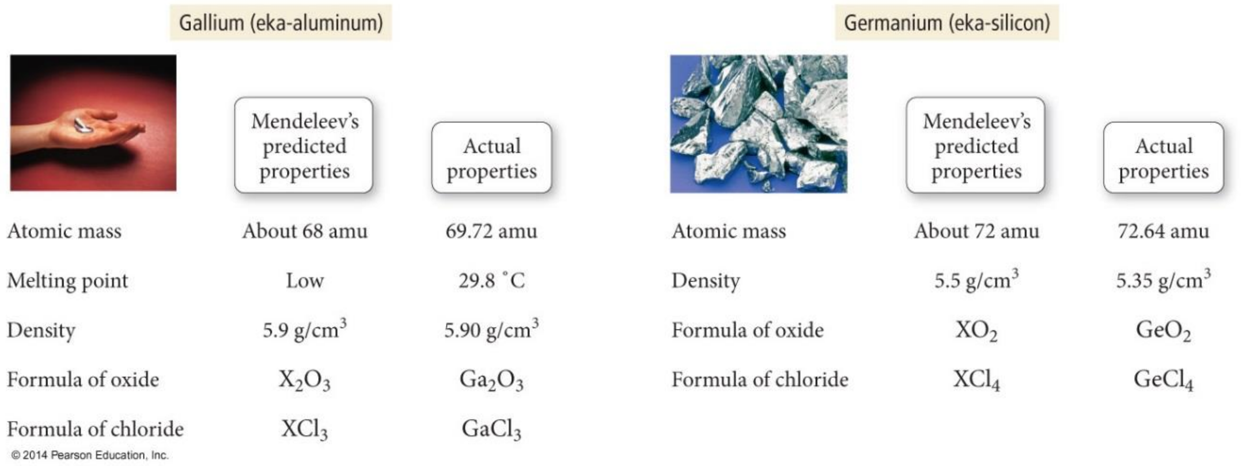
DEVELOPMENT OF THE PERIODIC TABLE

- Prior to the 1700s, relatively few element were known, and consisted mostly of metals used for coinage, jewelry and weapons. From early 1700s to mid-1800s, chemists discovered over 50 new elements.

- Attempts to organize these elements consisted efforts to group them into triads or octaves, with similar properties. These attempts did not lead to much insight about the properties of elements and were at times ridiculed by some.

- The modern periodic table is credited primarily to the Russian chemist Dmitri Mendeleev. Mendeleev's table is based on the ***periodic law***, which states that when elements are arranged in order of increasing mass, certain properties recur periodically. When arranged in this manner, elements with similar properties fall into the same column.

- Mendeleev's arrangement was a huge success, since it allowed him to predict the existence and properties of yet undiscovered elements, such as gallium and germanium. The comparison of the properties of these two elements based on Mendeleev's prediction and their actual properties are shown below.



Gallium (eka-aluminum)

	Mendeleev's predicted properties	Actual properties
Atomic mass	About 68 amu	69.72 amu
Melting point	Low	29.8 ˚C
Density	5.9 g/cm^3	5.90 g/cm^3
Formula of oxide	X_2O_3	Ga_2O_3
Formula of chloride	XCl_3	$GaCl_3$

Germanium (eka-silicon)

	Mendeleev's predicted properties	Actual properties
Atomic mass	About 72 amu	72.64 amu
Density	5.5 g/cm^3	5.35 g/cm^3
Formula of oxide	XO_2	GeO_2
Formula of chloride	XCl_4	$GeCl_4$

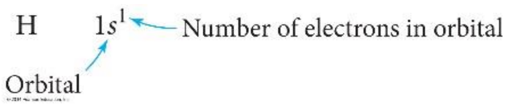
- Mendeleev's arrangement of elements based on mass did encounter some difficulties in explaining the behavior of some elements and was later improved by the English physicist Henry Mosely, who showed that listing elements by atomic number, rather than atomic mass, would resolve these problems.

- It is noteworthy to notice the scientific approach in practice in development of the periodic table. A number of observations led to a scientific law–the periodic law. Mendeleev's table, an expression of the periodic law, had predictive power, as laws usually do. However, it did not explain why the recurring of the properties occurs in elements. The theory that explains the reasons behind the periodic law is quantum-mechanical theory.

ELECTRON CONFIGURATION

- Quantum-mechanical theory describes the behavior of electrons in atoms. Since chemical bonding involves transfer or sharing of electrons, quantum-mechanical theory helps us understand and describe chemical behavior.

- Electrons in atoms exist within orbitals. An electron configuration for an atom shows the particular orbitals that electrons occupy for that atom. For example, the ground state–or lowest energy state-electron configuration for a hydrogen atom can be shown as:

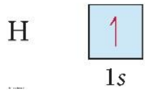


- Electrons generally occupy the lowest energy orbitals available. For hydrogen atom, the lowest energy orbital is 1s. In order to write similar electron configurations for multi-electron atoms, two additional concepts must be examined: the ***effects of electron spin*** and ***sublevel energy splitting***.

- Electron spin is a fundamental properly of the electron (like its negative charge). All electrons have the same amount of spin. However, the orientation of the electron spin is quantized.

- The spin quantum number (m_s)specifies the orientation of the spin of the electron, with only two possibilities that we call spin up ($m_s = +½$) and spin down ($m_s = –½$).

- The electron configuration of hydrogen can also be represented in a different way with an orbital diagram. In this diagram, the orbital is symbolized by a box and the electron is symbolized by an arrow. The orbital diagram for hydrogen is:



- In an orbital diagram, the direction of the arrow (pointing up or pointing down) represents the orientation of the electron's spin. The $m_s = +½$ is represented by an arrow pointing up (↑) and $m_s = –½$ is represented by an arrow pointing down (↓).

- In a collection of hydrogen atoms, the electrons in about half of the atoms are spin up and the electrons in the other half are spin down. When writing electron configuration for hydrogen atom, we conventionally represent the one electron as spin up.

ELECTRON CONFIGURATION

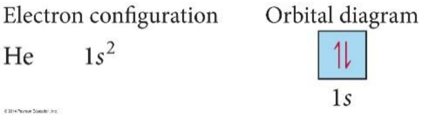
- The next atom, Helium, containing 2 electrons, has both electrons occupying the 1s orbital:

He $1s^2$

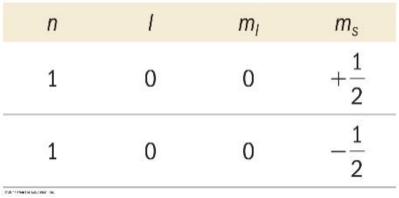
- Since both electrons in helium occupy the same orbital, how do the spins of the two align relative to one another? The answer to this question is addressed by the ***Pauli exclusion principle***, formulated by Wolfgang Pauli in 1925.

- The Pauli exclusion principle states that no two electrons in an atom have the same four quantum numbers. Since two electrons occupying the same orbital have the three identical quantum numbers (n, *l*, and m_l), they must have different spin quantum numbers.

- Since there are only two possible spin quantum numbers, the Pauli exclusion principle implies that each orbital can have a maximum of two electrons, with opposing spins. Therefore, the electron configuration and orbital diagram for helium is as follows:



- The table below shows the four quantum numbers for each of the two electrons in helium:



n	l	m_l	m_s
1	0	0	$+\frac{1}{2}$
1	0	0	$-\frac{1}{2}$

- Recall that the Shrodinger equation solutions studied earlier, determined the energies of the atomic orbitals for the hydrogen atom. When applying these equations to multi-electron atoms the solutions are only approximate, since the equation has terms to account for the interaction of the electrons with one another that make it too complicated to solve exactly.

SUBLEVEL ENERGY SPLITTING

- A major difference in the (approximate) solutions to the Shrodinger equation for multi-electron atoms compared to the solution for the hydrogen atom is the energy ordering of the orbitals.

