Chemical Periodicity
History of the Periodic Table
Dobereiner - Law of Triads
Early in the 19th century, scientists began to seek ways to classify the elements. One attempt was by Johann Dobereiner, a German chemist, in 1817. Dobereiner found that properties of calcium, barium, and strontium were very similar. He also noted that the atomic mass of strontium was about midway between those of calcium and barium. He grouped these three elements into what he termed a **triad** . Later, Dobereiner found several other groups of three elements with similar properties. In each case the middle element has an atomic mass about halfway between those of the first and third elements in the triad. Dobereiner's ideas were not taken seriously by others - they looked like coincidences, but the idea of trends had begun.

	Triad 1		Triad 2	
	name	atomic mass	name	atomic mass
first element	calcium	40.1	lithium	6.9
third element	barium	37.3	potassium	39.1
	Average mass	88.7	Average mass	23.0
second element	strontium	87.6	sodium	23.0

Newlands - Law of Octaves
In 1863 John Newlands, an English chemist, suggested a classification. He arranged the elements in order of their increasing atomic masses. He noted there appeared to be a repetition of similar properties every eighth element. Therefore, he placed seven elements in each group. He then arranged the 49 elements known at that time into seven groups of seven each. Newlands referred to his arrangement as the **Law of Octaves** because the same properties repeated every eight elements. Newlands' arrangement worked very well through the element Ca, after that the properties did not seem to match up as well with the vertical groups. For example, in the O, S, Fe, Se group, iron (Fe) does not belong in the same group as oxygen and sulfur. This left room for improvement. The obviously misplaced elements are in bold.

Li	Be	B	C	N	O	F
Na	Mg	Al	Si	P	S	Cl
K	Ca	**Cr**	Ti	**Mn**	**Fe**	**Co, Ni**
Cu	Zn	**Y**	**In**	As	Se	Br
Rb	Sr	**La,Ce**	Zr	Nb, **Mo**	**Ru, Rh**	**Pd**

Mendeleev
In 1869, Dmitri Mendeleev, a Russian chemist, proposed a similar idea. He suggested that the properties of the elements were a function of their atomic masses. However, Mendeleev believed that similar properties occurred after periods (horizontal rows) that could vary in length. Although he placed seven elements in each of his first two rows, he placed seventeen elements in each of the next two. However Mendeleev took it one step further in predicting that some elements may not be discovered yet and left blank spots in the periodic table. He even went so far as to predict a name and the properties of these yet to be discovered elements. It later turned out he was very close on his predictions. Below

is a version of his early periodic table. Mendeleev stated that the properties of the elements are a periodic function of their atomic masses. This statement is called the **periodic law**. There was a problem with Mendeleev's table of elements - tellurium and iodine seemed in the wrong columns if they were placed only by atomic mass. However Mendeleev assumed the mass was measured incorrectly and placed them according to their properties. He figured that later measurements would prove him correct.

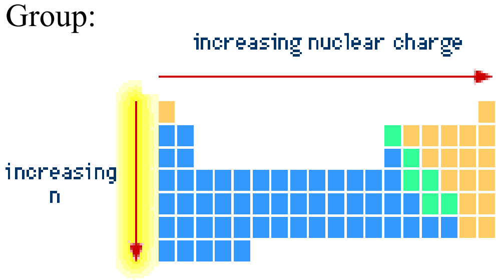
H							
Li	Be	B	C	N	O	F	
Na	Mg	Al	Si	P	S	Cl	
K	Ca	---	Ti	V	Cr	Mn	Fe, Co, Ni
Cu	Zn	---	---	As	Se	Br	Ru, Rh, Pd
Ag	Cd	In	Sn	Sb	Te	I	
Cs	Ba						

Moseley

More inconsistencies were found with early versions of the periodic table. Henry Moseley, in 1913, found the reason for the inconsistencies. He performed X-ray experiments on the elements and found that each element has an integral positive charge, the atomic number. As a result of Moseley's work, the periodic law was revised. It now has as its basis the atomic numbers of the elements instead of the atomic masses. The modern statement of the **periodic law** is *the properties of the elements are a periodic function of their atomic numbers.* The atomic number indicates the number of protons in the nucleus of each atom of the element. Because an atom is electrically neutral, the atomic number also indicates the number of electrons surrounding the nucleus. Certain electron arrangements are repeated periodically as atoms increase in atomic number. As you have already seen, atoms with similar electron configurations are placed in the same column. This table is called the periodic table of the elements.

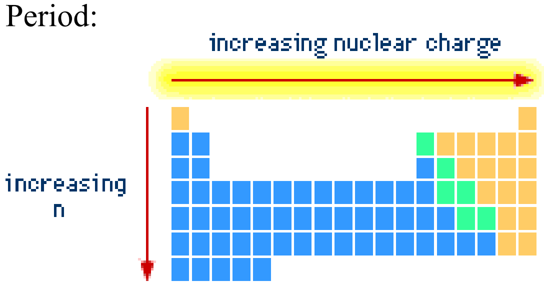
Periodic Trends

Group:



1. Orbitals are larger.
2. Electrons are farther from the nucleus.
3. Valence electrons are less tightly bound.

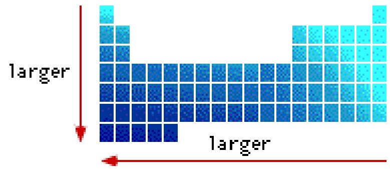
Period:



