Professor K

Section 8

Electron Configuration
Periodic Table

Schrödinger

- Cannot be solved for multielectron atoms
- We must assume the orbitals are all hydrogen-like

Differences

- In the H atom, all subshells (s,p,d,f) of a principal shell are at the same energy
- This varies for other elements, though all orbitals within a subshell are at the same energy level. (2 slides ahead) (DEGENERATE orbitals)
- Orbital energies are lower in multielectron atoms than in H. (WHY????)
- In multielectron atoms, for higher numbered principal shells, some subshells have nearly identical energies. (WHY???)

REMINDER

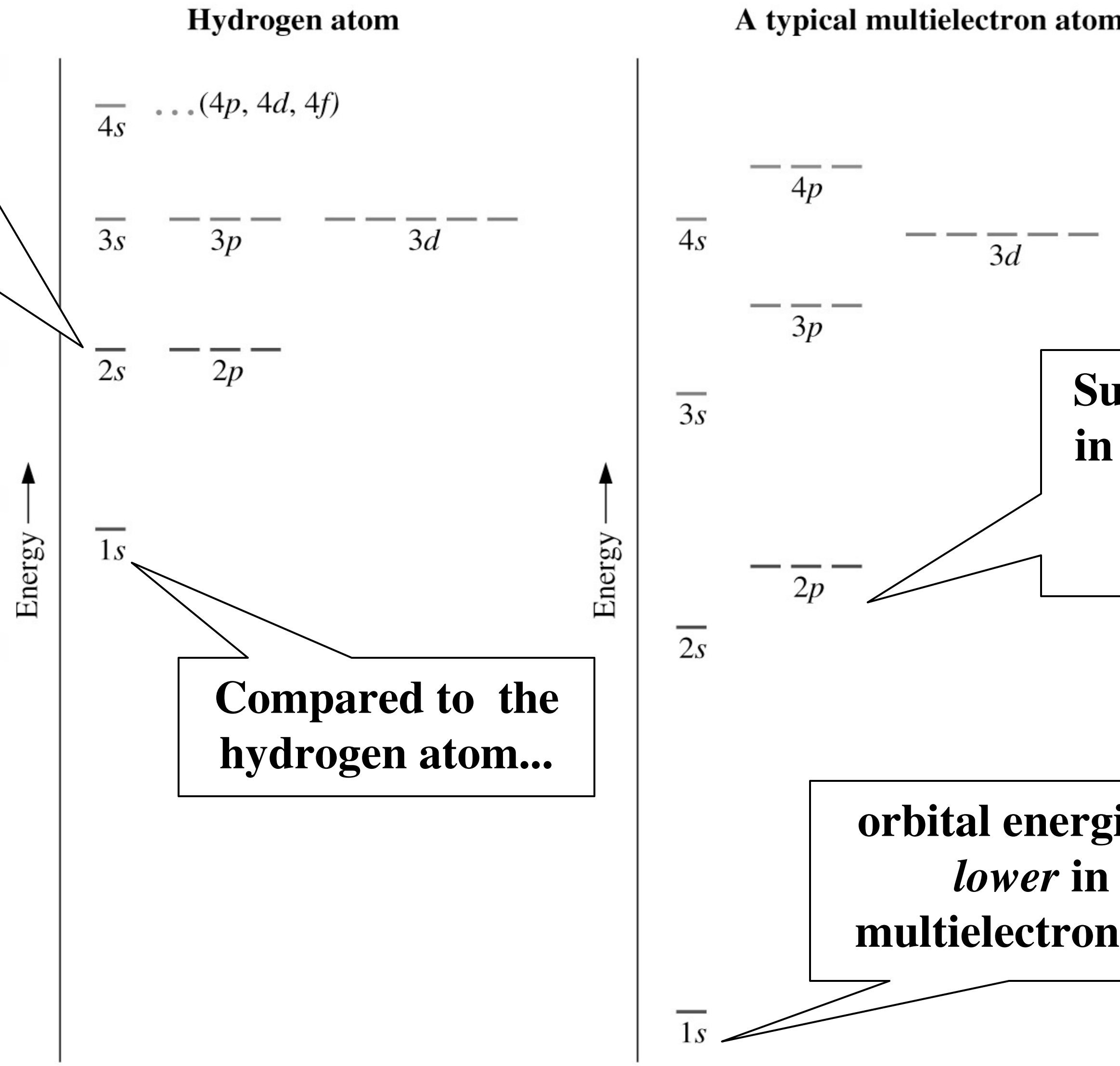
ORBITALS

ARE

REGIONS OF PROBABILITY

Orbital energy diagrams

Subshells within a shell are at the *same* energy level in hydrogen: 2*s* = 2*p*.



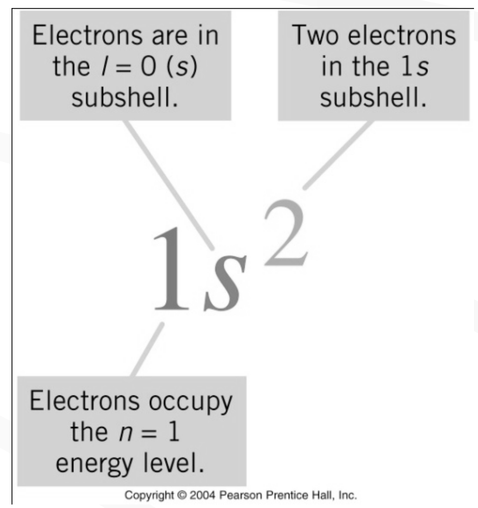
Compared to the hydrogen atom...

Subshells are *split* in a multielectron atom: 2*s* < 2*p*.

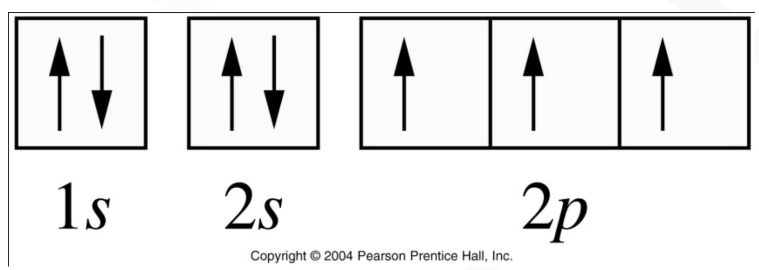
orbital energies are *lower* in a multielectron atom.