- In energy levels that have several sublevels (2 and above) the energy of the sublevel depends on the value of *l*. We therefore say that the energies of the sublevels are split. In general, the lower the value of *l* within a principal level, the lower the energy (E) of the corresponding orbital. Therefore:

$$E(\text{s orbital}) < E(\text{p orbital}) < E(\text{d orbital}) < E(\text{f orbital})$$

- Splitting of the sublevels in this way is affected by 3 factors. We will examine the first two factors to gain better insight into the properties of electrons.
  - ➢ Coulomb's law
  - ➢ shielding of electrons
  - ➢ penetration and overlapping of orbitals

Coulomb's law:

- The attraction and repulsion of charged particles are described by Coulomb's law, which states that the potential energy (E) of two charged particles depends on their charges (q_1 and q_2) and on their separation (r):

$$E = \frac{1}{4\pi\varepsilon_0}\frac{q_1q_2}{r} \qquad \varepsilon_0 = 8.85\text{x}10^{-12}\ \text{C/J}\bullet\text{m}$$

- The following conclusions can be drawn from Coulomb's law":
  - ➢ For like particles, the potential energy (E) is positive and decreases as r increases. Since systems tend toward lower potential energy, like charge repel each other.
  - ➢ For opposite charges, the potential energy (E) is negative and becomes more negative as r decreases. Therefore, opposite charge attract each other.
  - ➢ The magnitude of the interaction between charged particles increases as the charges of the particles increase. Therefore, an electron with a charge of –1 is more strongly attracted to a nucleus with a charge of +2+ than one with a charge of +1.
- **Examples:**
  1. According to Coulomb's law, what happens to the PE of two oppositely charged particles as they get closer together?

     a) The PE decreases b) The PE increases c) The PE does not change

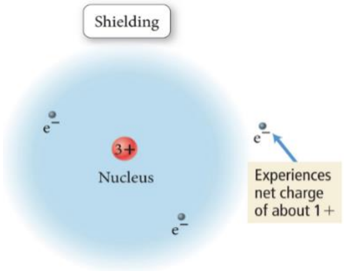
  2. According to Coulomb's law, which pair of charged particles has the lowest PE?
     a) A particle with 1- charge separated 150 pm from a particle with a 2+ charge.
     b) A particle with 1- charge separated by 150 pm from a particle with 1+ charge.
     c) A particle with 1- charge separated by 100 pm from a particle with 3+ charge.

SUBLEVEL ENERGY SPLITTING

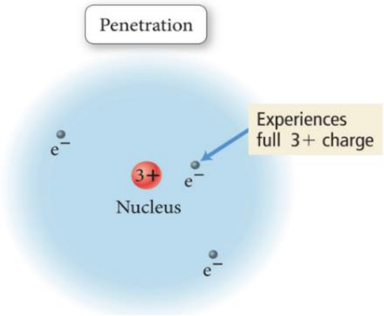
Shielding Effect:

- In multi-electron atoms, any electron experiences the positive charge of the nucleus (attractive) and the negative charge of the other electrons (repulsive). The repulsion of one electron by the others can be thought of as screening or ***shielding*** that electron from the full effect of the nuclear charge.

- For example, consider the lithium ion (Li^+), which has the same electron configuration as helium ($1s^2$). If a 3rd electron is brought towards the Li^+, when far from the nucleus, it would experience a net 1+ charge of the nucleus through the shielding of the 2– charge of the other 2 electrons.



- Therefore, the ***effective nuclear charge*** (Z_{eff}) the 3rd electron experiences is approximately 1+ (3+ from the nucleus and 2– from the other electrons). The inner electrons shield the outer electron from the full nuclear charge.

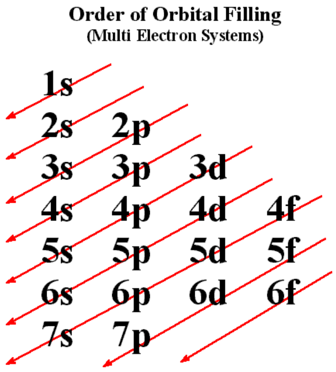


SUBLEVEL SPLITTING

- The diagram next shows the energy ordering of a number of orbitals in a multi-electron atom due to the effects of shielding and penetration.

- The ordering of the orbitals based on their energies, can be summarized in increasing order as:

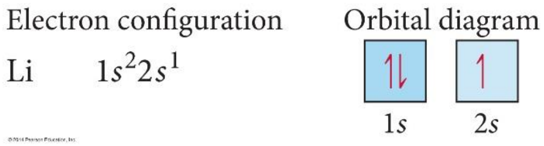
1s < 2s < 2p < 3s < 3p < **4s** < **3d** < 4p < **5s** < **4d** < 5p < **6s** < **4f** < 6p

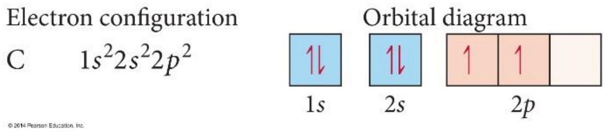


ELECTRON CONFIGURATION

- The ground-state electron configuration of atoms can be done systematically by remembering that electrons occupy lower energy orbitals first and that only two electrons (with opposing spins) are allowed in each orbital. This pattern of orbital filling is known as ***aufbau principle***.

- The ground state configurations for lithium and carbon are shown below:





- Note that the 2p electrons occupy the p orbitals (equal energy) singly, rather than pairing in one orbital. This effect is called ***Hund's rule***, that states that when filling degenerate orbitals, electrons fill them singly first, with parallel spins. This occurs due to the atom's tendency to find the lowest energy state possible.

- To summarize the orbital filling:

  - The orbitals fill lower energy orbitals first in order to minimize the energy of the atom. The orbitals fill in the following order:

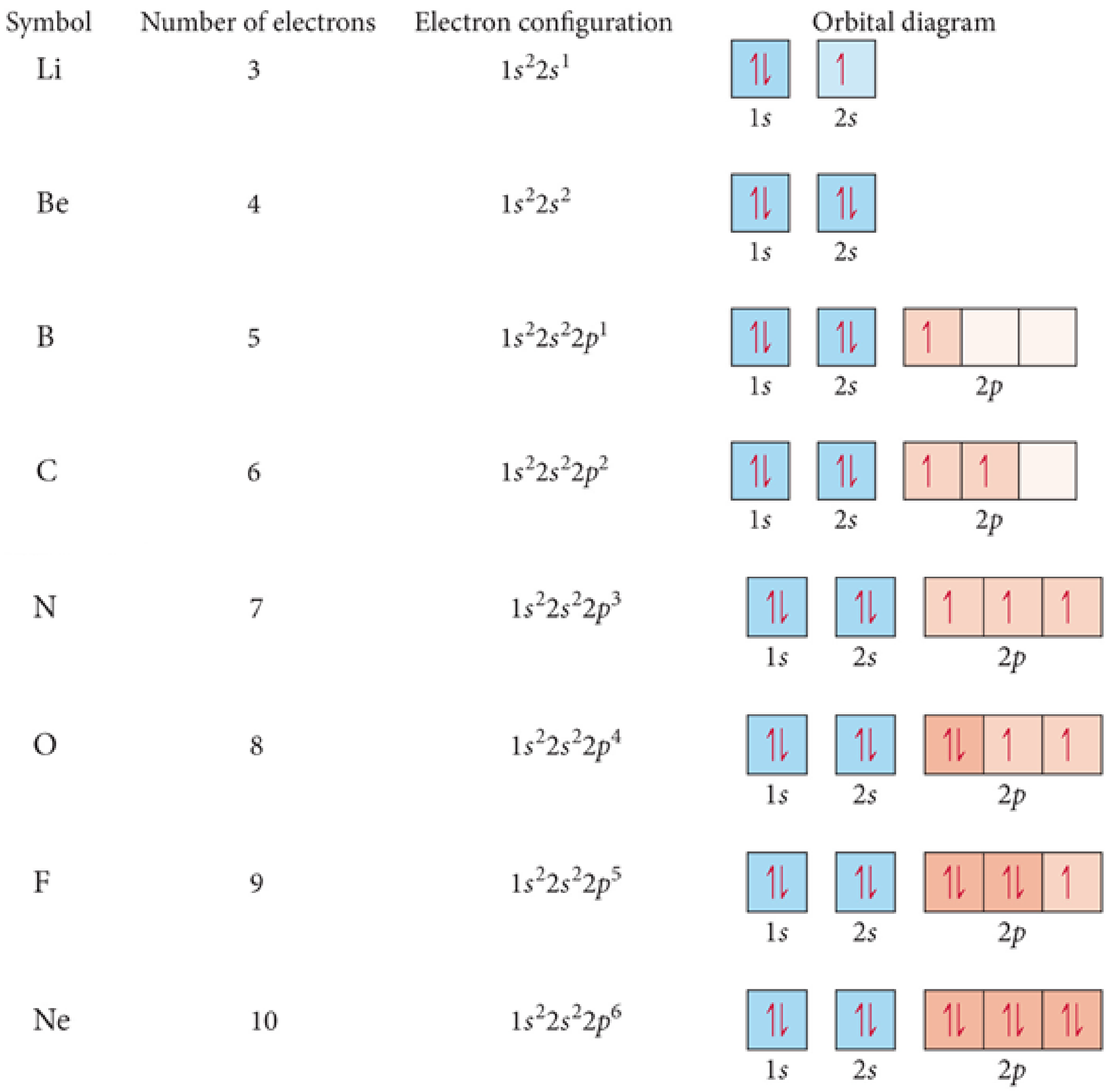
    1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s

