Chemical periodicity

How atomic structure shapes the periodic table

Our goal in this lesson is to help you understand how the shape and organization of the modern periodic table are direct consequences of the atomic electronic structure of the elements.

We begin with the image you saw in the

preceding lesson, showing the long form of the table with the "block" structure emphasized. You will recall that the two *f* blocks are written at the bottom merely to keep the table from becoming inconveniently wide; these two blocks actually go in between La-Hf and Ac-Db, respectively, in the *d* block.

1 How the periodic table is organized

A very simple way of organizing the chemical elements is to make a long a long horizontal list of the elements in order of their increasing atomic number. It would begin this way:

> H He Li Be B C N O F Ne Na Mg Al Si P S Cl Ar K Ca...

Now if we look at the various physical and chemical *properties* of these elements, we would find that their values tend to increase or decrease with Z in a manner that reveals a repeating pattern— that is, a *periodicity*. For the elements listed above, these breaks can be indicated by the vertical bars shown here in color:

> H **He** | Li Be B C N O F **Ne** | Na Mg Al Si P S Cl **Ar** | Ca ...

Periods

To construct the table, we place each sequence in a separate row, which we call a *period*. The rows are aligned in such a way that the elements in each vertical column possess certain similarities. Thus the first short-period elements H and He are chemically similar to the elements Li and Ne at the beginning and end of the second period. The first period is split in order to place H above Li and He above Ne, thus defining the various *groups*.

Take a moment to see how the above image relates to the complete periodic table, which we reproduce below. Notice how the *d*-block Groups 3 - 12 have been squeezed in beginning at the third period, where Scandium is the first element at which the 3d shell begins to fill.

The "block" nomenclature of the periodic table refers to the sub-orbital type (quantum number l, or s-p-d-f classification) of the highest-energy orbitals that are occupied in a given element.

- For $n=1$ there is no p block, and the s block is split so that helium is placed in the same group as the other inert gases, which it resembles chemically.
- For the second period ($n=2$) there is a p block but no d block; in the usual "long form" of the periodic table it is customary to leave a gap between these two blocks in order to accommodate the d blocks that occur at $n=3$ and above.
- At $n=6$ we introduce an f block, but in order to hold the table to reasonable dimensions the f blocks are placed below the main body of the table.

Groups

Each column of the periodic table is known as a *group*. The elements belonging to a given group bear a strong similarity in their chemical behaviors.

In the past, two different systems of Roman numerals and letters were used to denote the various groups. North Americans added the letter B to denote the d-block groups and A for the others; this is the system shown in the table above.

The the rest of the world used A for the d-block elements and B for the others. In 1985, a new international system was adopted in which the columns were simply labeled 1-18. Although this system was initially resisted by North American chemists

who predicted that it would leave students hopelessly confused, the "one to eighteen" system gradually became accepted as the older chemists died off and the Americans cought up with the rest of the world.

Families

Chemists have long found it convenient to refer to the elements of different groups, and in some cases of spans of groups by the names indicated in the table shown below. The two of these that are most important for you to know are the *noble gases* and the *transition metals*.

2 How electron structures shape the periodic table

The properties of an atom depend ultimately on the number of electrons in the various orbitals, and on the nuclear charge which determines the compactness of the orbitals.

The shell model of the atom

In order to relate the properties of the elements to their locations in the periodic table, it is often convenient to make use of a simplified view of the atom in which the nucleus is surrounded by one or more concentric spherical "shells", each of which consists of the highest-principal quantum number orbitals (always *s*- and *p*-orbitals) that contain at least one electron.

As with any scientific model, the shell model offers a simplified view that helps us to understand and correlate diverse phenomena. The principal simplification here is that it deals only with the **main group elements** of the *s*- and *p*-blocks, omitting the *d*- and *f*-block elements whose properties tend to be less closely tied to their group numbers.
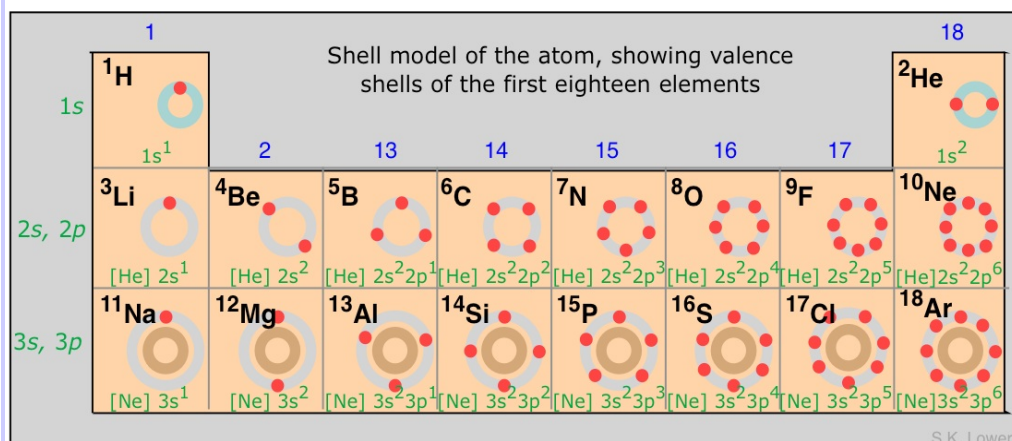
This diagram shows the first three rows of what are known as the *representative elements*— that is, the *s*- and *p*-block elements only. As we move farther down (into the fourth row and below), the presence of
d-electrons exerts a complicating influence which allows elements to exhibit multiple valances. This effect is especially noticeable in the transition-metal elements, and is the reason for not including the d-block with the representative elements.

