Mendeleev

- order elements by atomic mass
- saw a repeating pattern of properties
- **Periodic Law** – When the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically
- put elements with similar properties in the same column
- used pattern to predict properties of undiscovered elements
- where atomic mass order did not fit other properties, he re-ordered by other properties
  - ✓ Te & I

Mendeleev's Predictions

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)

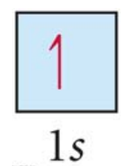
	Mendeleev's predicted properties	Actual properties
Atomic mass	About 72 amu	72.64 amu
Density	5.5 g/cm^3	5.35 g/cm^3
Formula of oxide	XO_2	GeO_2
Formula of chloride	XCl_4	$GeCl_4$

What vs. Why

- Mendeleev's Periodic Law allows us to predict what the properties of an element will be based on its position on the table
- it doesn't explain why the pattern exists
- Quantum Mechanics is a theory that explains why the periodic trends in the properties exist

Spin Quantum Number, m_s

- spin quantum number describes how the electron spins on its axis
  - ✓ clockwise or counterclockwise
  - ✓ **spin up** or **spin down**
- spins must cancel in an orbital
  - ✓ **paired**
- m_s can have values of ±½



Pauli Exclusion Principle

- no two electrons in an atom may have the same set of 4 quantum numbers
- therefore no orbital may have more than 2 electrons, and they must have with opposite spins
- knowing the number orbitals in a sublevel allows us to determine the maximum number of electrons in the sublevel
  - ✓ *s* sublevel has 1 orbital, therefore it can hold 2 electrons
  - ✓ *p* sublevel has 3 orbitals, therefore it can hold 6 electrons
  - ✓ *d* sublevel has 5 orbitals, therefore it can hold 10 electrons
  - ✓ *f* sublevel has 7 orbitals, therefore it can hold 14 electrons

Allowed Quantum Numbers

Quantum Number	*Values*	*Number of Values*	*Significance*
Principal, n	1, 2, 3, ...	-	distance from nucleus
Azimuthal, *l*	0, 1, 2, ..., n-1	n	shape of orbital
Magnetic, m_l	-*l*,...,0,...+*l*	2*l* + 1	orientation of orbital
Spin, m_s	-½, +½	2	direction of electron spin

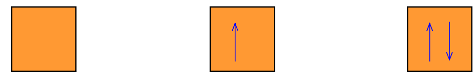
Electron Configurations

- the **ground state** of the electron is the lowest energy orbital it can occupy
- the distribution of electrons into the various orbitals in an atom in its ground state is called its **electron configuration**
- the number designates the principal energy level
- the letter designates the sublevel and type of orbital
- the superscript designates the number of electrons in that sublevel
- He = $1s^2$

Orbital diagram

Orbital Diagrams

- we often represent an orbital as a square and the electrons in that orbital as arrows
  - ✓ the direction of the arrow represents the spin of the electron

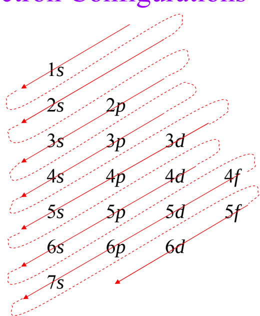


unoccupied orbital | orbital with 1 electron | orbital with 2 electrons

Order of Subshell Filling in Ground State Electron Configurations

start by drawing a diagram putting each energy shell on a row and listing the subshells, (*s, p, d, f*), for that shell in order of energy, (left-to-right)

next, draw arrows through the diagonals, looping back to the next diagonal each time



Filling the Orbitals with Electrons

- energy shells fill from lowest energy to high
- subshells fill from lowest energy to high
  - ✓ $s \rightarrow p \rightarrow d \rightarrow f$
  - ✓ Aufbau Principle
- orbitals that are in the same subshell have the same energy
- no more than 2 electrons per orbital
  - ✓ Pauli Exclusion Principle
- when filling orbitals that have the same energy, place one electron in each before completing pairs
  - ✓ Hund's Rule