  - Orbitals can hold no more than 2 electrons each. When two electrons occupy the same orbital, their spins are opposite (Pauli exclusion principle).

  - When orbitals of identical energy are available, electrons first occupy these orbitals singly with parallel spins rather than in pairs. Once the orbitals of equal energy are half full, the electrons start to pair (Hund's rule).

ELECTRON CONFIGURATION

- The electron configuration and orbital diagrams for the elements with atomic numbers 3-10 are shown below:



Symbol	Number of electrons	Electron configuration	Orbital diagram
Li	3	$1s^2 2s^1$	⇅ ↑ 1s 2s
Be	4	$1s^2 2s^2$	⇅ ⇅ 1s 2s
B	5	$1s^2 2s^2 2p^1$	⇅ ⇅ ↑ ☐ ☐ 1s 2s 2p
C	6	$1s^2 2s^2 2p^2$	⇅ ⇅ ↑ ↑ ☐ 1s 2s 2p
N	7	$1s^2 2s^2 2p^3$	⇅ ⇅ ↑ ↑ ↑ 1s 2s 2p
O	8	$1s^2 2s^2 2p^4$	⇅ ⇅ ⇅ ↑ ↑ 1s 2s 2p
F	9	$1s^2 2s^2 2p^5$	⇅ ⇅ ⇅ ⇅ ↑ 1s 2s 2p
Ne	10	$1s^2 2s^2 2p^6$	⇅ ⇅ ⇅ ⇅ ⇅ 1s 2s 2p

- The electron configuration of large atoms can be written more compactly by using [X] as the symbol for the inner electrons. [X] represents the symbol of the noble gas having the same number of electrons as the inner electrons of the atom.

- For example, the electron configuration of Na can be written as:

$[Ne]\ 3s^1$ where [Ne] represents the Na inner electrons ($1s^2\ 2s^2\ 2p^6$)

ELECTRON CONFIGURATION

Examples:

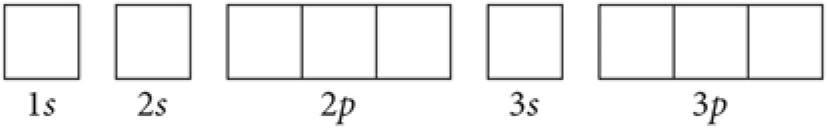
1. Using only a periodic table, write complete and condensed electron configurations for each element shown below:

   a) Mg

   b) P

   c) Br

2. Write the orbital diagram for sulfur and determine the number of unpaired electrons.

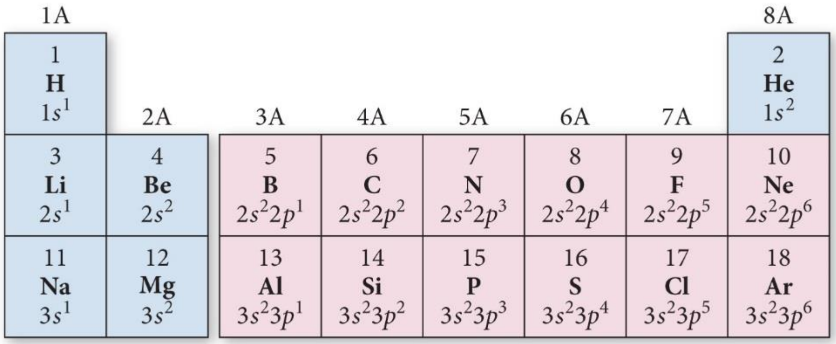


3. Assign a set of quantum numbers that identify the last electron that enters an orbital in problem 2 above.

ELECTRON CONFIGURATION & THE PERIODIC TABLE

- Recall that Mendeleev arranged the periodic table so that the elements with similar chemical properties lie in the same column. The chemical property of an element and its electron configuration can be observed by superimposing the configuration of the first 18 elements with their position on the periodic table.

Outer Electron Configurations of Elements 1–18

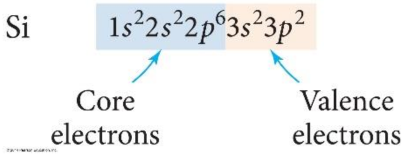


1A	2A	3A	4A	5A	6A	7A	8A
1 **H** $1s^1$							2 **He** $1s^2$
3 **Li** $2s^1$	4 **Be** $2s^2$	5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
11 **Na** $3s^1$	12 **Mg** $3s^2$	13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$

- Note that across a period, the electrons fill the orbitals in the correct order. Furthermore, as we move down a column, while the principal quantum number increases by one, the number of electrons in the outermost energy level (highest n value) remains the same. The electrons are called the ***valence electrons***.

- The key connection between the atom's chemical properties and its atomic structure lies in the number of valence electrons. For main group elements, the valence electrons are those in the outermost principal energy level. For transition elements, the outermost d electrons are also counted (even though these are not in an outermost principal energy level).