The electrons (denoted by the red dots) in the outer-most shell of an atom are the ones that interact most readily with other atoms, and thus play a major role in governing the chemistry of an element. Notice the use of noble-gas symbols to simplify the electron-configuration notation.

In particular, the number of outer-shell electrons (which is given by the rightmost digit in the *group number*) is a major determinant of an element's "combining power", or **valence**. The general trend is for an atom to gain or lose electrons, either directly (leading to formation of **ions**) or by sharing electrons with other atoms so as to achieve an outer-shell configuration of s^2p^6. This configuration, known as an **octet**, corresponds to that of one of the noble-gas elements of Group 18.

- the elements in Groups 1, 2 and 13 tend to give up their valence electrons to form positive ions such as Na^+, Mg^{2+} and Al^{3+}, as well as compounds NaH, MgH_2 and AlH_3. The outer-shell configurations of the metal atoms in these species correspond to that of neon.
- elements in Groups 15-17 tend to acquire electrons, forming ions such as P^{3-}, S^{2-} and Cl^- or compounds such as PH_3, H_2S and HCl. The outer-shell configurations of these elements correspond to that of argon.
- the Group 14 elements do not normally form ions at all, but share electrons with other elements in tetravalent compounds such as CH_4.

Effective nuclear charge

Those electrons in the outmost or valence shell are especially important because they are the ones that can engage in the sharing and exchange that is responsible for chemical reactions; how tightly they are bound to the atom determines much of the chemistry of the element. The degree of binding is the result of two opposing forces: the attraction between the electron and the nucleus, and the repulsions between the electron in question and all the other

electrons in the atom. All that matters is the net force, the difference between the nuclear attraction and the totality of the electron-electron repulsions.

We can simplify the shell model even further by imagining that the valence shell electrons are the *only* electrons in the atom, and that the nuclear charge has whatever value would be required to bind these electrons as tightly as is observed experimentally. Because the number of electrons in this model is less than the atomic number Z, the required nuclear charge will also be smaller, and is known as the **effective nuclear charge**. Effective nuclear charge is essentially the positive charge that a valence electron "sees".

> Part of the difference between Z and $Z_{effective}$ is due to other electrons in the valence shell, but this is usually only a minor contributor because these electrons tend to act as if they are spread out in a diffuse spherical shell of larger radius. The main actors here are the electrons in the much more compact inner shells which surround the nucleus and exert what is often called a shielding or "*screening*" effect on the valence electrons.
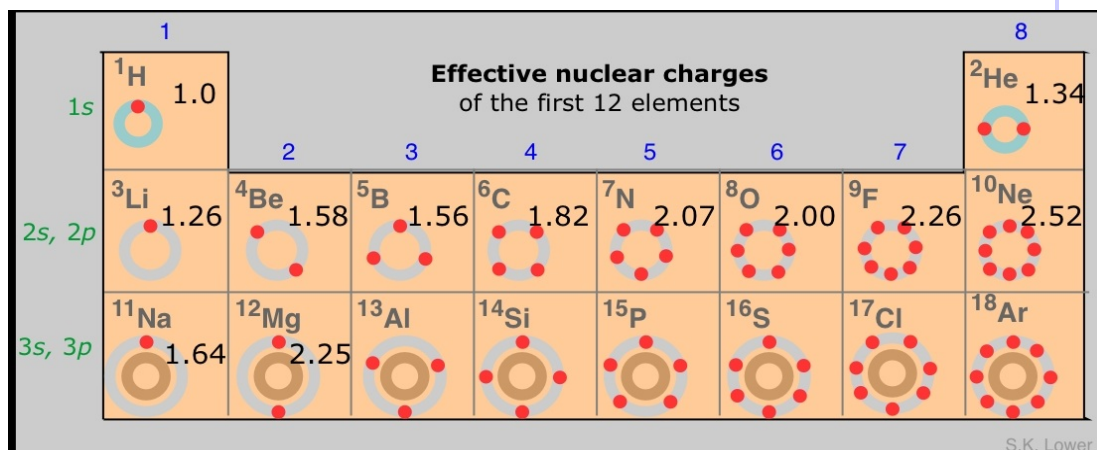
The formula for calculating effective nuclear charge is not very complicated, but we will skip a discussion of it here. An even simpler although rather crude procedure is to just subtract the number of inner-shell electrons from the nuclear charge; the result is a form of effective nuclear charge which is called the *core charge* of the atom.
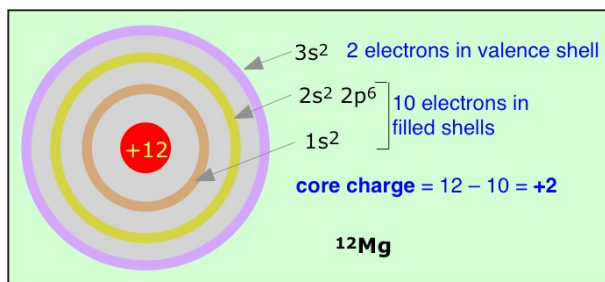
4 Periodic trends in atomic and ionic radii

The original purpose of the periodic table was to organize the the chemical elements in a manner that would make sense of the ways in which the oobserved physical and chemical properties of the elements vary with the atomic number.

In this section, we look at some of these trends and try to understand the reasons for them based on the electron structures of the elements.

Periodic trends in the sizes of atoms

What do we mean by the "size" of an atom?