Valence Electrons

- the electrons in all the subshells with the highest principal energy shell are called the **valence electrons**
- electrons in lower energy shells are called **core electrons**
- chemists have observed that one of the most important factors in the way an atom behaves, both chemically and physically, is the number of valence electrons

Electron Configuration of Atoms in their Ground State

- Kr = 36 electrons

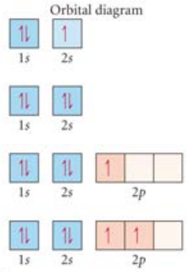
  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6$
  - ✓ there are 28 core electrons and 8 valence electrons
- Rb = 37 electrons

  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^1$

  $[Kr]5s^1$
- for the $5s^1$ electron in Rb the set of quantum numbers is $n = 5$, $l = 0$, $m_l = 0$, $m_s = +½$
- for an electron in the 2p sublevel, the set of quantum numbers is $n = 2$, $l = 1$, $m_l = -1$ or (0,+1), and $m_s = -½$ or (+½)

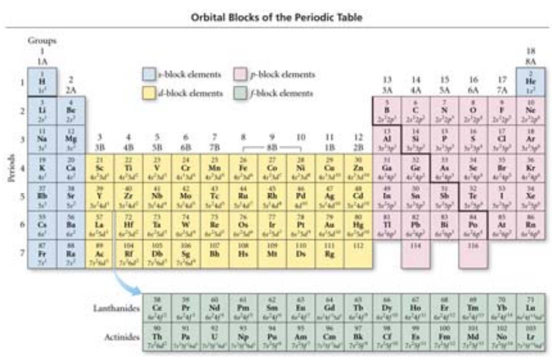
Electron Configurations

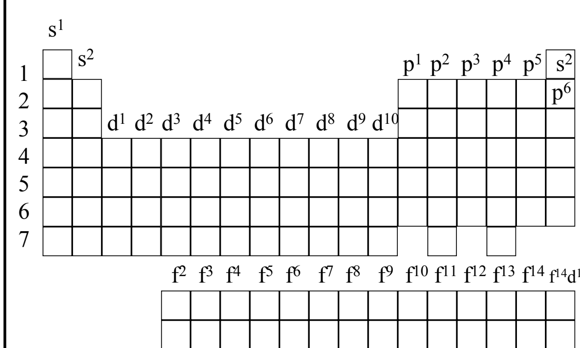
Symbol	Number of electrons	Electron configuration	Orbital diagram
Li	3	$1s^2 2s^1$	
Be	4	$1s^2 2s^2$	
B	5	$1s^2 2s^2 2p^1$	
C	6	$1s^2 2s^2 2p^2$	



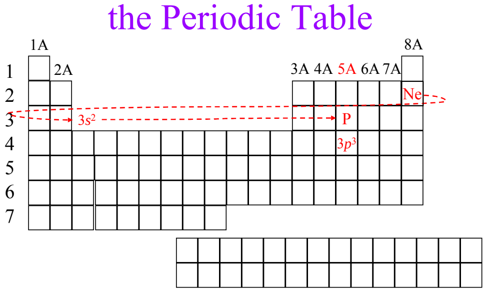
Electron Configuration & the Periodic Table

- the Group number corresponds to the number of valence electrons
- the length of each "block" is the maximum number of electrons the sublevel can hold
- the Period number corresponds to the principal energy level of the valence electrons





Electron Configuration from the Periodic Table



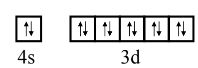
P = $[Ne]3s^2 3p^3$

P has 5 valence electrons

Transition Elements

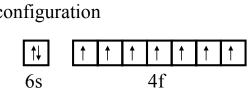
- for the *d* block metals, the principal energy level is one less than valence shell
  - ✓ one less than the Period number
  - ✓ sometimes *s* electron "promoted" to *d* sublevel