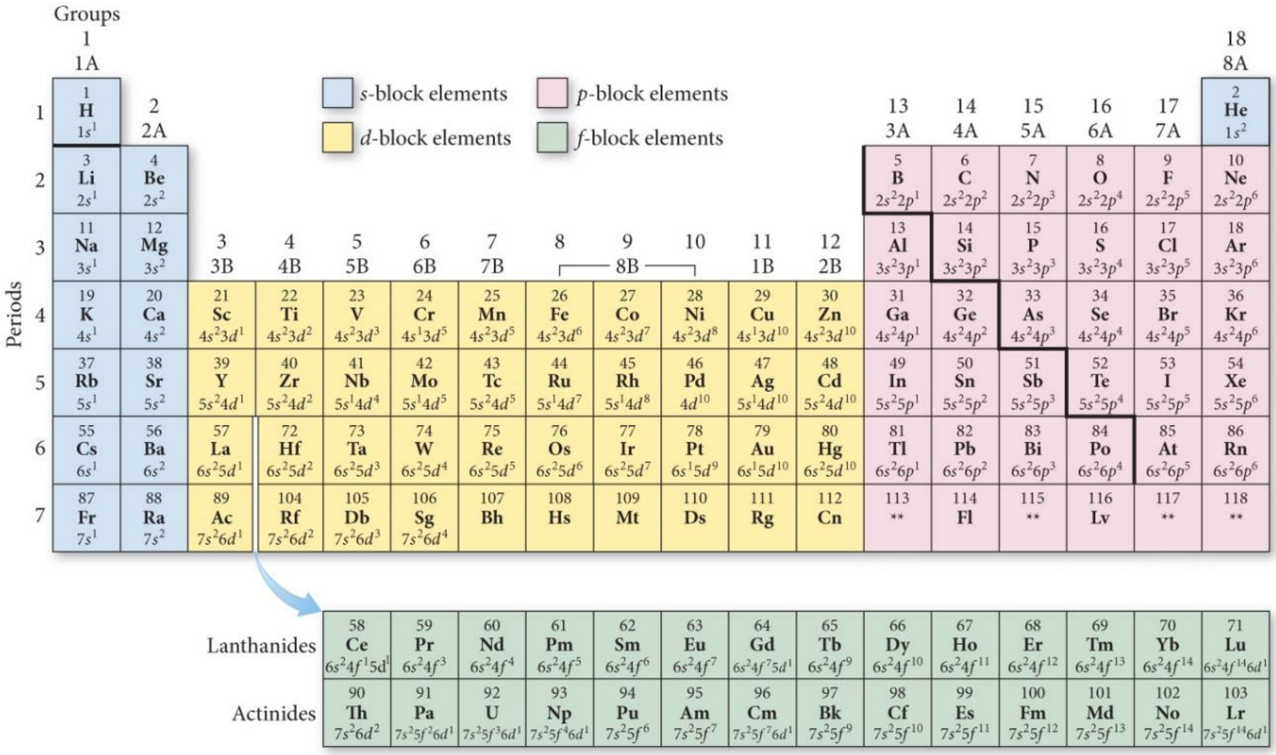
- The valence electrons are distinguished from all other electrons in a atom, which are called core electrons. The core electrons are those in complete principal energy levels and those in complete d and f sublevels. For example, silicon, has 4 valence electrons and 10 core electrons, as shown below:



ELECTRON CONFIGURATION & THE PERIODIC TABLE

- The periodic table can be divided into four blocks corresponding to the filling of the four quantum sublevels (s, p, d, and f).
- The group number of a main-group element is equal to the number of valence electrons for that element.
- The row number of a main-group element is equal to the highest principal quantum number for that element.

Orbital Blocks of the Periodic Table



- 🟦 *s*-block elements
- 🟨 *d*-block elements
- 🟥 *p*-block elements
- 🟩 *f*-block elements

Groups

Periods	1 1A	2 2A	3 3B	4 4B	5 5B	6 6B	7 7B	8 8B	9 8B	10 8B	11 1B	12 2B	13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1	1 **H** $1s^1$																	2 **He** $1s^2$
2	3 **Li** $2s^1$	4 **Be** $2s^2$											5 **B** $2s^22p^1$	6 **C** $2s^22p^2$	7 **N** $2s^22p^3$	8 **O** $2s^22p^4$	9 **F** $2s^22p^5$	10 **Ne** $2s^22p^6$
3	11 **Na** $3s^1$	12 **Mg** $3s^2$											13 **Al** $3s^23p^1$	14 **Si** $3s^23p^2$	15 **P** $3s^23p^3$	16 **S** $3s^23p^4$	17 **Cl** $3s^23p^5$	18 **Ar** $3s^23p^6$
4	19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $4s^23d^1$	22 **Ti** $4s^23d^2$	23 **V** $4s^23d^3$	24 **Cr** $4s^13d^5$	25 **Mn** $4s^23d^5$	26 **Fe** $4s^23d^6$	27 **Co** $4s^23d^7$	28 **Ni** $4s^23d^8$	29 **Cu** $4s^13d^{10}$	30 **Zn** $4s^23d^{10}$	31 **Ga** $4s^24p^1$	32 **Ge** $4s^24p^2$	33 **As** $4s^24p^3$	34 **Se** $4s^24p^4$	35 **Br** $4s^24p^5$	36 **Kr** $4s^24p^6$
5	37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $5s^24d^1$	40 **Zr** $5s^24d^2$	41 **Nb** $5s^14d^4$	42 **Mo** $5s^14d^5$	43 **Tc** $5s^24d^5$	44 **Ru** $5s^14d^7$	45 **Rh** $5s^14d^8$	46 **Pd** $4d^{10}$	47 **Ag** $5s^14d^{10}$	48 **Cd** $5s^24d^{10}$	49 **In** $5s^25p^1$	50 **Sn** $5s^25p^2$	51 **Sb** $5s^25p^3$	52 **Te** $5s^25p^4$	53 **I** $5s^25p^5$	54 **Xe** $5s^25p^6$
6	55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 **La** $6s^25d^1$	72 **Hf** $6s^25d^2$	73 **Ta** $6s^25d^3$	74 **W** $6s^25d^4$	75 **Re** $6s^25d^5$	76 **Os** $6s^25d^6$	77 **Ir** $6s^25d^7$	78 **Pt** $6s^15d^9$	79 **Au** $6s^15d^{10}$	80 **Hg** $6s^25d^{10}$	81 **Tl** $6s^26p^1$	82 **Pb** $6s^26p^2$	83 **Bi** $6s^26p^3$	84 **Po** $6s^26p^4$	85 **At** $6s^26p^5$	86 **Rn** $6s^26p^6$
7	87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **Ac** $7s^26d^1$	104 **Rf** $7s^26d^2$	105 **Db** $7s^26d^3$	106 **Sg** $7s^26d^4$	107 **Bh**	108 **Hs**	109 **Mt**	110 **Ds**	111 **Rg**	112 **Cn**	113 **	114 **Fl**	115 **	116 **Lv**	117 **	118 **

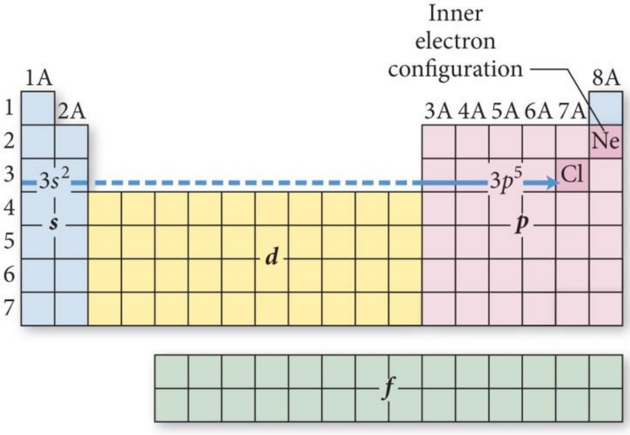
Lanthanides	58 **Ce** $6s^24f^15d^1$	59 **Pr** $6s^24f^3$	60 **Nd** $6s^24f^4$	61 **Pm** $6s^24f^5$	62 **Sm** $6s^24f^6$	63 **Eu** $6s^24f^7$	64 **Gd** $6s^24f^75d^1$	65 **Tb** $6s^24f^9$	66 **Dy** $6s^24f^{10}$	67 **Ho** $6s^24f^{11}$	68 **Er** $6s^24f^{12}$	69 **Tm** $6s^24f^{13}$	70 **Yb** $6s^24f^{14}$	71 **Lu** $6s^24f^{14}6d^1$
Actinides	90 **Th** $7s^26d^2$	91 **Pa** $7s^25f^26d^1$	92 **U** $7s^25f^36d^1$	93 **Np** $7s^25f^46d^1$	94 **Pu** $7s^25f^6$	95 **Am** $7s^25f^7$	96 **Cm** $7s^25f^76d^1$	97 **Bk** $7s^25f^9$	98 **Cf** $7s^25f^{10}$	99 **Es** $7s^25f^{11}$	100 **Fm** $7s^25f^{12}$	101 **Md** $7s^25f^{13}$	102 **No** $7s^25f^{14}$	103 **Lr** $7s^25f^{14}6d^1$

ELECTRON CONFIGURATION & THE PERIODIC TABLE

- The electron configuration of any element can be written based on its position in the periodic table.