The concept of "size" is somewhat ambiguous when applied to the scale of atoms and molecules. The reason for this is apparent when you recall that an atom has no definite boundary; there is a finite (but very small) probability of finding the electron of a hydrogen atom, for example, 1 cm, or even 1 km from the nucleus. It is not possible to specify a definite value for the radius of an isolated atom; the best we can do is to define a spherical shell within whose radius some arbitrary percentage of the electron density can be found.
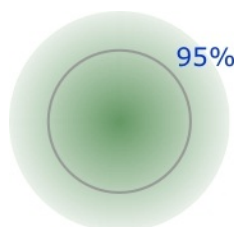
When an atom is combined with other atoms in a solid element or compound, an effective radius can be determined by observing the distances between adjacent rows of atoms in these solids. This is most commonly carried out by X-ray scattering experiments. Because of the different ways in which atoms can aggregate together, several different kinds of atomic radii can be defined.

> Distances on the atomic scale have traditionally been expressed in Ångstrom units (1Å = 10^{-8} cm = 10^{-10} m), but nowadays the picometer is preferred;

A rough idea of the size of a metallic atom can be obtained simply by measuring the *density* of a sample of the metal. This tells us the number of atoms per unit volume of the solid. The atoms are assumed to be spheres of radius r in contact with each other, each of which sits in a cubic box of edge length $2r$. The volume of each box is just the total volume of the solid divided by the number of atoms in that mass of the solid; the atomic radius is the cube root of r.

Although the radius of an atom or ion cannot be measured directly, in most cases it can be inferred from measurements of the distance between adjacent nuclei in a crystalline solid.
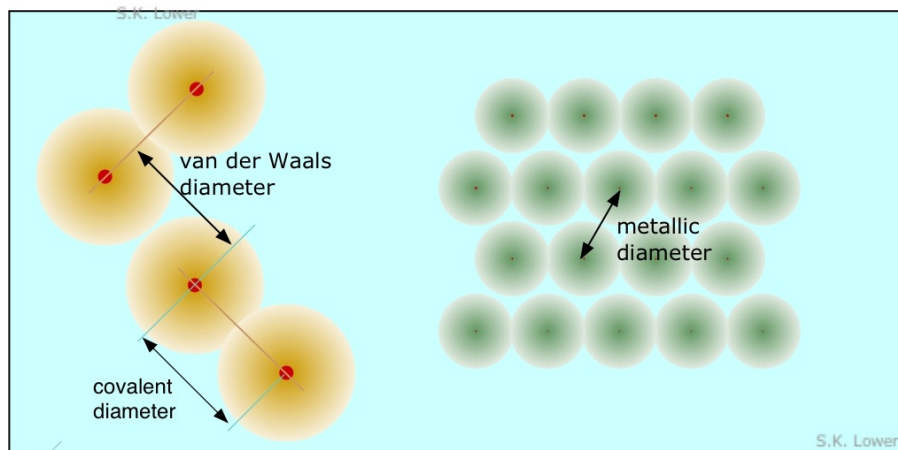
Because such solids fall into several different classes, several kinds of atomic radius are defined. Many atoms have several different radii; for example, sodium forms a metallic solid and thus has a metallic radius, it forms a gaseous molecule Na_2 in the vapor phase (covalent radius), and of course it forms ionic solids such as NaCl.

- **Metallic radius** is half the distance between nuclei in a metallic crystal.
- **Covalent radius** is half the distance between like atoms that are bonded together in a molecule.
- **van der Waals radius** is the effective radius of adjacent atoms which are not chemically bonded in a solid, but are presumably in "contact". An example would be the distance between the iodine atoms of adjacent I_2 molecules in crystalline iodine.

Many atoms have several different radii; for example, sodium forms a metallic solid and thus has a metallic radius, it forms a gaseous molecule Na_2 in the vapor phase (covalent radius), and of course it forms ionic solids as mentioned above.

Periodic trends in atomic radius

We would expect the size of an atom to depend mainly on the principal quantum number of the highest occupied orbital; in other words, on the "number of occupied electron shells". Since each row in the periodic table corresponds to an increment in n, atomic radius increases as we move down a column. The other important factor is the nuclear charge; the higher the atomic number, the more strongly will the electrons be drawn toward the nucleus, and the smaller the atom. This effect is responsible for the contraction we observe as we move across the periodic table from left to right.

Covalent radii - pm

Adapted from R.T. Sanderson's
Chemical Periodicity, Reinhold 1960

3.7 H																	.93 He
13.4 Li	9.0 Be												.82 B	.87 C	.75 N	.73 O	.72 F	1.31 Ne
15.4 Na	13.0 Mg												1.18 Al	1.11 Si	1.06 P	1.02 S	.99 Cl	1.74 Ar
19.6 K	17.4 Ca	14.4 Sc	13.6 Tl	V	Cr	Mn	Fe	Co	Ni	1.38 Cu	1.31 Zn	1.26 Ga	1.22 Ge	1.19 As	1.16 Se	1.14 Br	1.74 Kr
21.1 Rb	19.2 Sc	16.2 Y	14.8 Zr	Nb	Mo	Tc	Ru	Rh	Pd	15.3 Ag	14.8 Cd	14.4 In	14.1 Sn	13.8 Sb	13.5 Ta	13.3 I	20.9 Xe
22.5 Cs	19.8 Ba	16.9 La	Hf	Ta	W	Re	Os	Ir	Pt	15.0 Au	14.9 Hg	14.8 Tl	14.7 Pb	14.6 Bi	Po	At	21.4 Rn

The figure shows a periodic table in which the sizes of the atoms are represented graphically. The apparent discontinuities in this diagram reflect the difficulty of comparing the radii of atoms of metallic and nonmetallic bonding types. Radii of the noble gas elements are estimates from those of nearby elements.