Electron configuration

- Describes the distribution of electrons among the various orbitals in the atom.
- Electron configuration is represented in two ways:
- *s p d f* notation
  - Numbers denote principal shell
  - Letters denote subshell
  - Superscripts denote number of electrons per subshell
  - Electrons occupy orbitals of the lowest energy available



- Orbital diagram



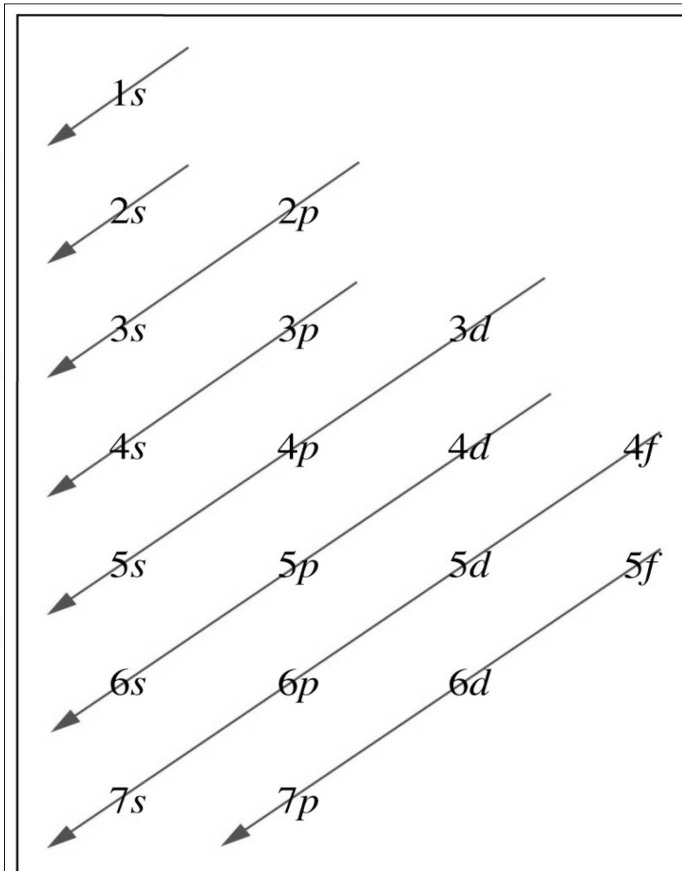
s p d f *notation (cont'd)*

- No two electrons can have the same set of 4 quantum numbers
- Thus, an orbital can accommodate at most 2 electrons (Wolfgang Pauli, 1926)– The *Pauli Exclusion Principle*
- Electrons enter empty orbitals whenever possible when faced with a set of identical-energy orbitals (Hund's rule)
- Electrons in half-filled orbitals have the same (parallel) spins
- Therefore, when drawing *ground state* electron configurations, the aufbau ("building up") principle is employed

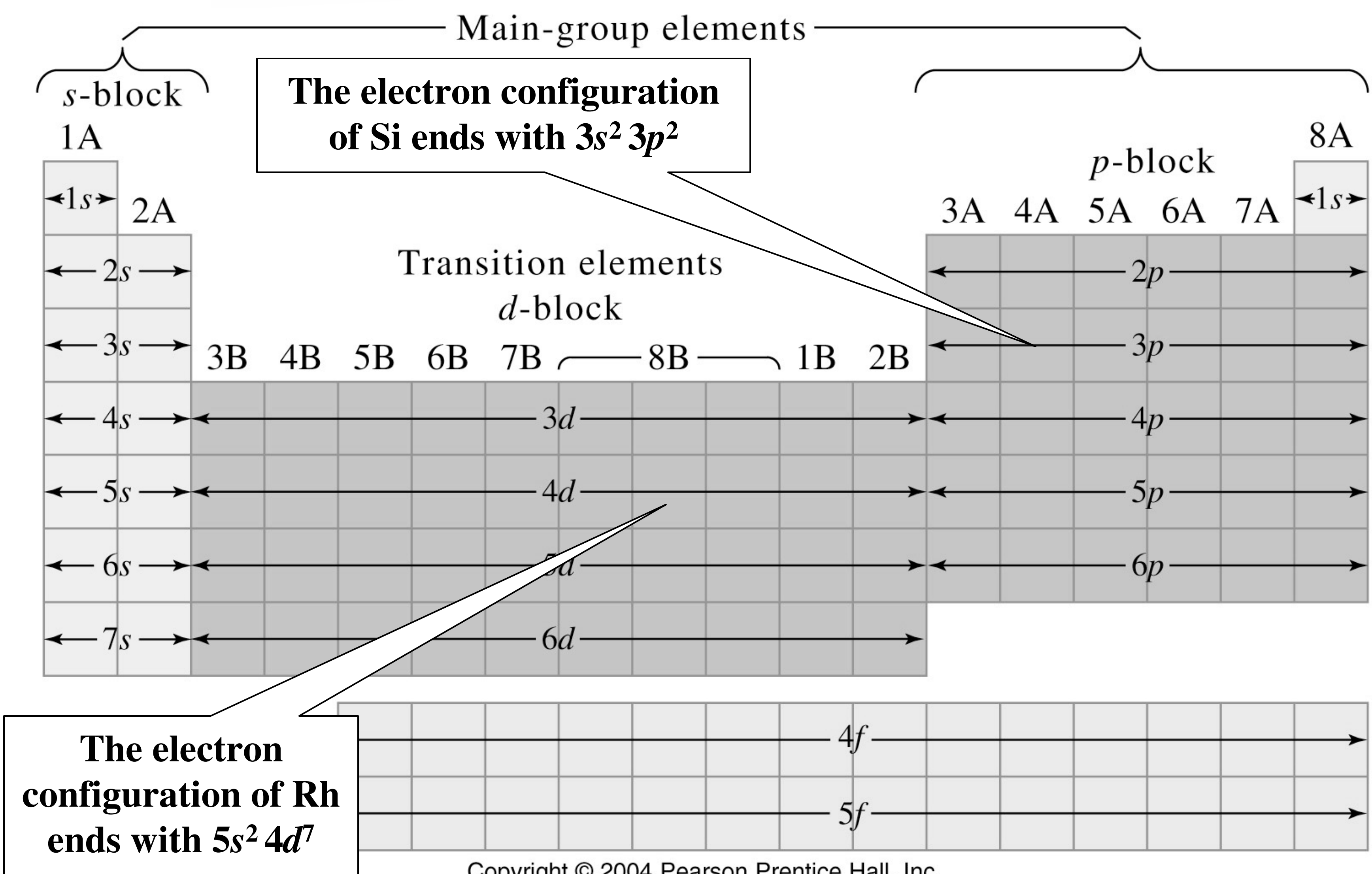
s p d f *notation (cont'd)*

- 1*s*, 2*s*, 2*p*, 3*s*, 3*p*, 4*s*, 3*d*, 4*p*, 5*s*, 4*d*, 5*p*, 6*s*, 4*f*, 5*d*, 6*p*, 7*s*, 5*f*, 6*d*, 7*p*

- To remember the above, don't use the figure... ***<u>USE THE PERIODIC TABLE</u>***