  Zn
  Z = 30, Period 4, Group 2B
  $[Ar]4s^2 3d^{10}$



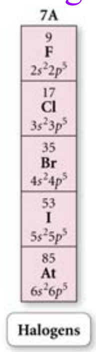
- for the *f* block metals, the principal energy level is two less than valence shell
  - ✓ two less than the Period number they really belong to
  - ✓ sometimes *d* electron in configuration

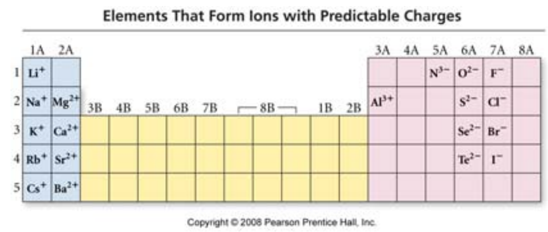
  Eu
  Z = 63, Period 6
  $[Xe]6s^2 4f^7$



Properties & Electron Configuration

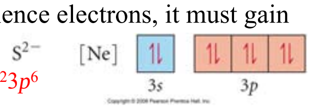
- ***elements in the same column have similar chemical and physical properties because they have the same number of valence electrons in the same kinds of orbitals***





Electron Configuration of Anions in their Ground State

- anions are formed when atoms gain enough electrons to have 8 valence electrons
  - ✓filling the *s* and *p* sublevels of the valence shell
- the sulfur atom has 6 valence electrons
  - S atom = $1s^22s^22p^63s^23p^4$
- in order to have 8 valence electrons, it must gain 2 more
  - S^{2-} anion = $1s^22s^22p^63s^23p^6$

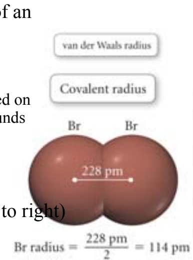


Electron Configuration of Cations in their Ground State

- cations are formed when an atom loses all its valence electrons
  - ✓resulting in a new lower energy level valence shell
  - ✓however the process is always endothermic
- the magnesium atom has 2 valence electrons
  - Mg atom = $1s^22s^22p^63s^2$
- when it forms a cation, it loses its valence electrons
  - Mg^{2+} cation = $1s^22s^22p^6$

Trend in Atomic Radius – Main Group

- Different methods for measuring the radius of an atom, and they give slightly different trends
  - ✓ van der Waals radius = nonbonding
  - ✓ covalent radius = bonding radius
  - ✓ atomic radius is an average radius of an atom based on measuring large numbers of elements and compounds
- Atomic Radius Increases down group
  - ✓ valence shell farther from nucleus
  - ✓ effective nuclear charge fairly close
- Atomic Radius Decreases across period (left to right)
  - ✓ adding electrons to same valence shell
  - ✓ effective nuclear charge increases
  - ✓ valence shell held closer

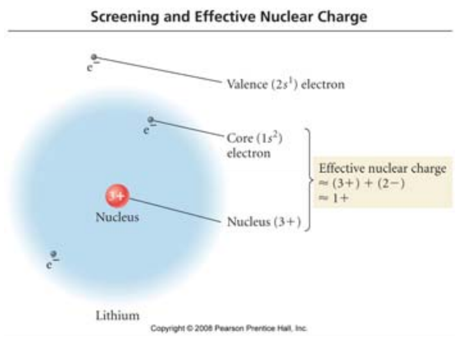


Effective Nuclear Charge

- in a multi-electron system, electrons are simultaneously attracted to the nucleus and repelled by each other
- outer electrons are ***shielded*** from full strength of nucleus
  - ✓screening effect
- **effective nuclear charge** is net positive charge that is attracting a particular electron
- **Z** is nuclear charge, **S** is electrons in lower energy levels
  - ✓electrons in same energy level contribute to screening, but very little
  - ✓effective nuclear charge on sublevels trend, *s* > *p* > *d* > *f*