How ionic radii are estimated

The size of an *ion* can be defined only for those present in *ionic solids*. When an ion dissolves in water, it acquires a *hydration shell* of loosely-attached H_2O molecules that increase its effective radius in ways that are difficult to define in a systematic way.

By observing the diffraction of X-rays by such an ionic crystal, it is an easy task to measure the distance between adjacent rows of Na^+ and Cl^- ions, but there is no unambiguous way to decide what portions of this distance are attributable to each ion. The best one can do is make estimates based on studies of several different ionic solids (LiI, KI, NaI, for example) that contain one ion in common. Many such estimates have been made, and they turn out to be remarkably consistent.

For example, the lithium ion is

Ionic radii are measured indirectly by comparing internuclear distances in salts whose positive ions vary in size

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sufficiently small that in LI, the iodide ions are in contact, so I-I distances are twice the ionic radius of I^-. This is not true for KI, but in this solid, adjacent potassium and iodide ions are in contact, allowing estimation of the K^+ ionic radius.

Comparing the radii of atoms and their ions

A positive ion is always smaller than the neutral atom, owing to the diminished electron-electron repulsion. If a second electron is lost, the ion gets even smaller; for example, the ionic radius of Fe^{2+} is 76 pm, while that of Fe^{3+} is 65 pm. If formation of the ion involves complete emptying of the outer shell, then

the decrease in radius is especially great.

The hydrogen ion H$^+$ is in a class by itself; having no electron cloud at all, its radius is that of the bare proton, or about 0.1 pm— a contraction of 99.999%! Because the unit positive charge is concentrated into such a small volume of space, the *charge density* of the hydrogen ion is extremely high; it interacts very strongly with other matter, including water molecules, and in aqueous solution it exists only as the *hydronium ion* H$_3$O$^+$.

Negative ions are always larger than the parent ion; the addition of one or more electrons to an existing shell increases ***electron-electron repulsion*** which results in a general expansion of the atom.

Ionic radii

Ions are colored red and blue; parent atoms brown.
Radii are in picometers.
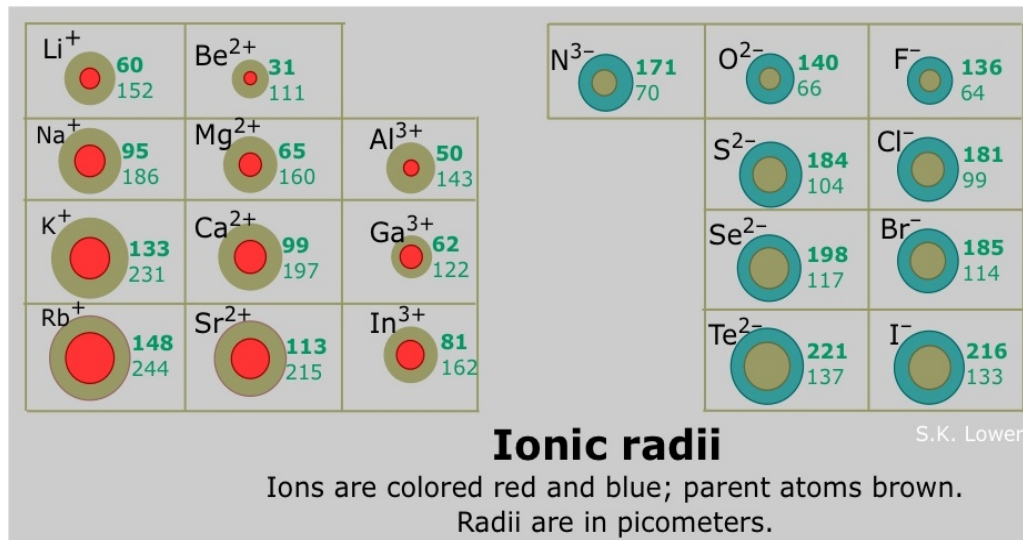
Periodic trends in ionic radii

The best way of visualizing these trends is to compare the radii of an *isoelectronic series* — a sequence of species all having the s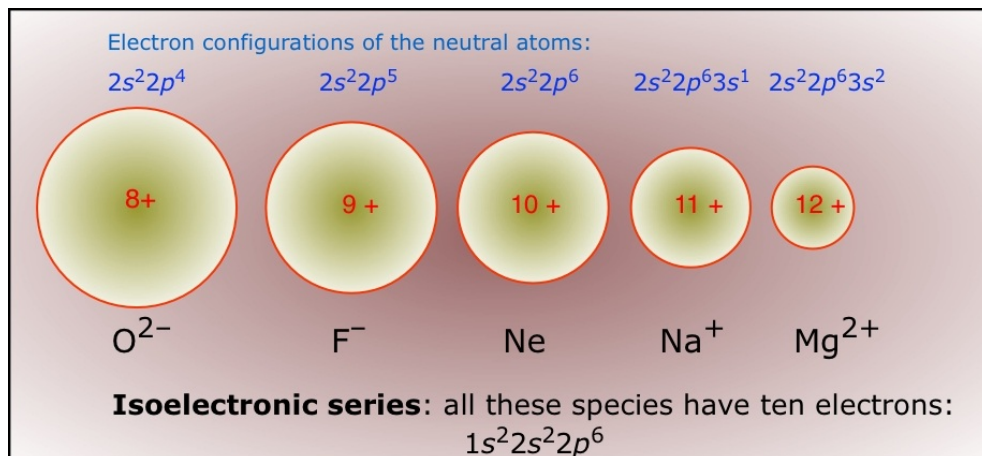ame number of electrons (and thus the same amount of electron-electron repulsion) but differing in nuclear charge. Of course, only one member of such a sequence can be a neutral atom (neon in the series shown below.) The effect of increasing nuclear charge on the radius is clearly seen.