- For example, when writing electron configuration for Cl, it can be seen that the inner electrons have the electron configuration of the previous noble gas (Ne) and the outer electron configuration is $3s^2\ 3p^5$.

- Note that Cl is in group 7 and therefore has seven valence electrons.



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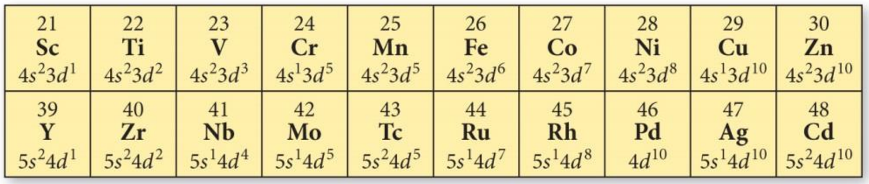
Examples:

1. Using a periodic table, write electron configuration for Ge, and identify the valence and core electrons.

2. Using a periodic table, write the condensed electron configuration of Bi (Z=83)

ELECTRON CONFIGURATION OF TRANSITION ELEMENTS

- The electron configuration of the transition elements (d block) exhibit trends that differ from those of main-group elements. As we move across a period in the d block, the d orbitals begin to fill as shown below:



21	22	23	24	25	26	27	28	29	30
Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
$4s^23d^1$	$4s^23d^2$	$4s^23d^3$	$4s^13d^5$	$4s^23d^5$	$4s^23d^6$	$4s^23d^7$	$4s^23d^8$	$4s^13d^{10}$	$4s^23d^{10}$
39	40	41	42	43	44	45	46	47	48
Y	**Zr**	**Nb**	**Mo**	**Tc**	**Ru**	**Rh**	**Pd**	**Ag**	**Cd**
$5s^24d^1$	$5s^24d^2$	$5s^14d^4$	$5s^14d^5$	$5s^24d^5$	$5s^14d^7$	$5s^14d^8$	$4d^{10}$	$5s^14d^{10}$	$5s^24d^{10}$

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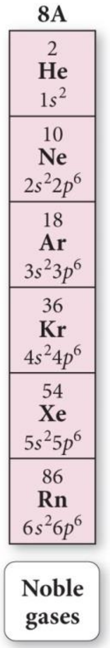
- The principal quantum number of the d orbitals that fill across each period is one less than the period number. For example, the 3d orbitals begin filling in the fourth period. This is because the 4s orbitals are slightly lower energy than 3d orbitals (as discussed earlier).

- Another irregularity that occurs in the 3d orbital filling is the configuration of Cr and Cu (which have configurations of $4s^1\ 3d^x$) compared to the other elements configuration of $4s^2\ 3d^x$. This is due to the stability of a half-filled sublevel (as in Cr) and a completely filled sublevel (as in Cu).

- Actual electron configuration of elements are definitively determined (through spectroscopy) and do not always conform to the general pattern. Nonetheless, the patterns described above can be used to accurately predict electron configuration of most elements in the periodic table.

- We can now see how quantum-mechanical model accounts for the chemical properties of the elements, and how it accounts for the periodic law. The chemical properties of elements are largely determined by the number of valence electrons they contain. Their properties are periodic, because the number of valence electrons is periodic.

- For example, noble gases all have eight valence electrons (except He), and they all have full outer energy levels and are particularly stable and unreactive.



8A
2 **He** $1s^2$
10 **Ne** $2s^22p^6$
18 **Ar** $3s^23p^6$
36 **Kr** $4s^24p^6$
54 **Xe** $5s^25p^6$
86 **Rn** $6s^26p^6$
Noble gases

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CONCEPT REVIEW

1. What is effective nuclear charge (Z_{eff})?

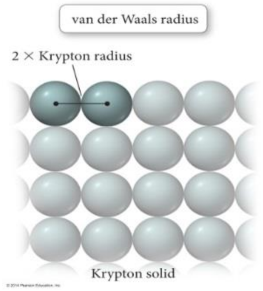
2. How does Z_{eff} change moving down a group? Why?

3. How does Z_{eff} change moving across a period? Why?

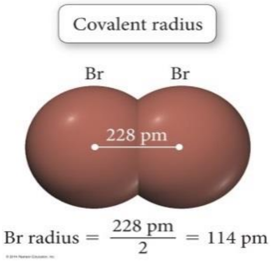
ATOMIC RADII

- Most of the volume of an atom is taken up by its electrons occupying a quantum-mechanical orbital. The orbitals do not have a defined boundary and represent only statistical probability distribution for where the electron is found. So how do we define the size of the atom?

- One way to do so, it to consider the distance between nonbonding atoms. An atomic radius determined this way is called the ***nonbonding atomic radius*** or the ***van der Waals radius***.



- Another way to define the atomic size, called the ***bonding atomic radius*** or ***covalent radius***, is defined as follows:
  - ***Nonmetals:*** one-half the distance between two of the atoms bonded together.
  - ***Metals:*** one-half the distance between two of the atoms next to each other in a crystal.

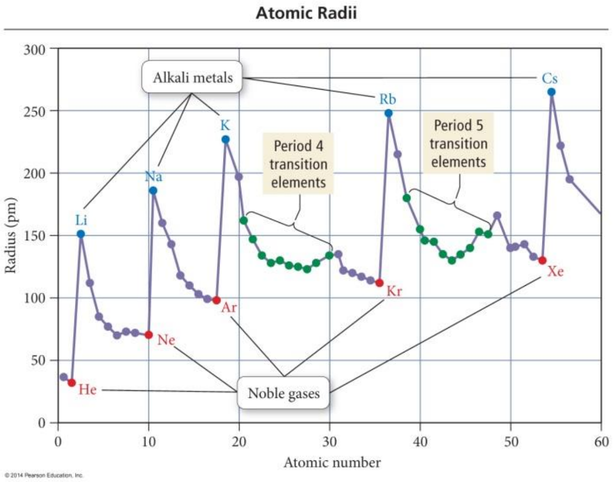


- Using this method, atomic radii can be assigned to all elements in the periodic table that form chemical bonds or form metallic crystals.

- A more general term, atomic radius, refers to a set of average bonding radii determined from measurements on a large number of elements and compounds. The atomic radius–radius of an atom when bonded to another atom–is always smaller than the van der Waals radius.

- The approximate bond length of any two covalently bonded atoms is the sum of their atomic radii. For example, the bond length for ICl is iodine's atomic radius (133 pm) plus chlorine's atomic radius (99 pm) for a bond length of 232 pm.

- The diagram below shows the atomic radius of elements as a function of their atomic number. Note the periodic trend: atomic radii peak with each alkali metal.



ATOMIC RADII

- The general trends in the atomic radii of main-group elements can be summarized as follows:

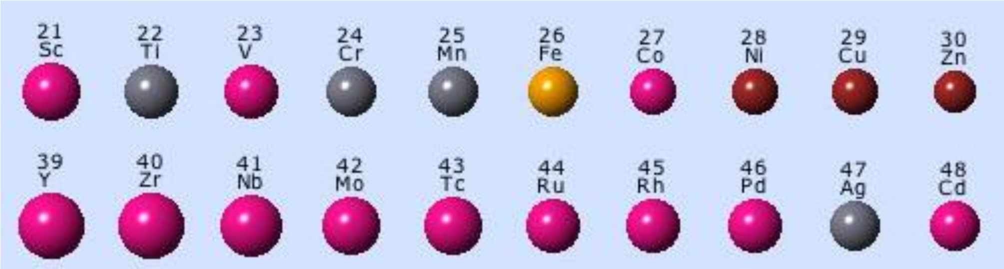
  - Moving down a group, atomic radius increases.