Using the periodic table to write e^- configurations



Exceptions to aufbau

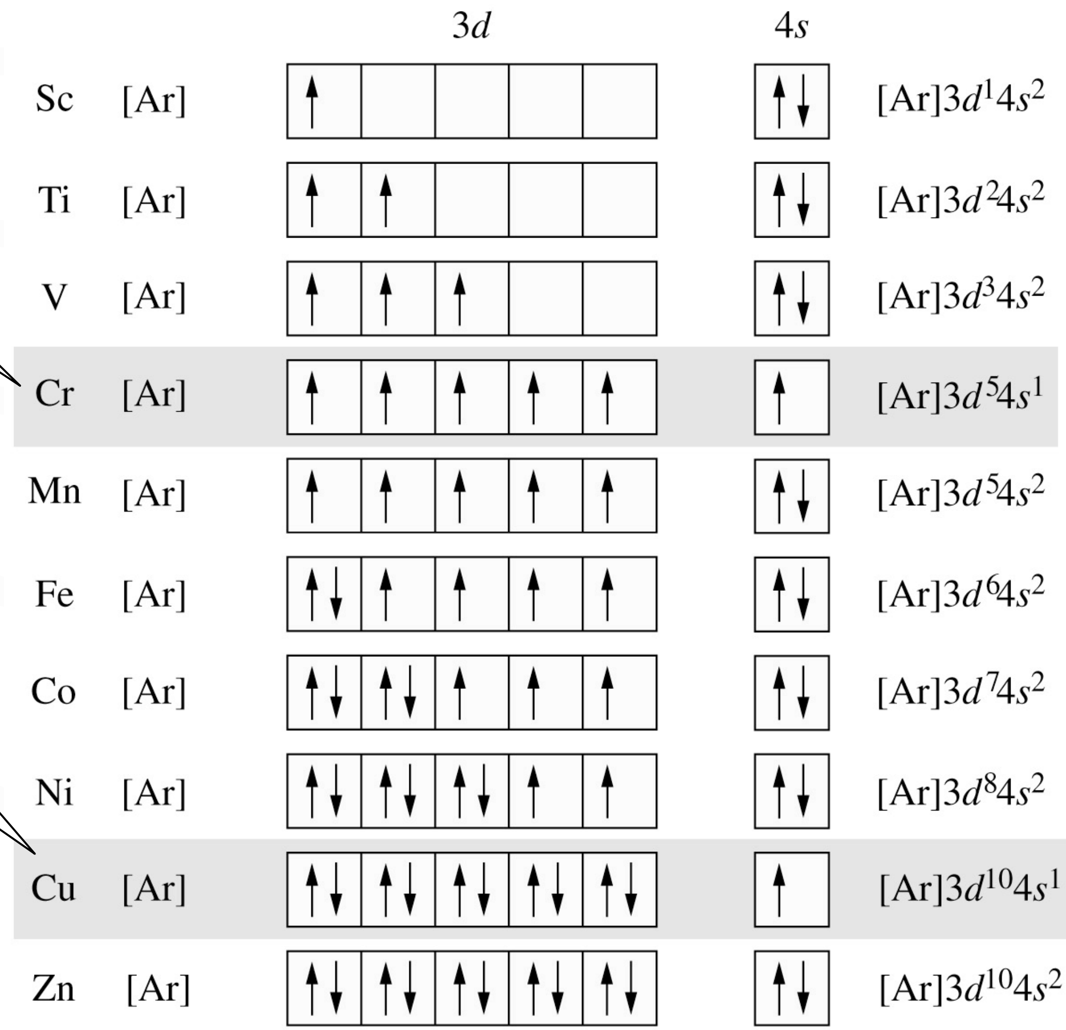
- Cr and Cu are examples where the observed configuration (confirmed experimentally) is not as expected due to a *hyperstability* of a FILLED or HALF-FILLED subshell

Exceptions to the Aufbau principle (cont'd)

Half-filled *d* subshell plus half-filled *s* subshell has slightly lower in energy than $s^2\,d^4$.

Filled *d* subshell plus half-filled *s* subshell has slightly lower in energy than $s^2\,d^9$.

More exceptions occur farther down the periodic table. They aren't always predictable, because energy levels get closer together.



Exceptions to the Aufbau principle (cont'd)

1A	2A	3B	4B	5B	6B	7B	8B	8B	8B	1B	2B	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** $3s^23p^6$
19 **K** $4s^1$	20 **Ca** $4s^2$	21 **Sc** $3d^14s^2$	22 **Ti** $3d^24s^2$	23 **V** $3d^34s^2$	24 **Cr** $3d^54s^1$	25 **Mn** $3d^54s^2$	26 **Fe** $3d^64s^2$	27 **Co** $3d^74s^2$	28 **Ni** $3d^84s^2$	29 **Cu** $3d^{10}4s^1$	30 **Zn** $3d^{10}4s^2$	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** $4s^24p^6$
37 **Rb** $5s^1$	38 **Sr** $5s^2$	39 **Y** $4d^15s^2$	40 **Zr** $4d^25s^2$	41 **Nb** $4d^45s^1$	42 **Mo** $4d^55s^1$	43 **Tc** $4d^55s^2$	44 **Ru** $4d^75s^1$	45 **Rh** $4d^85s^1$	46 **Pd** $4d^{10}$	47 **Ag** $4d^{10}5s^1$	48 **Cd** $4d^{10}5s^2$	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** $5s^25p^6$
55 **Cs** $6s^1$	56 **Ba** $6s^2$	57 ***La** $5d^16s^2$	72 **Hf** $5d^26s^2$	73 **Ta** $5d^36s^2$	74 **W** $5d^46s^2$	75 **Re** $5d^56s^2$	76 **Os** $5d^66s^2$	77 **Ir** $5d^76s^2$	78 **Pt** $5d^96s^1$	79 **Au** $5d^{10}6s^1$	80 **Hg** $5d^{10}6s^2$	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** $6s^26p^6$
87 **Fr** $7s^1$	88 **Ra** $7s^2$	89 **†Ac** $6d^17s^2$	104 **Rf** $6d^27s^2$	105 **Db** $6d^37s^2$	106 **Sg** $6d^47s^2$	107 **Bh**	108 **Hs**	109 **Mt**	110	111	112						

*	58 **Ce** $4f^26s^2$	59 **Pr** $4f^36s^2$	60 **Nd** $4f^46s^2$	61 **Pm** $4f^56s^2$	62 **Sm** $4f^66s^2$	63 **Eu** $4f^76s^2$	64 **Gd** $4f^75d^16s^2$	65 **Tb** $4f^96s^2$	66 **Dy** $4f^{10}6s^2$	67 **Ho** $4f^{11}6s^2$	68 **Er** $4f^{12}6s^2$	69 **Tm** $4f^{13}6s^2$	70 **Yb** $4f^{14}6s^2$	71 **Lu** $4f^{14}5d^16s^2$
†	90 **Th** $6d^27s^2$	91 **Pa** $5f^26d^17s^2$	92 **U** $5f^36d^17s^2$	93 **Np** $5f^46d^17s^2$	94 **Pu** $5f^67s^2$	95 **Am** $5f^77s^2$	96 **Cm** $5f^76d^17s^2$	97 **Bk** $5f^97s^2$	98 **Cf** $5f^{10}7s^2$	99 **Es** $5f^{11}7s^2$	100 **Fm** $5f^{12}7s^2$	101 **Md** $5f^{13}7s^2$	102 **No** $5f^{14}7s^2$	103 **Lr** $5f^{14}6d^17s^2$

s-block elements

d-block elements

p-block elements

f-block elements

Example

- What is the electron configuration of Cs?