Electron configurations of the neutral atoms:

$2s^22p^4$ $2s^22p^5$ $2s^22p^6$ $2s^22p^63s^1$ $2s^22p^63s^2$

8+   9 +   10 +   11 +   12 +

O^{2-} F$^-$ Ne   Na$^+$ Mg^{2+}

Isoelectronic series: all these species have ten electrons: $1s^22s^22p^6$

4 Periodic trends in the energetics of ion formation

Chemical reactions are based largely on the interactions between the most loosely bound electrons in atoms, so it is not surprising that the tendency of an atom to gain, lose or share electrons should play an important role in determining its chemical properties.

Periodic trends in ionization energy

This term always refers to the formation of *positive* ions. In order to remove an electron from an atom, work must be done to overcome the electrostatic attraction between the electron and the nucleus; this work is called the ***ionization energy*** of the atom and corresponds to the exothermic process

$$\text{M}(g) \rightarrow \text{M}^+(g) + \text{e}^-$$
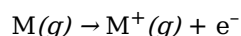
in which M(*g*) stands for any isolated (gaseous) atom.

An atom has as many ionization energies as it has electrons. Electrons are always removed from the highest-energy occupied orbital. An examination of the successive ionization energies of the first ten elements (below) provides experimental confirmation that the binding of the two innermost electrons (1*s* orbital) is significantly different from that of the *n*=2 electrons.Successive ionization energies of an atom increase rapidly as reduced electron-electron repulsion causes the electron shells to contract, thus binding the electrons even more tightly to the nucleus.

The table lists the energies, in electron volts, required to remove each successive electron from the first ten elements.

It's worth taking some time to examine the rather abrupt jumps in the sequence E1 through E10 as the atomic number increases. kkNote the very large jumps in the energies required to remove electrons from the 1s orbitals of atoms of the second-row elements Li-Ne.

	H	He	Li	Be	B	C	N	O	F	Ne
E1	1.3	2.4	0.5	0.9	0.8	1.1	1.4	1.3	1.7	2.1
E2		5.3	7.3	1.7	2.4	2.3	2.8	3.4	3.4	4.0
E3			12	15	3.7	4.6	4.6	5.3	6.0	6.1
E4				21	25	6.2	7.5	7.5	8.4	9.4
E5					33	38	9.4	11	11	12
E6						47	53	13	15	15
E7							64	71	18	19
E8								84	92	23
E9									106	115
E10										130

electrons removed from *n*=1 shell

electrons removed from *n*=2 shell

Ionization energies increase with the nuclear charge *Z* as we move *across* the periodic table. They decrease as we move *down* the table because in each period the electron is being removed from a shell one step farther from the nucleus than in the atom immediately above it. This results in the familiar zig-zag lines when the first ionization energies are plotted as a function of Z.

Ionization energies of the first 20 elements
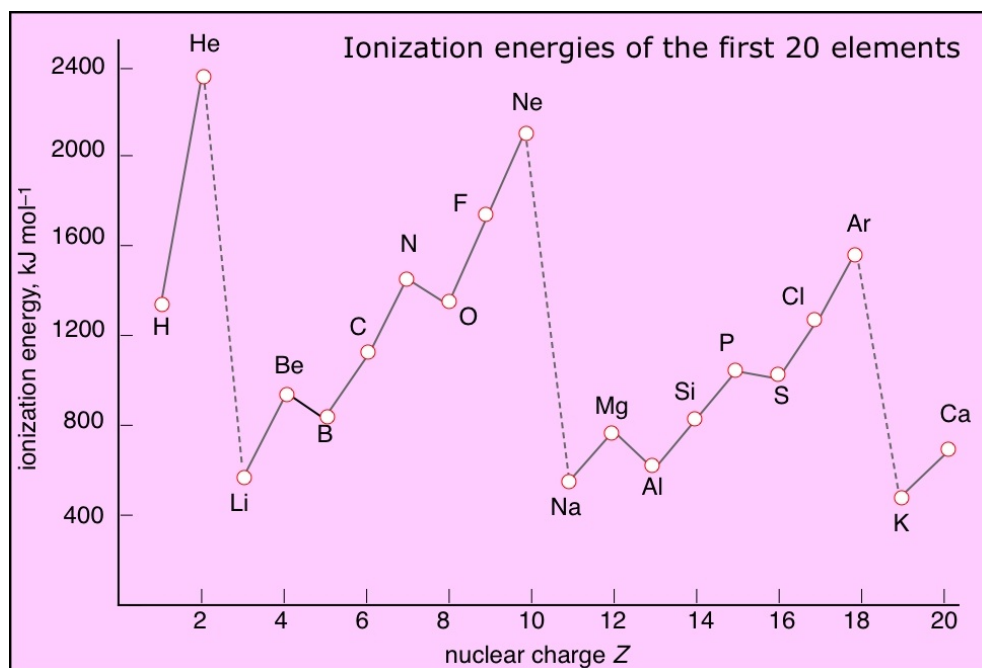
This more detailed plot of the ionization energies of the atoms of the first ten elements reveals some interesting irregularities that can be related to the slightly lower energies (greater stabilities) of electrons in half-filled (spin-unpaired) relative to completely-filled subshells.