    This trend can be explained by noting that the principal quantum number (n) of the electrons in the outermost energy level increases, as you move down a group, causing the electrons to occupy larger orbitals and therefore increases atomic radii.

  - Moving across a period, the atomic radius generally decreases.

    This trend can be explained by the fact that moving across a period increases effective nuclear charge (Z_{eff}) experienced by the electrons in the outermost energy level, resulting in a stronger attraction between them and the nucleus, and decreasing atomic radii.

- The atomic radii of the transition elements stays relatively constant moving across a period.



- This can be explained by the fact that due to the filling of the d orbitals, the effective nuclear charge experienced by the electrons in the outermost energy level for these elements remains constant, keeping the atomic radius approximately constant.

- When evaluating atomic radius of elements, it is important to not just assume the general trend that the lower the position of the element the larger its atomic radius. For example, Ga lies under Al in group 3A, but is has a smaller radius. What could be a possible cause for this deviation from the general trend?

- Ga has a greater nuclear charge than Al, but it is also expected to have a greater shielding due to the larger number of core electrons, making its Z_{eff} similar to Al. Some of Ga core electrons are in the "d" orbital, and have poor shielding due to the shape of the orbitals. As a result, Ga has a greater Z_{eff} than Al, making it slightly smaller.

Examples:

1. Which electrons experience the greatest effective nuclear charge?

   a) The valence electrons in Mg
   b) The valence electrons in Al
   c) The valence electrons in S

2. Select the larger atom in each pair listed below:

   a) N or F

   b) C or Ge

   c) N or Al

3. Arrange the following elements in order of decreasing atomic radius: S, Ca, F, Rb, Si

ELECTRON CONFIGURATION & MAGNETIC PROPERTIES

- The electron configuration of main-group monatomic ions can be deduced from the electron configuration of the neutral atom and the charge of the ion. For anions, add the number of electrons indicated by the magnitude of the charge, and for cations, subtract the number of electrons indicated by the magnitude of the charge. For example,

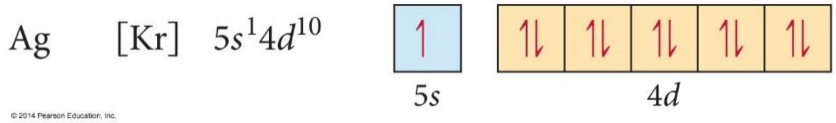
F	$1s^2\ 2s^2\ 2p^5$	F^-	$1s^2\ 2s^2\ 2p^6$
Na	$1s^2\ 2s^2\ 2p^6\ 3s^1$	Na^+	$1s^2\ 2s^2\ 2p^6\ 3s^0$

- For transition element cations, remove the electrons in the highest n-value orbitals first, even if they do not correspond to the reverse order of filling. For example,

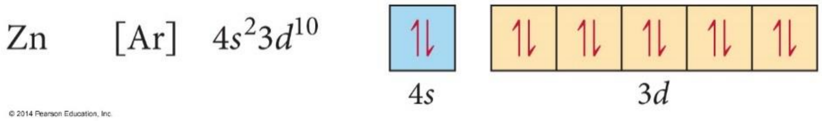
V	$[Ar]\ 4s^2\ 3d^3$	V^{2+}	$[Ar]\ 4s^0\ 3d^3$

- The loss of electrons contrary to the filing order for the transition metals is due to the stability of the resulting configurations and is supported by experimental observations.

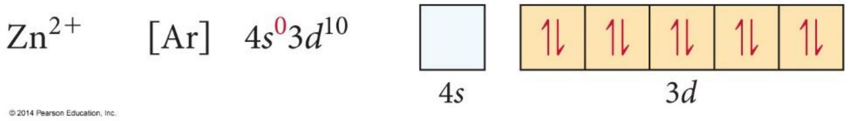
- Since an unpaired electron generates a magnetic field due to its spin, an atom or ion that has unpaired electrons is attracted to an external magnetic field and is called ***paramagnetic***. For example, Ag is paramagnetic due to its unpaired 5s electron as shown below:



- In contrast, atoms or ions that do not have unpaired electrons are repelled by an external magnetic field and are called diamagnetic. For example, Zn is diamagnetic as shown below:



- The observation that Zn^{2+} is diamagnetic is confirmation that the transition metal ions lose the 4s electrons before losing 3d electrons (shown below), since the opposite would have led to unpaired d electrons for the ion.



Examples:

1. Palladium (Z=46) is diamagnetic. Use this information to determine which of the following electron configurations is consistent with this fact.

   a) $[Kr]\ 5s^2 4d^8$ b) $[Kr]\ 4d^{10}$ c) $[Kr]\ 5s^1 4d^9$

2. How many unpaired electrons are in a nickel (III) ion, Ni^{3+}?

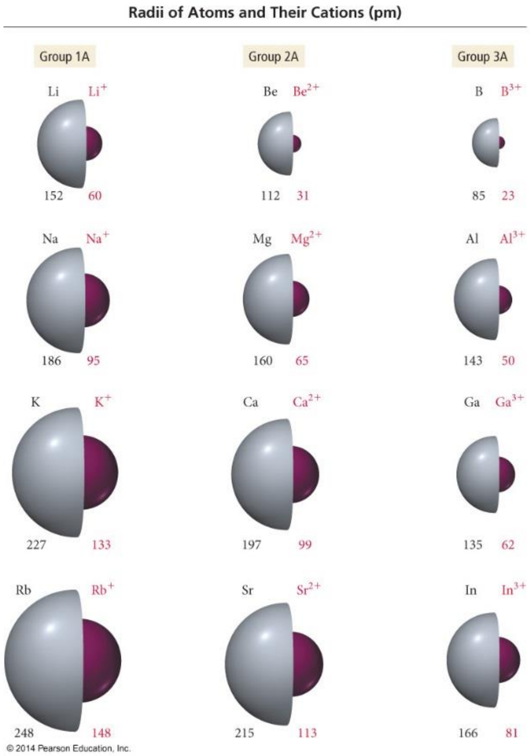
   a) 1 b) 2 c) 3 d) 4

IONIC RADII

- What happens to the radius of an atom when it becomes an ion?

- When metals lose electrons and become cations, they lose an outer energy level, and therefore become much smaller in size. This trend is the same with all cations and their atom.

- As nonmetals gain electrons and become anions, they add electrons to their outermost energy level without increasing nuclear charge. The additional electrons increase the repulsion among the outermost electrons and increase the size of the anion compared to the atom.


Radii of Atoms and Their Cations (pm)

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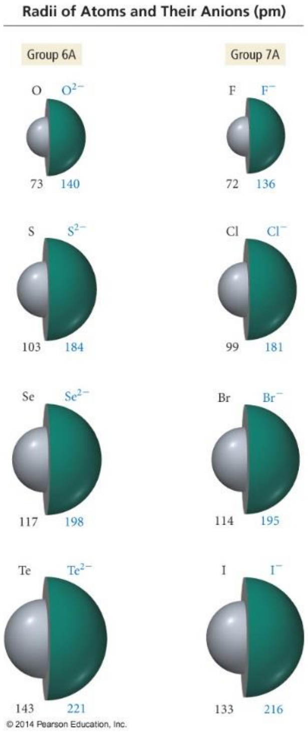
Radii of Atoms and Their Anions (pm)

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Examples:

1. Choose the large atom or ion from each pair:

   a) S or S^{2-} b) Ca or Ca^{2+} c) Br^{-} or Kr

2. Arrange the following in order of increasing radius: Ca^{2+}, Ar, Cl^{-}

IONIZATION ENERGY

- ***The ionization energy (IE)*** of an atom is the energy required to remove an electron from the atom or ion in the gaseous state. Ionization energy is always positive because removing an electron always requires energy.