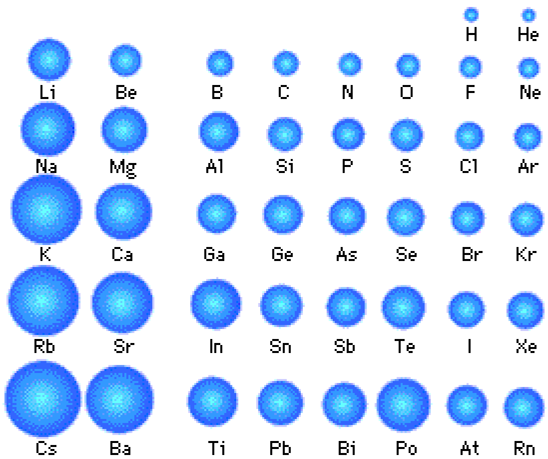
1. Electrostatic attraction increases.
2. Electrons are pulled closer to the nucleus.
3. Valence electrons are more tightly held.

Atomic Radius:

- Atomic radii increase with increasing **electron shielding**.
- Atomic radii decrease with increasing **effective nuclear charge**.
- **Cations** have smaller radii than their neutral atoms.
- **Anions** have larger radii than their neutral atoms.



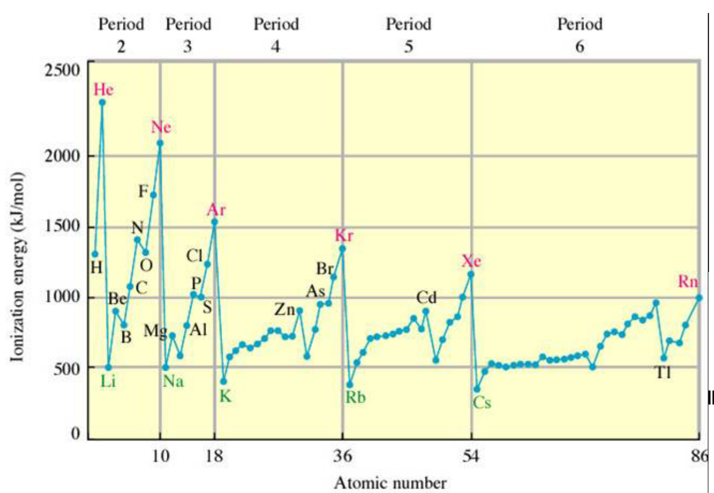
Periodic Trends in Atomic Size

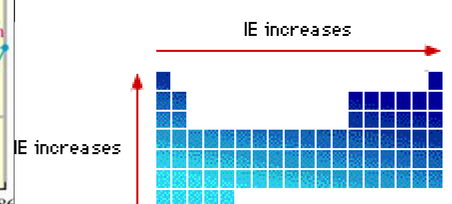


Atomic Size by Element

FirstIonization potential:

- **Ionization energy (IE)** is the energy necessary to remove an electron from an atom, molecule or ion.
- Moving down a group, ionization energy decreases because of increased **electron shielding.**
- Moving across a row from left to right ionization energy increases because of increased **effective nuclear charge**.





$atom(g) + IE \longrightarrow atom^{+}(g) + e^{-}(g)$

Electron Affinity

- **Electron affinity (EA)** is the energy released when an electron is added to a neutral atom.

- Electron affinity generally increases in magnitude toward the top and the right on the periodic table.

- As you move **down a group**, less energy is released (becomes more positive or number is larger which means less energy released) because the **atomic radius is larger** resulting in a weaker attraction between the nucleus and valence energy level. If an atoms valence energy level is further from the nucleus less energy lost when an electron is added to an atom.

- · As you move **across a period**, more energy is released **effective nuclear charge increases** across a period and the additional electron will be closer to the nucleus.

Electronegativity:

- **Electronegativity** is a parameter describing the ability of an atom to attract additional electron density to itself.

- Electronegativity decreases down a group due to increased electron shielding.

- Due to increasing **nuclear charge**, electronegativity increases moving across a **period** from left to right.

Exercises:

1. In each of the following pairs, circle the species with the *higher* first ionization energy:

(a) Li or Cs (b) Cl^- or Ar (c) Ca or Br (d) Na^+ or Ne (e) B or Be

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2. In each of the following pairs, circle the species with the *larger* atomic radius:

(a) Mg or Ba (b) S or S^{2-} (c) Cu^{+2} or Cu (d) He or H^- (e) Na or Cl

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3. *Circle* the best choice in each list:

(a) highest *first* ionization energy: C, N, Si

(b) largest radius: S^{2-}, Cl^{-}, Cl

(c) highest electronegativity: As, Sn, S

(d) smallest atom: Na, Li, Be

(e) most paramagnetic: Fe, Co, Ni

(f) lowest *first* ionization energy: K, Na, Ca

(g) highest *second* ionization energy: Na, Mg, Al

(h) lowest *second* ionization energy: Ar, K, Ca

Answers (be sure you can explain the reason for each answer!):
1. (a) Li; (b) Ar (isoelectronic pair); (c) Br; (d) Na^+ (isoelectronic pair); (e) Be (common exception: what is the rule here?).
2. (a) Ba; (b) S^{2-}; (c) Cu; (d) H^- (isoelectronic pair); (e) Na.
3. (a) N; (b) S^{2-} (S^{2-} and Cl^- are isoelectronic); (c) S; (d) Be; (e) Fe (hint: determine no. of unpaired spins for each element); (f) K; (g) Na; (h) Ca.