Finally, a more comprehensive survey of the ionization energies of the main group elements is shown below.
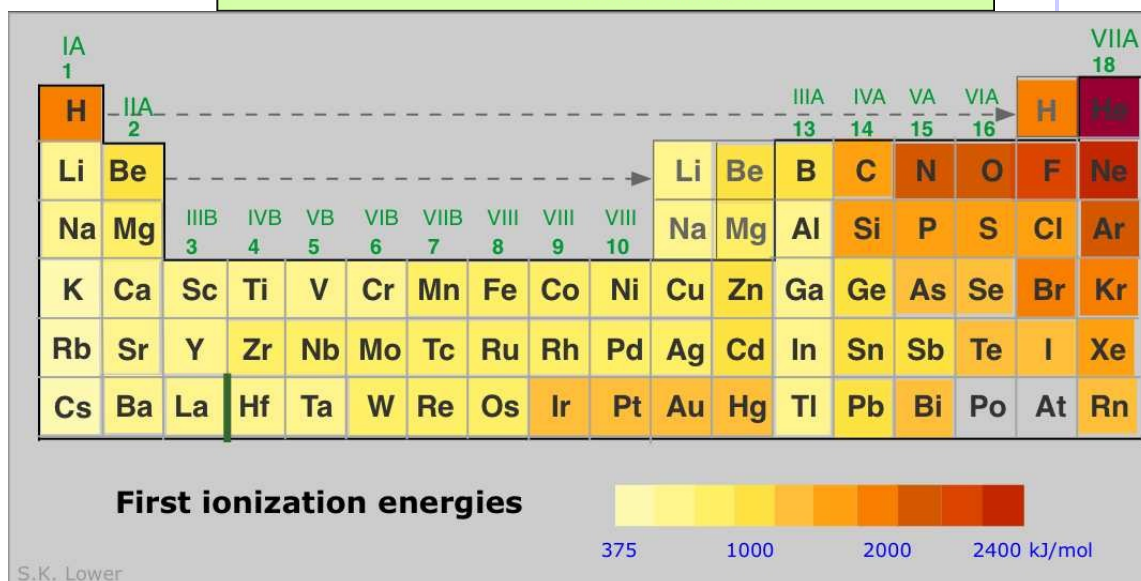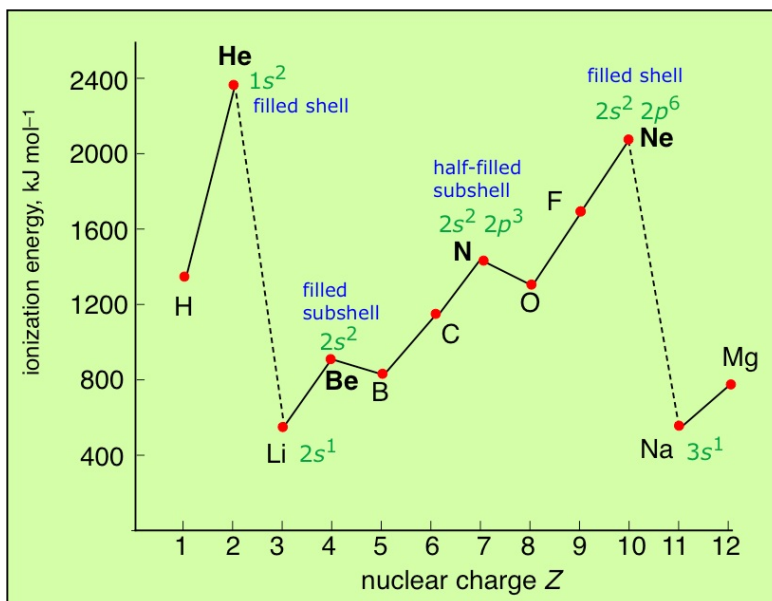
Some points to note:

- The noble gases have the highest IE's of any element in the period. This has nothing to do with any mysterious "special stability" of the s^2p^6 electron configuration; it is simply a matter of the high nuclear charge acting on more contracted orbitals.

- IE's (as well as many other properties) tend not to vary greatly amongst the *d*-block elements. This reflects the fact that as the more-compact *d* orbitals are being filled, they exert a screening effect that partly offsets that increasing nuclear charge on the outermost *s* orbitals of higher principal quantum number.

- Each of the Group 13 elements has a lower first-IE than that of the element preceding it. The reversal of the IE trend in this group is often attributed to the more easy removal of the single outer-shell p electron compared to that of electrons contained in filled (and thus spin-paired) *s*- and *d*-orbitals in the preceding elements.

Electron affinity

Formation of a negative ion occurs when an electron from some external source enters the atom and become incorporated into the lowest energy orbital that possesses a vacancy. Because the entering electron is attracted to the positive nucleus, the formation of negative ions is usually exothermic. The energy given off is the **electron affinity** of the atom. For some atoms, the electron affinity appears to be slightly negative, suggesting that electron-electron repulsion is the dominant factor in these instances.

> In general, electron affinities tend to be much smaller than ionization energies, suggesting that they are controlled by opposing factors having similar magnitudes. These two factors are, as before, the nuclear charge and electron-electron repulsion. But the latter, only a minor actor in positive ion formation, is now much more significant. One reason for this is that the electrons contained in the inner shells of the atom exert a collective negative charge that partially cancels the charge of the nucleus, thus exerting a so-called shielding effect which diminishes the tendency for negative ions to form.

Because of these opposing effects, the periodic trends in electron affinities are not as clear as are those of ionization energies. This is particularly evident in

the first few rows of the periodic table, in which small effects tend to be magnified anyway because an added electron produces a large percentage increase in the number of electrons in the atom.