- ***Noble-gas-core (condensed) abbreviation***: Another example of chemists' shorthand. The portion of the config. that corresponds to the electron config. of the nearest previous noble gas is replaced with a bracketed chemical symbol. It's easier to write …

  (Z = 3) Li **[He]**$2s^1$

  (Z = 22) Ti **[Ar]**$4s^2 3d^2$

Example

- Give the complete ground-state electron configuration of a strontium atom
  (a) in *spdf* notation and
  (b) in the noble-gas-core abbreviated notation
  (c) in the orbital box diagram notation.

Valence electrons

- The outermost shell of electrons is known as the *valence shell*
- The inner electrons are the *core electrons*
- When writing the configuration of *ions*, add or remove electrons to/from the valence shell
- Often results in noble gas configuration
- EXCEPTION: Transition elements- outer *s* electrons are lost first
- If two species have the same electron configuration, they are said to be *isoelectronic*

Valence electrons and core electrons

- The ***valence shell*** is the outermost occupied principal shell. The valence shell contains the ***valence electrons***.
- For main group elements, the number of valence shell electrons is the same as the periodic table group number (2A elements: two valence electrons, etc.)

  The period number is the same as the principal quantum number n of the electrons in the valence shell.
- Electrons in inner shells are called ***core electrons.***

Five valence electrons, for which $n = 4$

Example: As $[Ar]\ 4s^2\ 3d^{10} 4p^3$

28 core electrons

Electron configurations of ions

- To obtain the electron configuration of an ***anion*** by the aufbau process, we simply ***add*** the additional electrons to the valence shell of the neutral nonmetal atom.
- The number added often completes the shell.
- A nonmetal monatomic ion usually attains the electron configuration of a noble gas atom.

O^{2-} : [Ne]

Br^{-} : [Kr]

Electron configurations of ions (cont'd)

- A metal atom loses electrons to form a ***cation***.
- Electrons are ***removed*** from the configuration of the atom.
- The first electrons lost are those of the ***highest principal*** quantum number.
- If there are two subshells with the same highest principal quantum number, electrons are lost from the subshell with the higher *l*.

Electron configurations of ions *(cont'd)*

Atom	Ion	(or)
F $1s^2\,2s^2 2p^5$	F^- $1s^2\,2s^2 2p^6$	[Ne]
S [Ne] $3s^2\,3p^4$	S^{2-} [Ne] $3s^2\,3p^6$	[Ar]
Sr [Kr] $5s^2$	Sr^{2+} [Kr] $\cancel{5s^2}$	[Kr]
Ti [Ar] $4s^2\,3d^2$	Ti^{4+} [Ar] $\cancel{4s^2\,3d^2}$	[Ar]
Fe [Ar] $4s^2\,3d^6$	Fe^{2+} [Ar] $\cancel{4s^2}\,3d^6$	[Ar] $3d^6$

What would be the configuration of Fe^{3+}? Of Sn^{2+}?

Valence **electrons are lost first.**

e^{-} configuration of ions (cont'd)

Table 8.3 Electron Configurations of Some Metal Ions

Noble Gas			Pseudo–Noble Gas[a]		18 + 2[b]	Various	
Li^{+}	Be^{2+}	Al^{3+}	Cu^{+}	Zn^{2+}	In^{+}	Cr^{2+}:	$[Ar]3d^4$
Na^{+}	Mg^{2+}		Ag^{+}	Cd^{2+}	Tl^{+}	Cr^{3+}:	$[Ar]3d^3$
K^{+}	Ca^{2+}		Au^{+}	Hg^{2+}	Sn^{2+}	Mn^{2+}:	$[Ar]3d^5$
Rb^{+}	Sr^{2+}				Pb^{2+}	Mn^{3+}:	$[Ar]3d^4$
Cs^{+}	Ba^{2+}				Sb^{3+}	Fe^{2+}:	$[Ar]3d^6$
					Bi^{3+}	Fe^{3+}:	$[Ar]3d^5$
						Co^{2+}:	$[Ar]3d^7$
						Co^{3+}:	$[Ar]3d^6$
						Ni^{2+}:	$[Ar]3d^8$

[a] In the pseudo–noble gas configuration, all valence electrons are lost and the remaining $(n-1)$ shell has 18 electrons in the configuration $(n-1)s^2(n-1)p^6(n-1)d^{10}$.

[b] In the 18 + 2 configuration, $(n-1)s^2(n-1)p^6(n-1)d^{10}ns^2$, two valence electrons remain.

Magnetism

- *Diamagnetic* atoms have all electrons paired
- *Paramagnetic* atoms have some unpaired electrons
- *Ferromagnetism* is the exceptionally strong attractions of a magnetic field for iron and a few other substances.
- Despite the fact that your instructor's thesis centered on this topic, we will not discuss it further

Periodic properties

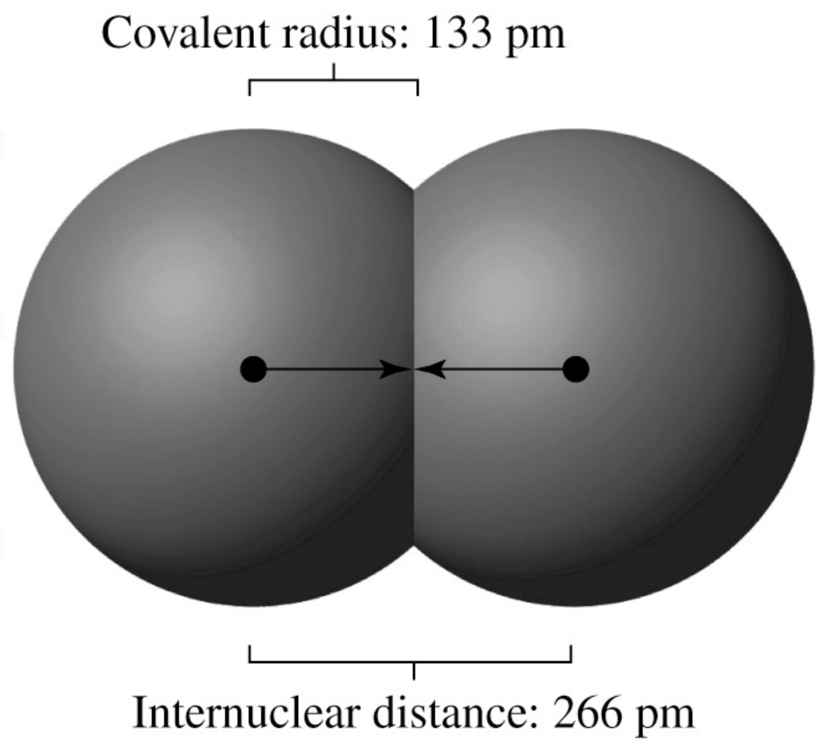
- Certain physical and chemical properties recur at regular intervals (Mendeleev, anyone?), and/or vary in regular fashion, when the elements are arranged according to increasing atomic number.
- Melting point, boiling point, hardness, density, physical state, and chemical reactivity are periodic properties.
- We will examine several periodic properties that are readily explained using electron configurations.
  - Atomic radii
  - Effective nuclear charge
  - Covalent radii
  - Ionic radii
  - Ionization energy
  - Electron affinity

Periodic properties: atomic radius

- Half the distance between the nuclei of two atoms is the ***atomic radius.***

  Covalent radius: half the distance between the nuclei of two identical atoms joined in a *molecule*.