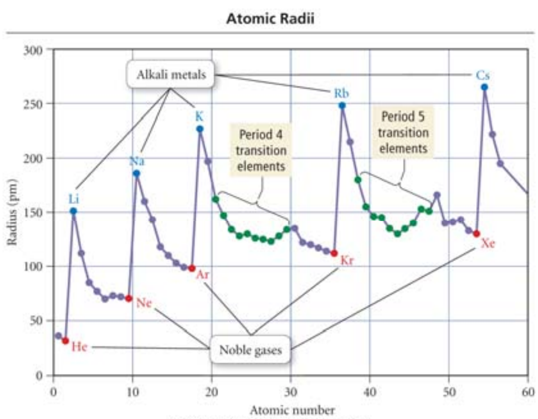
$$Z_{effective} = Z - S$$

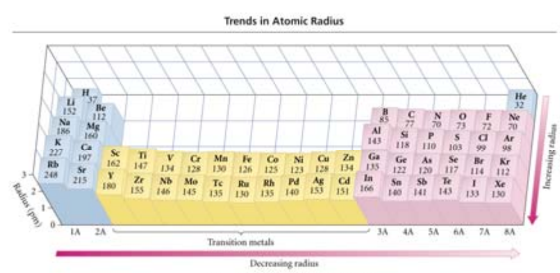
Screening & Effective Nuclear Charge



Trends in Atomic Radius Transition Metals

- increase in size down the Group
- atomic radii of transition metals roughly the same size across the *d* block
  - ✓must less difference than across main group elements
  - ✓valence shell ns^2, not the *d* electrons
  - ✓effective nuclear charge on the ns^2 electrons approximately the same





Electron Configuration of Cations in their Ground State

- cations form when the atom loses electrons from the valence shell
- for transition metals electrons, may be removed from the sublevel closest to the valence shell

Al atom = $1s^22s^22p^63s^23p^1$

Al^{+3} ion = $1s^22s^22p^6$

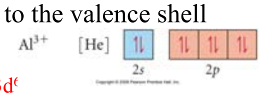
Fe atom = $1s^22s^22p^63s^23p^64s^23d^6$

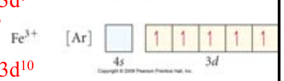
Fe^{+2} ion = $1s^22s^22p^63s^23p^63d^6$

Fe^{+3} ion = $1s^22s^22p^63s^23p^63d^5$

Cu atom = $1s^22s^22p^63s^23p^64s^13d^{10}$

Cu^{+1} ion = $1s^22s^22p^63s^23p^63d^{10}$





Magnetic Properties of Transition Metal Atoms & Ions

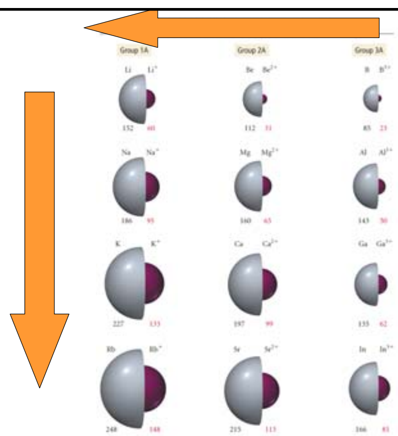
- electron configurations that result in unpaired electrons mean that the atom or ion will have a net magnetic field – this is called **paramagnetism**
  - ✓will be attracted to a magnetic field
- electron configurations that result in all paired electrons mean that the atom or ion will have no magnetic field – this is called **diamagnetism**
  - ✓slightly repelled by a magnetic field
- both Zn atoms and Zn^{2+} ions are diamagnetic, showing that the two 4*s* electrons are lost before the 3*d*
  - ✓Zn atoms $[Ar]4s^23d^{10}$
  - ✓Zn^{2+} ions $[Ar]4s^03d^{10}$

