2| = 2.27$. This value is greater than 1.7, and therefore indicates a complete electron exchange occurs.

Pauling Scale of Electronegativity

Linus Pauling was the original scientist to describe the phenomena of electronegativity. The best way to describe his method is to look at a hypothetical molecule that we will call XY. By comparing the measured X-Y bond energy with the theoretical X-Y bond energy (computed as the average of the X-X bond energy and the Y-Y bond energy), we can describe the relative affinities of these two atoms with respect to each other.

$$\Delta \text{ Bond Energies} = (X-Y)_{\text{measured}} - (X-Y)_{\text{expected}}$$

If the electronegativities of X and Y are the same, then we would expect the measured bond energy to equal the theoretical (expected) bond energy and therefore the Δ bond energies would be zero. If the electronegativities of these atoms are not the same, we would see a polar molecule where one atom would start to pull electron density toward itself, causing it to become partially negative.

By doing some careful experiments and calculations, Pauling came up with a slightly more sophisticated equation for the relative electronegativities of two atoms in a molecule: $EN(X) - EN(Y) = 0.102 (\Delta^{1/2})$. In that equation, the factor 0.102 is simply a conversion factor between kJ and eV to keep the units consistent with bond energies.

By assigning a value of 4.0 to Fluorine (the most electronegative element), Pauling was able to set up relative values for all of the elements. This was when he first noticed the trend that the electronegativity of an atom was determined by its position on the periodic table and that the electronegativity tended to increase as you moved left to right and bottom to top along the table. The range of values for Pauling's scale of electronegativity ranges from Fluorine (most electronegative = 4.0) to Francium (least electronegative = 0.7). Furthermore, if the electronegativity difference between two atoms is very large, then the bond type tends to be more ionic, however if the difference in electronegativity is small then it is a nonpolar covalent bond.

The major drawback of this method is that it is not possible often to have values of X-X bond energy and the Y-Y bond energy by simple thermochemical calculation.

Mulliken Electronegativity

A method for estimating electronegativity was developed by Robert Mulliken (1896–1986; Nobel Prize in Chemistry 1966) who noticed that elements with large first ionization energies tend to have very negative electron affinities and gain electrons in chemical reactions. Conversely, elements with small first ionization energies tend to have slightly negative (or even positive) electron affinities and lose electrons in chemical reactions. Mulliken recognized that an atom's tendency to gain or lose electrons could therefore be described quantitatively by the average of the values of its first ionization energy and the absolute value of its electron affinity.

Robert S. Mulliken proposed that the arithmetic mean of the first ionization energy (E_{I1}) and the electron affinity (E_{ea}) should be a measure of the tendency of an atom to attract electrons. As this definition is not dependent on an arbitrary relative scale, it has also been termed *absolute electronegativity*. Using our definition of electron affinity, we can write Mulliken's original expression for electronegativity as follows: Mulliken's definition used the magnitude of the ionization energy and the electron affinity. By definition, the magnitude of a quantity is a positive number. Our definition of electron affinity produces negative values for the electron affinity for most elements, so vertical lines indicating absolute value are needed in the Equation to make sure that we are adding two positive numbers in the numerator.

$$\chi = |E_{I1} + E_{ea}| / 2$$

Elements with a large first ionization energy and a very negative electron affinity have a large positive value in the numerator of Equation , so their electronegativity is high. Elements with small first ionization energy and a small electron affinity have a small positive value for the numerator in Equation, so they have a low electronegativity. Inserting the appropriate data into Equation gives a Mulliken electronegativity value for fluorine of 1004.6 kJ/mol. To compare Mulliken's electronegativity values with those obtained by Pauling, Mulliken's values are divided by 252.4 kJ/mol, which gives Pauling's value (3.98).

However, it is more usual to use a linear transformation to transform these absolute values into values that resemble the more familiar Pauling values. For ionization energies and electron affinities in electronvolts:

$$\chi_{\text{Mulliken}} = 0.187(E_{\text{I1}} + E_{\text{ea}}) + 0.17$$

and for energies in kJ/mol,

$$\chi_{\text{Mulliken}} = (1.97 \times 10^{-3})(E_{\text{I1}} + E_{\text{ea}}) + 0.19$$