  Metallic radius: half the distance between the nuclei of adjacent atoms in a *solid metal*.

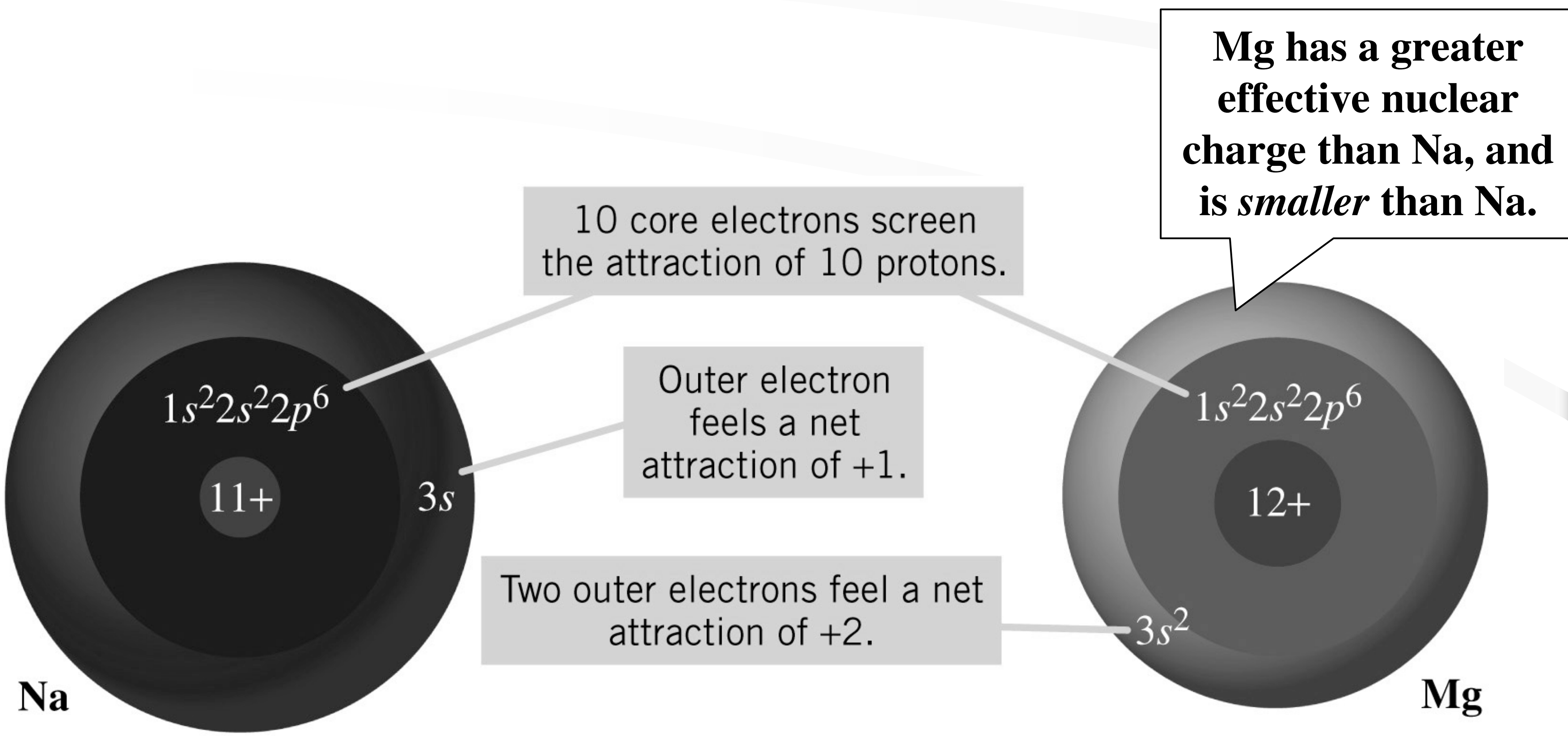


Atomic radius (cont'd)

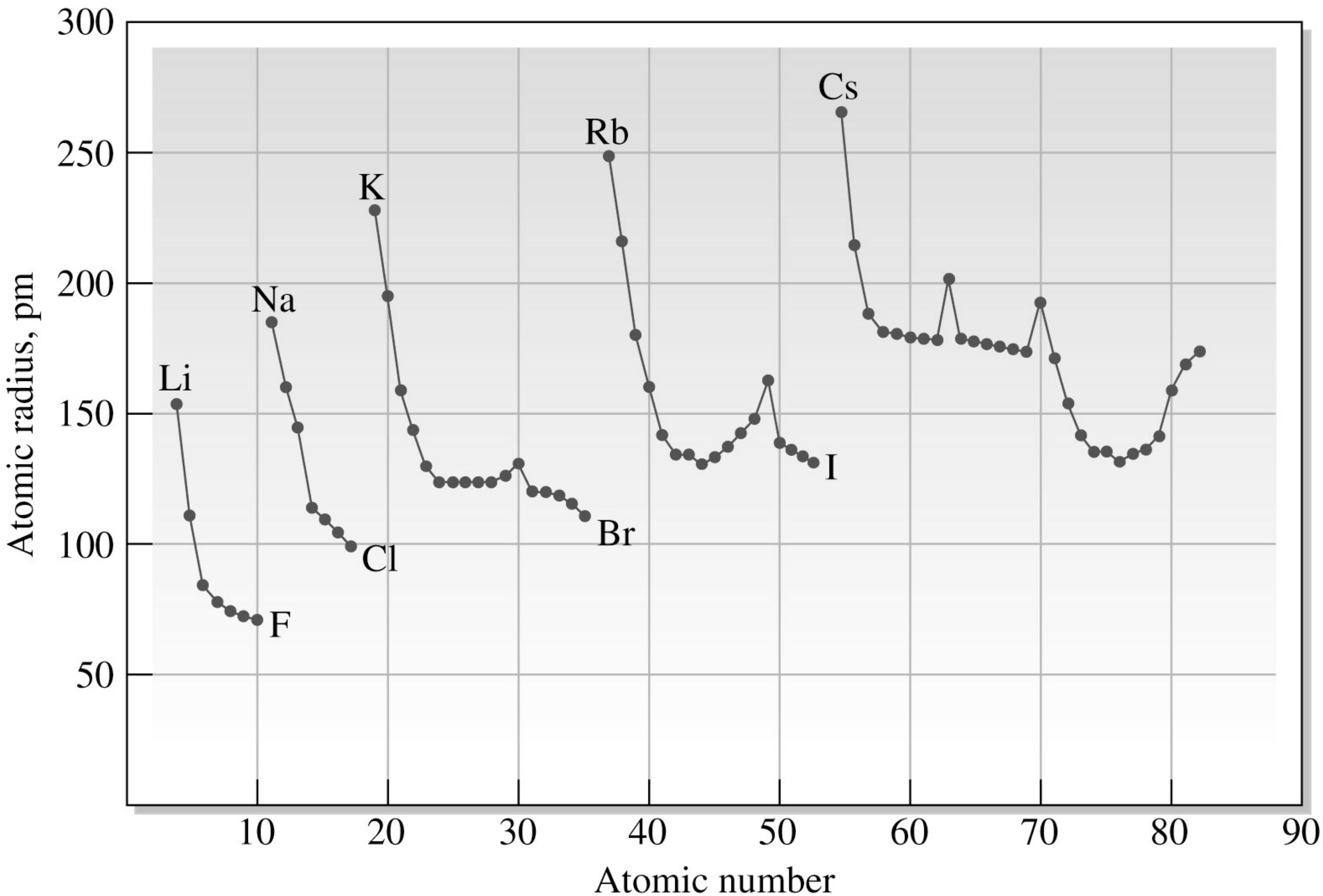
- Atomic radius ***increases*** from top to bottom within a group.
- The value of *n* increases, moving down the periodic table.
- The value of *n* relates to the ***distance*** of an electron from the nucleus.
- Often in Angstroms (10^{-10}m) or picometers (10^{-12}m)