- The energy required to remove the first electron is called the ***first ionization energy (IE_1)***. For example, the first ionization energy of sodium can be represented by the following equation:

$$\text{Na (g)} \rightarrow \text{Na}^{+}\text{ (g)} + 1\ e^{-} \qquad IE_1 = 496 \text{ kJ/mol}$$

- The energy to remove the second electron is the ***second ionization energy (IE_2),*** and the energy required to remove the 3rd electron is the third ionization energy (IE_3), and so on. The second ionization energy for sodium can be represented as:

$$\text{Na}^{+}\text{ (g)} \rightarrow \text{Na}^{2+}\text{ (g)} + 1\ e^{-} \qquad IE_2 = 4560 \text{ kJ/mol}$$

- Note that the second ionization energy is not the energy required to remove two electrons (that quantity is the sum of IE_1 and IE_2). Also note that the second ionization energy for Na is much greater than first ionization energy, since it removed electrons from a complete energy level (core electron).

Examples:

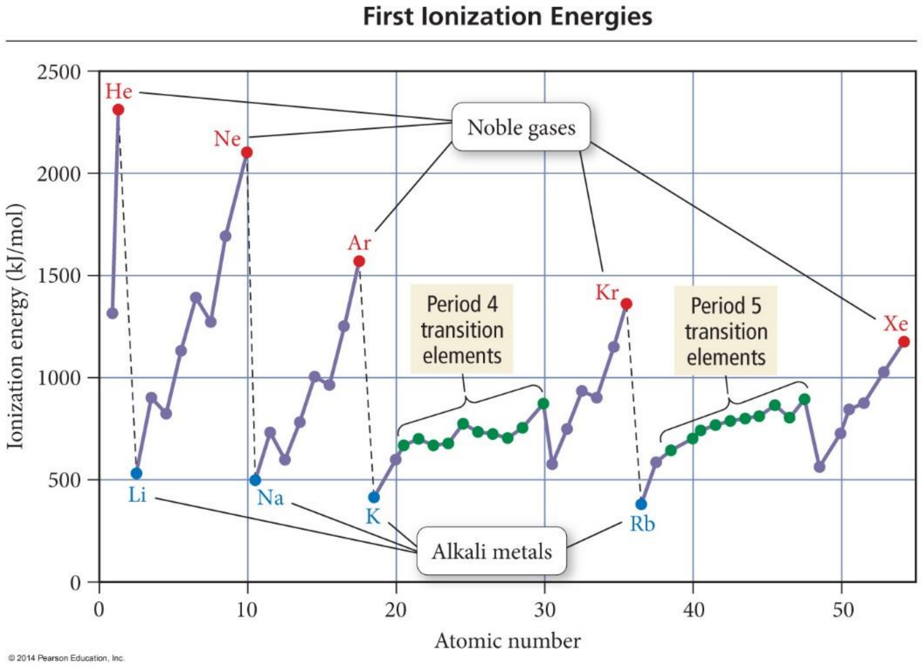
1. Based on the concept of ionization energies discussed above, explain why valence electrons are more important than core electrons in determining the reactivity and bonding in atoms.

2. Based on the definition of ionization energy, construct a relationship between atomic radius and ionization energy.

IONIZATION ENERGY

Trends in First Ionization Energy:

- The first ionization energies of the elements through Xe are shown below.



- Note the trend in the ionization energy, peaking at each noble gas and bottoming at each alkali metal. The general trends in the first ionization energy of elements can be summarized as follows:

    - Ionization energy generally decreases as we move down a group in the periodic table because the electrons in the outermost energy level are increasingly farther away from the nucleus and are therefore held less tightly.

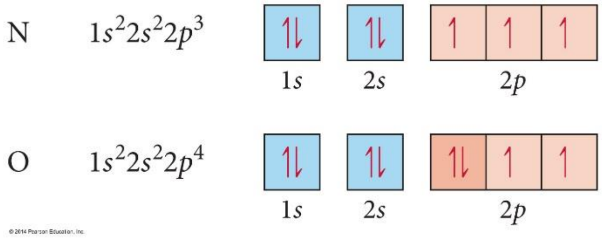
    - Ionization energy generally increases as we move across a period in the periodic table because electrons in the outermost energy level generally experience a larger effective nuclear charge (Z_{eff}).

- Careful examination of the ionization energies indicate some exceptions to the general trends noted above. For example, B has a lower ionization energy than Be, even though it lies to the right of Be in the same period.

- This exceptions is caused by the change in going from s block to p block. The electron lost by B is in 2p orbital (incomplete sublevel) compared to the electron lost in Be, which is in 2s orbital (complete sublevel). Due to the stability of the complete sublevel, it requires more energy to remove the 2s electron than the 2p electron, resulting in a higher ionization energy for Be than B. Similar exceptions occur with Al and Ga in the lower periods.

IONIZATION ENERGY

- Another exception occurs between N and O. Although O is to the right of N, it has lower ionization energy compared to N. This exceptions can be explained based on the stability of half-filled sublevel present in N (shown below). Exceptions for similar reason occur for S and Se, in the same group as O.



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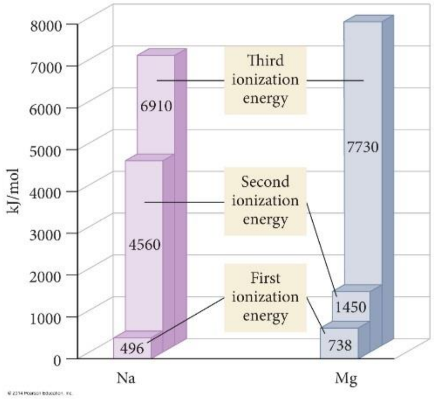
Trends in Second and Succesive Ionization Energies:



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- Shown on the right are the 1st, 2nd and 3rd ionization energies for Na and Mg. Note the large increase between 1st and 2nd IEs for Na and between 2nd and 3rd IEs for Mg. What is the cause of these large increases?

- These trends can be understood by examining the electron configurations for Na and Mg:

  Na [Ne] $3s^1$ Mg [Ne] $3s^2$

- The large increase observed between the 1st and 2nd IEs for Na is due to the loss of the core electrons for IE_2. For Mg, the core electrons are removed for the 3rd IE and therefore the corresponding large increase between IE_2 and IE_3.

- Reviewing successive IE for other elements in the 3rd period indicates a fairly uniform increase with each successive removal of valence electron, and a large increase for the removal of the first core electrons in each atom.

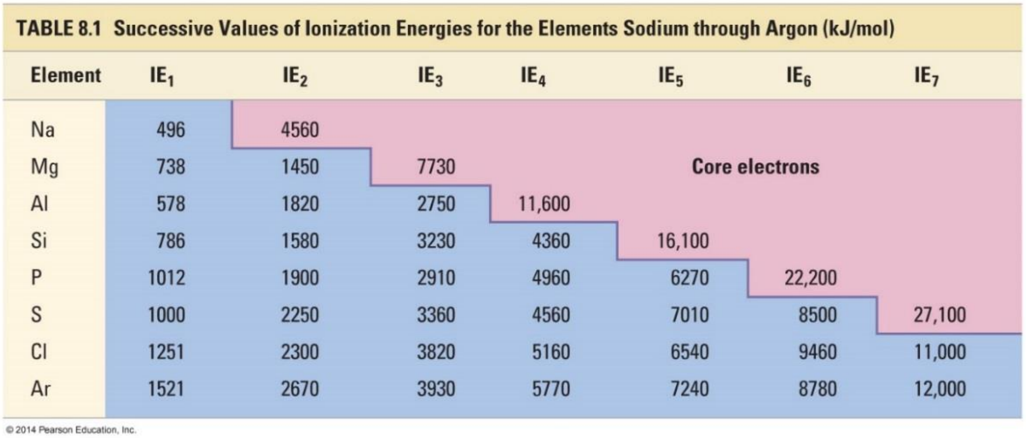

TABLE 8.1 Successive Values of Ionization Energies for the Elements Sodium through Argon (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7
Na	496	4560					
Mg	738	1450	7730				
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
P	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
Cl	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

Core electrons

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IONIZATION ENERGY

Examples:

1. Determine which element in each set has higher ionization energy:

    a) Al or S

    b) As or Sb

    c) Ca or Sr

2. Arrange the following elements in order of decreasing first ionization energy: S, Ca, F, Rb, Si.

3. The following successive ionization energies were observed for a 2nd period element:

IE_1 = 1086 kJ/mol
IE_2 = 2353 kJ/mol
IE_3 = 4620 kJ/mol
IE_4 = 6222 kJ/mol
IE_5 = 37829 kJ/mol
IE_6 = 47276 kJ/mol

To which element do these ionization energy values belong?