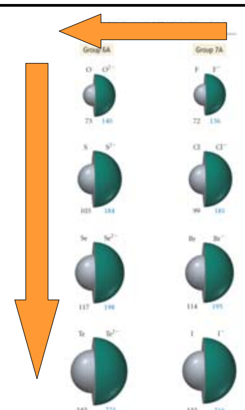
Trends in Ionic Radius

- Ions in same group have same charge
- Ion size increases down the group
  - ✓ higher valence shell, larger
- Cations smaller than neutral atom; Anions bigger than neutral atom
- Cations smaller than anions
  - ✓ except Rb^{+1} & Cs^{+1} bigger or same size as F^{-1} and O^{-2}
- Larger positive charge = smaller cation
  - ✓ for isoelectronic species
  - ✓ isoelectronic = same electron configuration
- Larger negative charge = larger anion
  - ✓ for isoelectronic series

Periodic Pattern - Ionic Radius (Å)

1A	2A	3A	4A	5A	6A	7A
H: -1, +1						
Li +1 0.68	Be +2 0.31	B +3 0.23	C -4	N -3 1.71	O -2 1.40	F -1 1.33
Na +1 0.97	Mg +2 0.66	Al +3 0.51	Si -4	P -3 2.12	S -2 1.84	Cl -1 1.81
K +1 1.33	Ca +2 0.99	Ga +3 0.62; +1	Ge -4	As -3 2.22	Se -2 1.98	Br -1 1.96
Rb +1 1.47	Sr +2 1.13	In +3 0.81; +1	Sn +4 0.71; +2	Sb	Te -2 2.21	I -1 2.20
Cs +1 1.69	Ba +2 1.35	Tl +3 0.95; +1	Pb +4 0.84; +2	Bi		



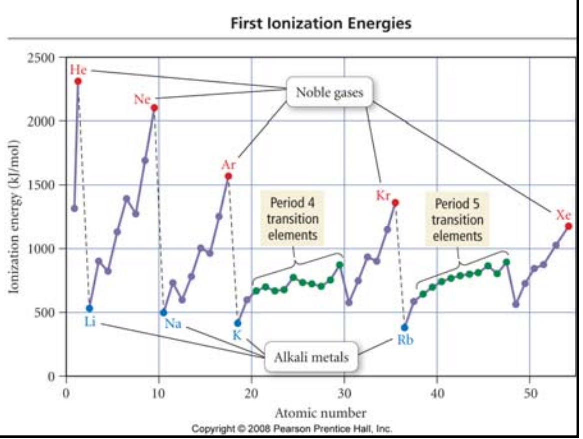


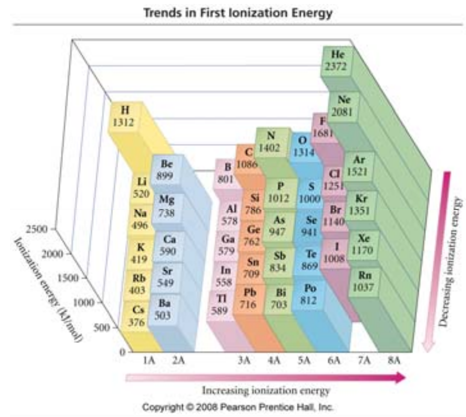
Ionization Energy

- minimum energy needed to remove an electron from an atom
  - ✓ gas state
  - ✓ endothermic process
  - ✓ valence electron easiest to remove
  - ✓ $M(g) + IE_1 \rightarrow M^{1+}(g) + 1\ e^-$
  - ✓ $M^{+1}(g) + IE_2 \rightarrow M^{2+}(g) + 1\ e^-$
    - ➢ first ionization energy = energy to remove electron from neutral atom; 2nd IE = energy to remove from +1 ion; etc.