Atomic radius (cont'd)

- Atomic radius ***decreases*** from left to right within a period.
- Why? The ***effective nuclear charge*** (Z_{eff}) increases from left to right, increasing the attraction of the nucleus for the valence electrons, and making the atom smaller.



Atomic radii of the elements

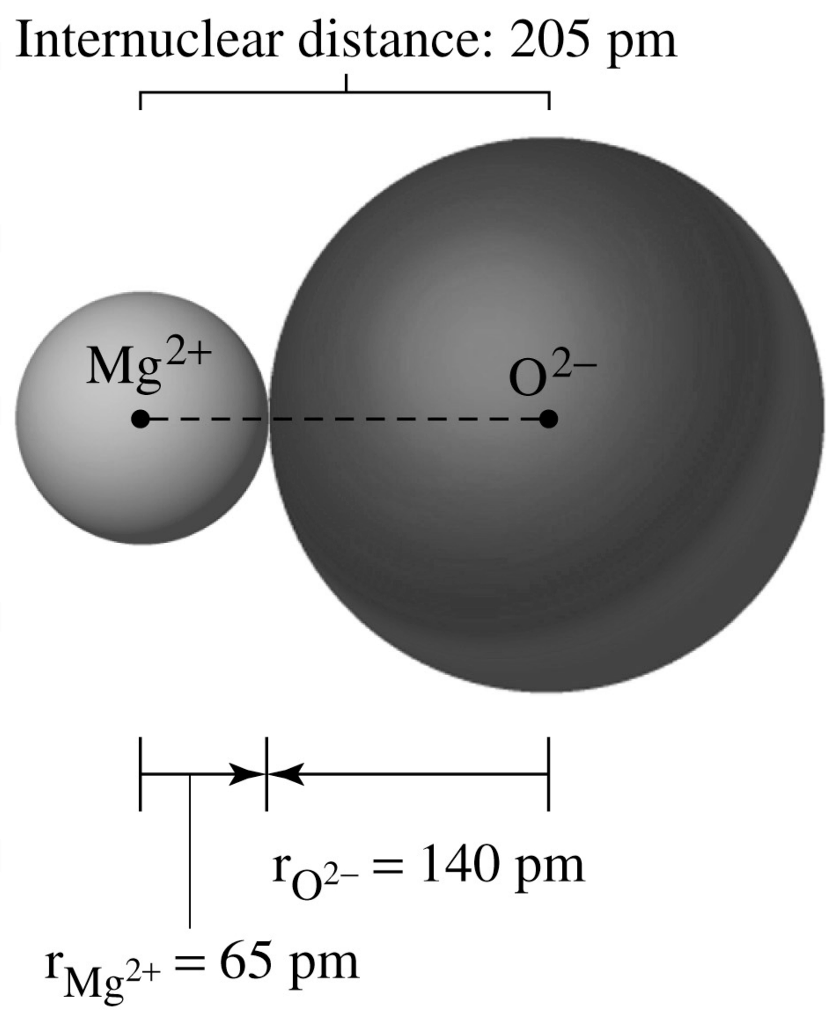


Example

- With reference only to a periodic table, arrange each set of elements in order of increasing atomic radius:
  - (a) Mg, S, Si
  - (b) As, N, P
  - (c) As, Sb, Se

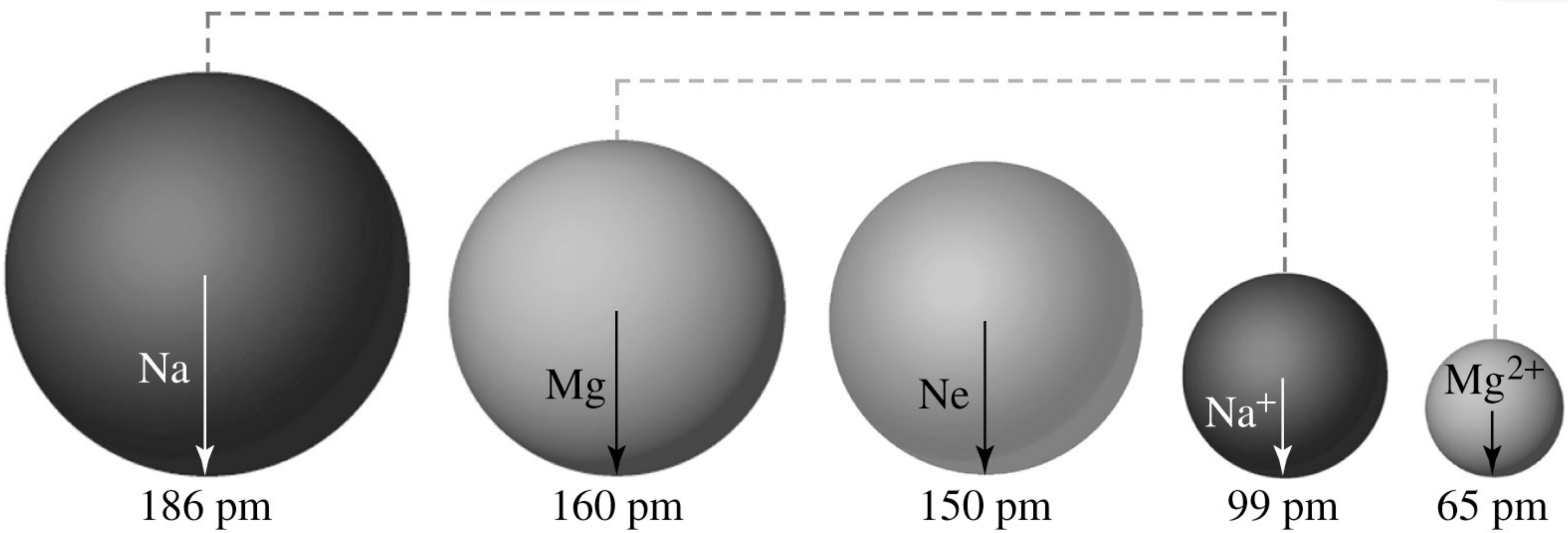
Ionic radii

The ***ionic radius*** of each ion is the portion of the distance between the nuclei occupied by that ion.