Electron affinities in kJ released per mole of mononegative ions formed

IA 1																	VIIIA 18
H 73	IIA 2											IIIA 13	IVA 14	VA 15	VIA 16	VIIA 17	He −21
Li 60	Be −19											B 27	C 122	N −7	O 141	F 328	Ne −29
Na 53	Mg −19	IIIB 3	IVB 4	VB 5	VIB 6	VIIB 7	VIII 8	VIII 9	VIII 10	IB 11	IIB 12	Al 43	Si 134	P 72	S 200	Cl 349	Ar −35
K 48	Ca −10	Sc 18	Ti 8	V 51	Cr 64	Mn	Fe 16	Co 64	Ni 112	Cu 118	Zn −47	Ga 29	Ge 116	As 78	Se 195	Br 325	Kr −39
Rb 47	Sr	Y 30	Zr 41	Nb 86	Mo 72	Tc 53	Ru 101	Rh 110	Pd 54	Ag 126	Cd −32	In 29	Sn 116	Sb 103	Te 190	I 295	Xe −41
Cs 45	Ba	La	Hf	Ta 31	W 79	Re 14	Os 106	Ir 101	Pt 205	Au 223	Hg −61	Tl 20	Pb 35	Bi 91	Po 183	At 270	Rn −41
Fr 44	Ra	Ac	Db	Jl	Rf	Bh	Hn	Mt									

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In general, we can say that electron affinities become more exothermic as we move from left to right across a period (owing to increased nuclear charge and smaller atom size). There are some interesting irregularities, however:

- In the Group 2 elements, the filled 2*s* orbital apparently shields the nucleus so effectively that the electron affinities are slightly endothermic.
- The Group 15 elements have rather low values, due possibly to the need to place the added electron in a half-filled *p* orbital; why the electron affinity of nitrogen should be endothermic is not clear. The vertical trend is for electron affinity to become less exothermic in successive periods owing to better shielding of the nucleus by more inner shells and the greater size of the atom, but here also there are some apparent anomalies.

Electronegativity

When two elements are joined in a chemical bond, the element that attracts the shared electrons more strongly is more *electronegative*. Elements with low electronegativities (the metallic elements) are said to be *electropositive*.

> It is important to understand that electronegativities are properties of atoms that are chemically bound to each other; there is no way of measuring the electronegativity of an isolated atom.

Moreover, the same atom can exhibit different electronegativities in different chemical environments, so the "electronegativity of an element" is only a general guide to its chemical behavior rather than an exact specification of its behavior in a particular compound. Nevertheless, electronegativity is eminently useful in summarizing the chemical behavior of an element. You will make considerable use of electronegativity when you study chemical bonding and the chemistry of the individual elements.

Because there is no single definition of electronegativity, any numerical scale for measuring it must of necessity be somewhat arbitrary. Most such scales are themselves based on atomic properties that are directly measurable and which relate in one way or the other to electron-attracting propensity.

The most widely used of these scales was devised by Linus Pauling and is related to ionization energy and electron affinity.

The Pauling scale runs from 0 to 4; the highest electron affinity, 4.0, is assigned to fluorine, while cesium has the lowest value of 0.7. Values less than about 2.2 are usually associated with electropositive, or metallic character. In the representation of the scale shown in figure, the elements are arranged in rows corresponding to their locations in the periodic table. The correlation is obvious; electronegativity is associated with the higher rows and the rightmost columns.

The location of **hydrogen** on this scale reflects some of the significant chemical properties of this element. Although it acts like a metallic element in many respects (forming a positive ion, for example), it can also form hydride-ion (H⁻) solids with the more electropositive elements, and of course its ability to share electrons with carbon and other *p*-block elements gives rise to a very rich chemistry, including, of course, the millions of organic compounds.

electropositive ⟷ electronegative

1   2   13   14   15   16   17

Li Be B   C   N   O   F

Na Mg Al Si P   S   Cl

K   Ca Ga Ge As Se Br

Rb Sr In Sn Sb Ta I

H

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1   2   3   4
electronegativity (dimensionless units)