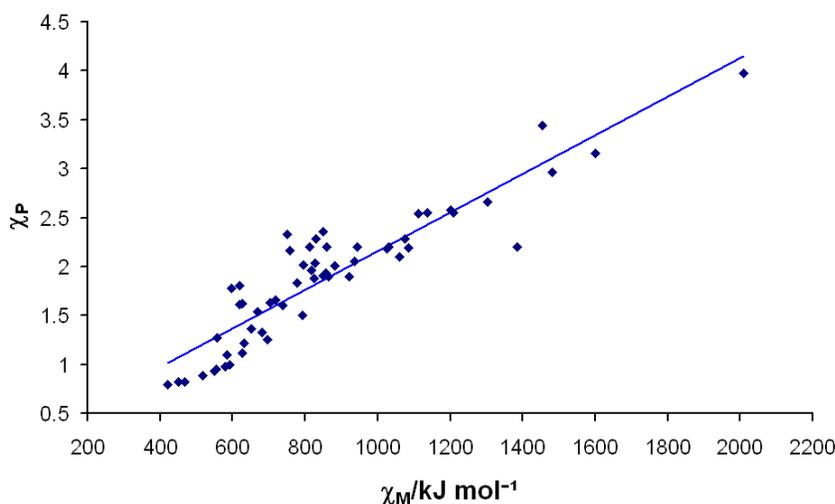
The Mulliken electronegativity can only be calculated for an element for which the electron affinity is known, fifty-seven elements as of 2006. The Mulliken electronegativity of an atom is sometimes said to be the negative of the chemical potential. By inserting the energetic definitions of the ionization potential and electron affinity into the Mulliken electronegativity, it is possible to show that the Mulliken chemical potential is a finite difference approximation of the electronic energy with respect to the number of electrons, i.e.,

$$\mu_{\text{Mulliken}} = -\chi_{\text{Mulliken}} = -E_{\text{I1}} + E_{\text{ea}2}$$

All electronegativity scales give essentially the same results for one element relative to another. Even though the Mulliken scale is based on the properties of individual *atoms* and the Pauling scale is based on the properties of atoms in *molecules*, they both apparently measure the same basic property of an element. In the following discussion, we will focus on the relationship between electronegativity and the tendency of *atoms* to form positive or negative ions. We will therefore be implicitly using the Mulliken definition of electronegativity. Because of the parallels between the Mulliken and Pauling definitions, however, the conclusions are likely to apply to atoms in molecules as well.

Significance

Despite being developed from a very different set of principles than Pauling Electronegativity, which is based on bond dissociation energies, there is a good correlation between Mulliken and Pauling Electronegativities for the atoms, as shown in the plot below.



Although Pauling electronegativities are usually what are found in textbooks, the Mulliken electronegativity more intuitively corresponds to the "ability of an atom to draw electrons toward itself in bonding," and is probably a better indicator of that property. However, because of the good correlation between the two scales, using the Pauling scale is sufficient for most purposes.

Allred-Rochow Electronegativity

Allred-Rochow Electronegativity is a measure that determines the values of the electrostatic force exerted by the effective nuclear charge on the valence electrons. The value of the effective nuclear charges is estimated from Slater's rules. The higher charge, the more likely it will attract electrons. Although, Slater's rule are partly empirical. So the Allred-Rochow electronegativity is no more rigid than the Pauling Electronegativity.

Slater's rules

Slater's rules are rules that provides the values for the effective nuclear charge concept, or Z_{eff} . These rules are based on experimental data for electron promotion and ionization energies, and Z_{eff} is determined from this equation:

$$Z_{\text{eff}}=Z-S$$

Where

- Z is the nuclear charge,
- Z_{eff} is the effective nuclear charge, and
- S is the shielding constant

Through this equation, this tells us that electron may get reduced nuclear charge due to high shielding. Allred and Rochow used Z_{eff} because it is accurate due to the involvement of shielding that prevents electron to reach its true nuclear charge: Z . When an atom with filled s -shell attracts electrons, those electrons will go to the unfilled p -orbital. Since the electrons have the same negative charge, they will not only repel each other, but also repel the electrons from the filled s -shell. This creates a shielding effect where the inner core electrons will shield the outer core electrons from the nucleus. Not only would the outer core electrons experience effective nuclear charge, but it will make them easily removed from the outer shell. Thus, It is easier for outer electrons to penetrate the p shell, which has little likelihood of being near the nuclear, rather than the s shell. Consider this, each of the outer electron in the (ns, np) group contributes $S = 0.35$, $S = 0.85$ in the $(n - 1)$ shell, and $S = 1.00$ in the $(n - 2)$ or lower shells.

Allred and Rochow were two chemists who came up with the Allred-Rochow Electronegativity values by taking the electrostatic force exerted by effective nuclear charge, Z_{eff} , on the valence electron. To do so, they came up with an equation:

$$\chi_{\text{AR}}=[(3590 \times Z_{\text{eff}})/r_{\text{cov}}^2]+0.744$$

At the time, the values for the covalent radius, r_{cov} , were inaccurate. Allred and Rochow added certain perimeters so that it would more closely correspond to Pauling's electronegativity scale.

According to this scale, the electronegativities increases from left to right just like Pauling's scale because the Z is increasing. As we go down the group, it decreases because of the larger atomic size that increases the distance between the electrons and nucleus