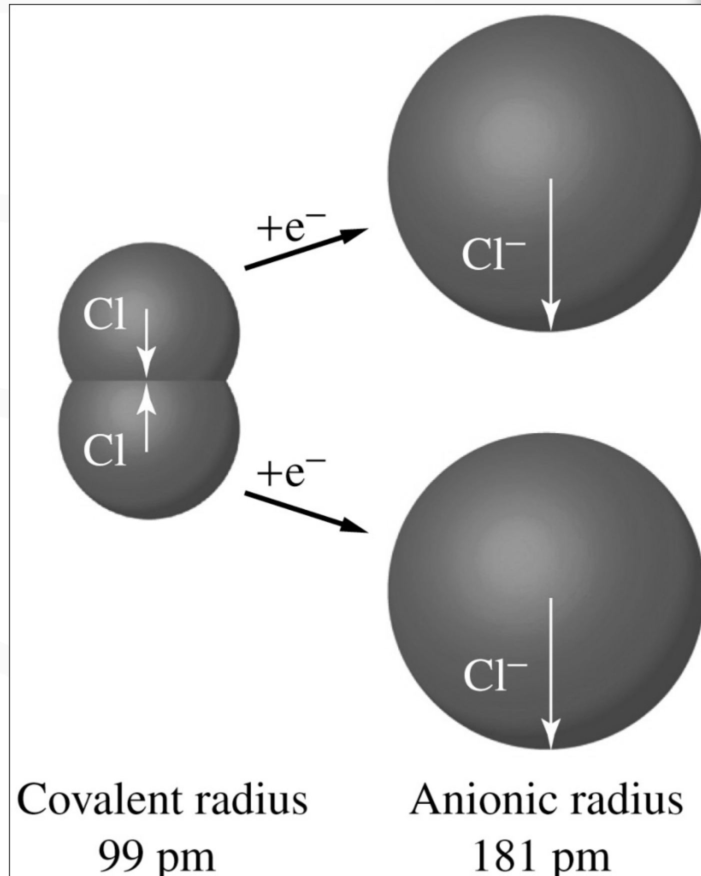
Ionic radii- cations

- *Cations* are **smaller** than the atoms from which they are formed; the value of *n* usually decreases. Also, there is less electron–electron repulsion.

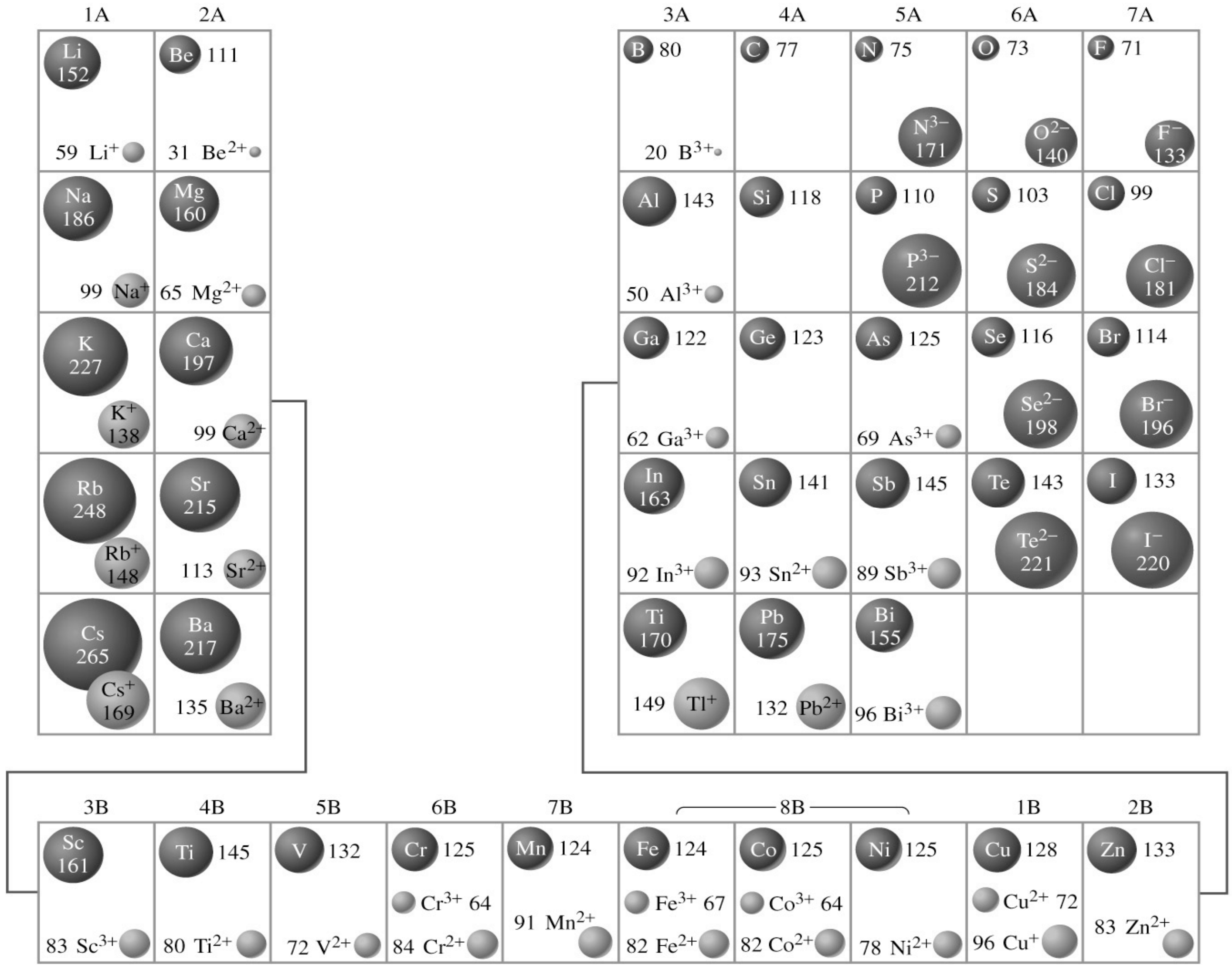


Ionic radii- anions

- ***Anions*** are ***larger*** than the atoms from which they are formed.
- Effective nuclear charge is unchanged, but additional electron(s) increase electron–electron repulsion.
- ***Isoelectronic*** species have the same electron configuration; size decreases with effective nuclear charge.



Some atomic and ionic radii



Example

- Refer to a periodic table, but not to the previous figure, and arrange the following species in the expected order of increasing radius:
  Ca^{2+}, Fe^{3+}, K^{+}, S^{2-}, Se^{2-}

Ionization energy

- ***Ionization energy*** (*IE*) is the energy required to remove an electron from a ground-state gaseous atom.
- *IE* is usually expressed in kJ per mole of atoms.

$$M(g) \rightarrow M^{+}(g) + e^{-} \qquad \Delta H = IE_1$$

$$M^{+}(g) \rightarrow M^{2+}(g) + e^{-} \qquad \Delta H = IE_2$$

$$M^{2+}(g) \rightarrow M^{3+}(g) + e^{-} \qquad \Delta H = IE_3$$

Trends in IE

- $I_1 < I_2 < I_3$
  - Removing an electron from a *positive ion* is more difficult than removing it from a *neutral atom*.
- A large jump in I occurs after valence electrons are completely removed (why?).
- I_1 ***decreases*** from top to bottom on the periodic table.
  - n increases; valence electron is farther from nucleus.
- I_1 generally ***increases*** from left to right, with exceptions.
  - Greater effective nuclear charge from left to right holds electrons more tightly.