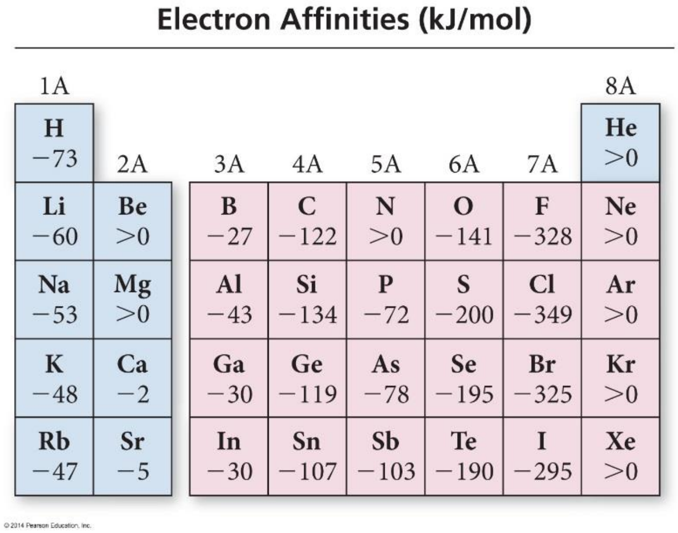
ELECTRON AFFINITY

- The ***electron affinity (EA)*** of an atom or ion is a the energy change associated with gaining an electron by the atom in the gaseous state.

- The electron affinity is usually–though not always–negative because the atom or ion usually releases energy when it gains an electron. Electron affinity can be represented by the following equation:

$$\text{Cl (g)} + 1\ e^{-} \rightarrow \text{Cl}^{-}\text{ (g)} \qquad \text{EA} = -349\ \text{kJ/mol}$$

- Electron affinities for a number of main group elements are shown below. As seen the trends in EA are not as regular as trends in other periodic properties we have studied earlier.



Electron Affinities (kJ/mol)

1A	2A	3A	4A	5A	6A	7A	8A
H −73							**He** >0
Li −60	**Be** >0	**B** −27	**C** −122	**N** >0	**O** −141	**F** −328	**Ne** >0
Na −53	**Mg** >0	**Al** −43	**Si** −134	**P** −72	**S** −200	**Cl** −349	**Ar** >0
K −48	**Ca** −2	**Ga** −30	**Ge** −119	**As** −78	**Se** −195	**Br** −325	**Kr** >0
Rb −47	**Sr** −5	**In** −30	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** >0

- Although no general trends in EA are present, the following observations are noteworthy:

  - Metals exhibit lower EA values (less negative) than nonmetals (more negative).

  - For main-group elements, EA becomes greater (more negative) as we move across the period. The exceptions to this general trend for group 2 and 5 elements can be explained by noting that elements in both these groups have filled or half-filled sublevels that are stable, causing these elements lower tendency to gain an electron.

METALLIC CHARACTER

- Another periodic property is the metallic character of elements. Earlier in this course we defined various characteristics to metals and nonmetals. We can generalize these properties as ***metallic character***, and summarize the following trends:

  - Moving across a period, metallic character decreases.

  - Moving down a group, metallic character increases.

- To illustrate the effect of these trends on the properties of elements, we look at the trend in the acid-base behavior of oxides of elements in period 3 and group 5.

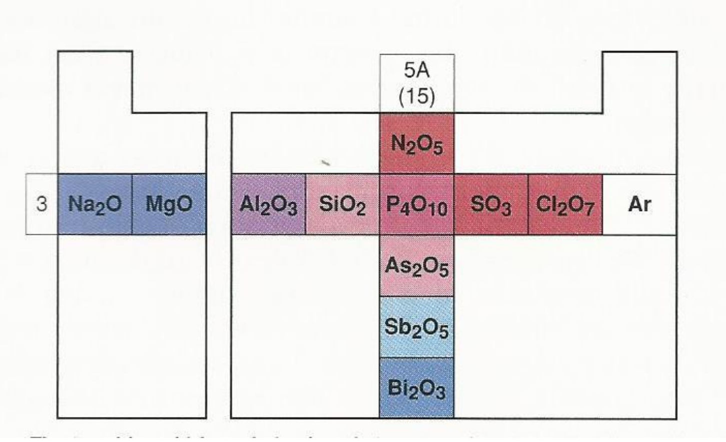
- In general, metals lose electron to oxygen to form ionic oxides that act as bases–they produce OH^- in aqueous solution. Nonmetal share electrons with oxygen to form covalent oxides that act as acids–they produce H^+ in aqueous solution.

$$Na_2O\ (s)\ +\ H_2O\ (l)\ \rightarrow\ 2\ NaOH\ (aq)$$

$$SO_2\ (g) +\ H_2O\ (l)\ \rightarrow\ H_2SO_3\ (aq)$$

- Metalloids form oxides that are ***amphoteric***–they can act both as an acid and a base.

- Acid-base properties of oxides of elements in period 3 and group 5 are shown below.



- Note that as the metallic character of elements decreases across the period, the oxides become more acidic (Na and Mg form strongly basic oxides, while Si through Cl form acidic oxides of increasing strength; Al forms amphoteric oxide).

- Also note that as the metallic character of elements increases down a group, the oxides become more basic (N, P and As form oxides of decreasing acidity, while Sb and Bi form oxides of increasing base strength).

METALLIC CHARACTER

Examples:

1. a) Why is calcium generally more reactive than magnesium?

   b) Why does Xe react with fluorine but not with iodine?

   c) Why is the first ionization energy of Se less than that of As?

2. Choose the more metallic element in each pair shown below:

a) Sn or Te

b) P or Sb

c) Ge or In

3. Arrange the following elements in order of increasing metallic character:
Si, Na, Cl, Rb

4. Which of the oxides shown below is the most basic?

   a) Bi_2O_3
   b) SiO_2
   c) Cs_2O
   d) Na_2O

ANSWERS TO IN-CHAPTER PROBLEMS:

Page	***Example No.***	***Answer***
4	1	a
	2	c
9	1a	$1s^2 2s^2 2p^6 2s^2$; [Ne] $3s^2$
	1b	$1s^2 2s^2 2p^6 2s^2 3p^3$; [Ne] $3s^2 3p^3$
	1c	$1s^2 2s^2 2p^6 2s^2 3p^6 4s^2 3d^{10} 4p^5$; [Ar] $4s^2 3d^{10} 4p^5$
	2	2 unpaired electrons
	3	$n = 3$; $l = 1$, $m_l = -1$; $m_s = -\frac{1}{2}$
12	1	$1s^2 2s^2 2p^6 2s^2 3p^6 \mathbf{4s^2} 3d^{10} \mathbf{4p^2}$
	2	[Xe] $\mathbf{6s^2} 4f^{14} 5d^{10} \mathbf{6p^3}$
17	1	c
	2	a) N; b) Ge; c) Al
	3	Rb > Ga > Si > S > F
18	1	b
	2	c
19	1	a) S^{2-}; b) Ca; c) Br^-
	2	$Ca^{2+} < Ar < Cl^-$
23	1	a) S; b) As; c) Ca
	2	F > S > Si > Ca > Rb
	3	carbon
26	2	a) Sn; b) Sb; c) In
	3	Cl < Si < Na < Rb
	4	c