What you should be able to do

Make sure you thoroughly understand the following essential concepts that have been presented above.
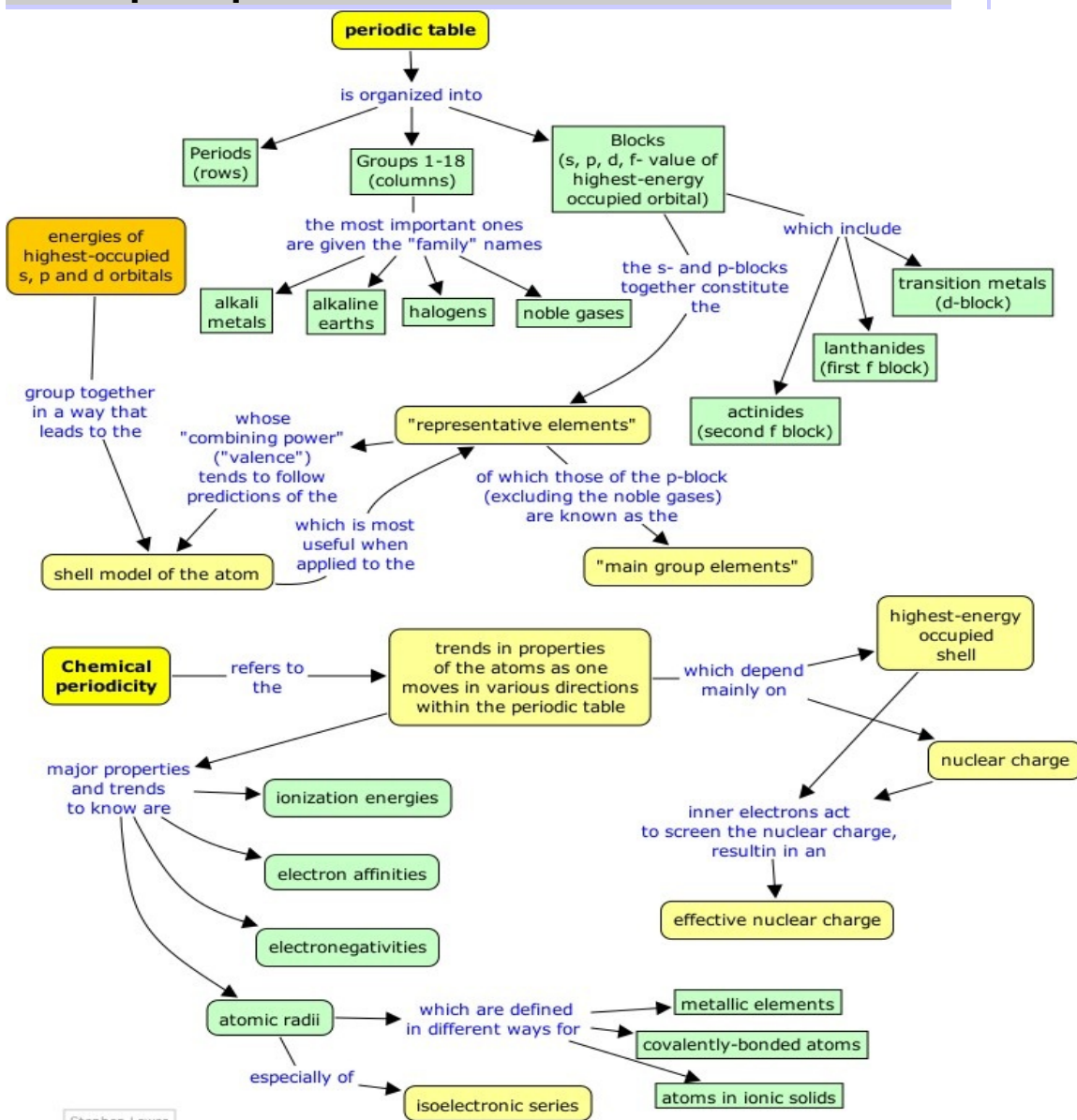
- You should be able to sketch out the general form of the periodic table and identify the various **blocks** and identify the **groups** corresponding to the **alkali metals**, the **transition elements**, the **halogens**, and the **noble gases**.

- For the first eighteen elements, you should be able to predict the formulas of typical binary compounds they can be expected to form with hydrogen and with oxygen.
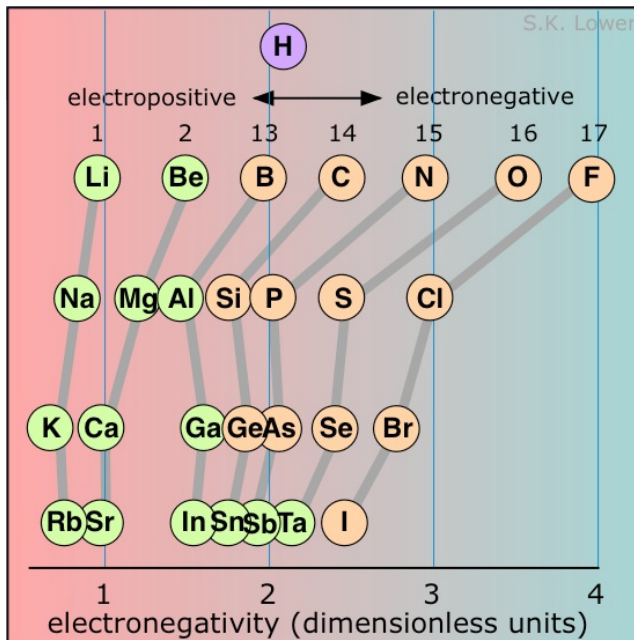
- Comment on the concept of the "size" of an atom, and give examples of how radii are defined in at least two classes of of substances.

- Define **ionization energy** and **electron affinity**, and explain the periodic general trends.

- State the meaning and significance of **electronegativity**.

Concept Map

periodic table

is organized into

Periods (rows)

Groups 1-18 (columns)

Blocks (s, p, d, f- value of highest-energy occupied orbital)

energies of highest-occupied s, p and d orbitals

the most important ones are given the "family" names

which include

the s- and p-blocks together constitute the

transition metals (d-block)

alkali metals

alkaline earths

halogens

noble gases

lanthanides (first f block)

actinides (second f block)

group together in a way that leads to the

whose "combining power" ("valence") tends to follow predictions of the

"representative elements"

of which those of the p-block (excluding the noble gases) are known as the

which is most useful when applied to the

shell model of the atom

"main group elements"

Chemical periodicity

refers to the

trends in properties of the atoms as one moves in various directions within the periodic table

which depend mainly on

highest-energy occupied shell

nuclear charge

major properties and trends to know are

ionization energies

electron affinities

electronegativities

inner electrons act to screen the nuclear charge, resultin in an

effective nuclear charge

atomic radii

which are defined in different ways for

especially of

isoelectronic series

metallic elements

covalently-bonded atoms

atoms in ionic solids

Stephen Lower