General Trends in 1st Ionization Energy

- larger the effective nuclear charge on the electron, the more energy it takes to remove it
- the farther the most probable distance the electron is from the nucleus, the less energy it takes to remove it
- 1st IE **decreases** down the group
  - ✓ valence electron farther from nucleus
- 1st IE generally **increases** across the period
  - ✓ effective nuclear charge increases





Irregularities in the Trend

- Ionization Energy generally increases from left to right across a Period
- except from 2A to 3A, 5A to 6A

Be 1s ↑↓ 2s ↑↓ 2p [ ][ ][ ]

B 1s ↑↓ 2s ↑↓ 2p [↑][ ][ ]

N 1s ↑↓ 2s ↑↓ 2p [↑][↑][↑]

O 1s ↑↓ 2s ↑↓ 2p [↑↓][↑][↑]

Which is easier to remove an electron from B or Be? Why?

Irregularities in the First Ionization Energy Trends

Be 1s ↑↓ 2s ↑↓ 2p [ ][ ][ ]

Be^+ 1s ↑↓ 2s ↑ 2p [ ][ ][ ]

To ionize Be you must break up a full sublevel, cost extra energy

B 1s ↑↓ 2s ↑↓ 2p [↑][ ][ ]

B^+ 1s ↑↓ 2s ↑↓ 2p [ ][ ][ ]

When you ionize B you get a full sublevel, costs less energy

Irregularities in the First Ionization Energy Trends

N 1s ↑↓ 2s ↑↓ 2p [↑][↑][↑]

N^+ 1s ↑↓ 2s ↑↓ 2p [↑][↑][ ]

To ionize N you must break up a half-full sublevel, cost extra energy

O 1s ↑↓ 2s ↑↓ 2p [↑↓][↑][↑]

O^+ 1s ↑↓ 2s ↑↓ 2p [↑][↑][↑]

When you ionize O you get a half-full sublevel, costs less energy

Trends in Successive Ionization Energies

- removal of each successive electron costs more energy
  - ✓ shrinkage in size due to having more protons than electrons
  - ✓ outer electrons closer to the nucleus, therefore harder to remove
- regular increase in energy for each successive valence electron
- large increase in energy when start removing core electrons

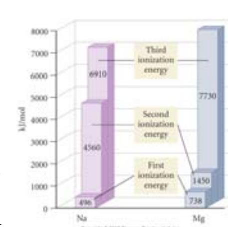


TABLE 8.1 Successive Values of Ionization Energies for the Elements Sodium through Argon (kJ/mol)

Element	IE_1	IE_2	IE_3	IE_5	IE_4	IE_6	IE_7
Na	496	4560					
Mg	738	1450	7730		Core electrons		
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

Trends in Electron Affinity

- energy released when an neutral atom gains an electron
  - ✓ gas state
  - ✓ $M(g) + 1e^- \rightarrow M^{-1}(g) + EA$
- defined as exothermic (-), but may actually be endothermic (+)
  - ✓ alkali earth metals & noble gases endothermic, WHY?
- more energy released (more -); the larger the EA
- generally increases across period
  - ✓ becomes more negative from left to right
  - ✓ not absolute
  - ✓ lowest EA in period = alkali earth metal or noble gas
  - ✓ highest EA in period = halogen

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

Metallic Character

- Metals
  - ✓ malleable & ductile
  - ✓ shiny, lusterous, reflect light
  - ✓ conduct heat and electricity
  - ✓ most oxides basic and ionic
  - ✓ form cations in solution
  - ✓ lose electrons in reactions - **oxidized**
- Nonmetals
  - ✓ brittle in solid state
  - ✓ dull
  - ✓ electrical and thermal insulators
  - ✓ most oxides are acidic and molecular
  - ✓ form anions and polyatomic anions
  - ✓ gain electrons in reactions - **reduced**
- metallic character increases left
- metallic character increase down

Trends in Metallic Character I