Selected ionization energies

Compare I_2 to I_1 for a 2A element, then for the corresponding 1A element.

Why is I_2 for each 1A element so *much* greater than I_1?

Why don't we see the *same* trend for each *2A element*? $I_2 > I_1$ … but only about twice as great …

Table 8.4 Ionization Energies of Group 1A and Group 2A Elements, kJ /mol

	1A	2A
	Li	Be
I_1	520	900
I_2	7298	1757
	Na	Mg
I_1	496	738
I_2	4562	1451
	K	Ca
I_1	419	590
I_2	3051	1145
	Rb	Sr
I_1	403	550
I_2	2633	1064
	Cs	Ba
I_1	376	503
I_2	2230	965

Selected ionization energies

General trend in I_1: An increase from left to right, but …

…I_1 drops, moving from 2A to 3A.

The electron being removed is now a *p* electron (higher energy, easier to remove than an *s*).

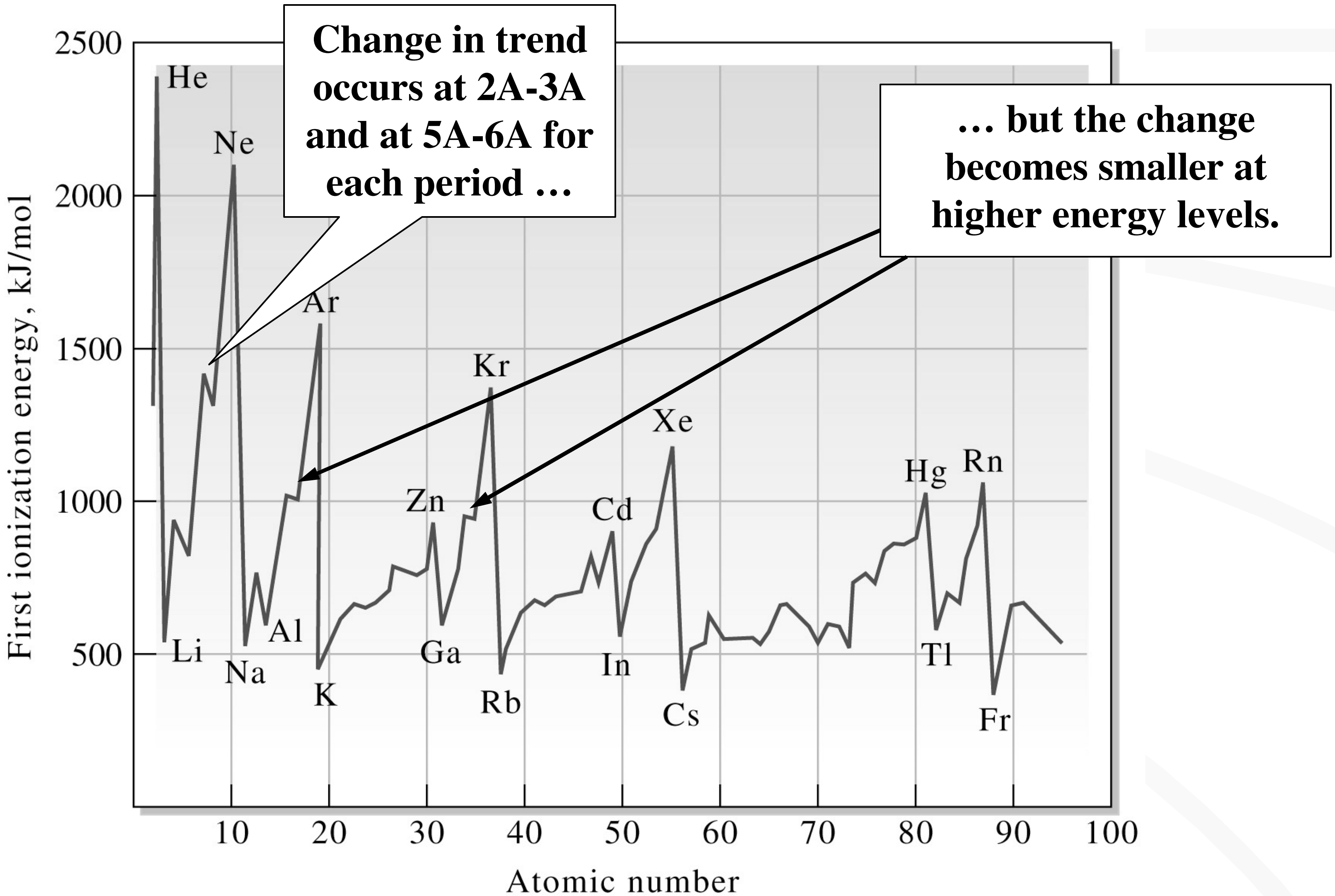
Table 8.5 Ionization [illegible]gies of the Second- and Third-Period Elements, kJ/mol

	1A	2A	3A	4A	5A	6A	7A	8A
	Li	Be	B	C	N	O	F	Ne
I_1	520	900	801	1086	1402	1314	1681	2081
I_2	7298	1757	2427	2352	2856	3388	3374	3952
	Na	Mg	Al	Si	P	S	Cl	Ar
I_1	496	738	578	787	1012	999	1251	1521
I_2	4562	1461	1817	1577	190[illegible]	2251	2298	2666

I_1 drops again between 5A and 6A.

Repulsion of the paired electron in 6A makes that electron easier to remove.

First ionization energies



Example

- Without reference to the previous figure, arrange each set of elements in the expected order of increasing first ionization energy.
  (a) Mg, S, Si
  (b) As, N, P
  (c) As, Ge, P

Electron affinity

Electron affinity (*EA*) is the energy change that occurs when an electron is added to a gaseous atom:

$$M(g) + e^- \rightarrow M^-(g) \qquad \Delta H = EA_1$$

- A ***negative*** electron affinity means that the process is ***exothermic***.
- Nonmetals generally have more affinity for electrons than metals do. (Nonmetals like to form anions!)
- Electron affinity generally is ***more*** negative or less positive on the right and toward the top of the periodic table.

Selected electron affinities

The halogens have a greater affinity for electrons than do the alkali metals, as expected.

Table 8.6 Some Selected First Electron Affinities, kJ/mol

1A	2A	3A	4A	5A	6A	7A	8A
Li	Be	B	C	N	O	F	Ne
−60	>0	−27	−154	≈0	−141	−328	>0
Na					S	Cl	
−53					−200	−349	
K					Se	Br	
−48					−195	−325	
Rb					Te	I	
−47					−190	−295	
Cs					Po	At	
−46					−183	−270	

Other periodic properties (overview)

- Metallic character
  - Increases top to bottom
  - Decreases left to right
- Flame color
  - Due to electronic transitions
- Oxidizing and reducing power
  - Think of how easy it is to gain or lose electron(s)
- Acidic and basic character
  - Ditto!

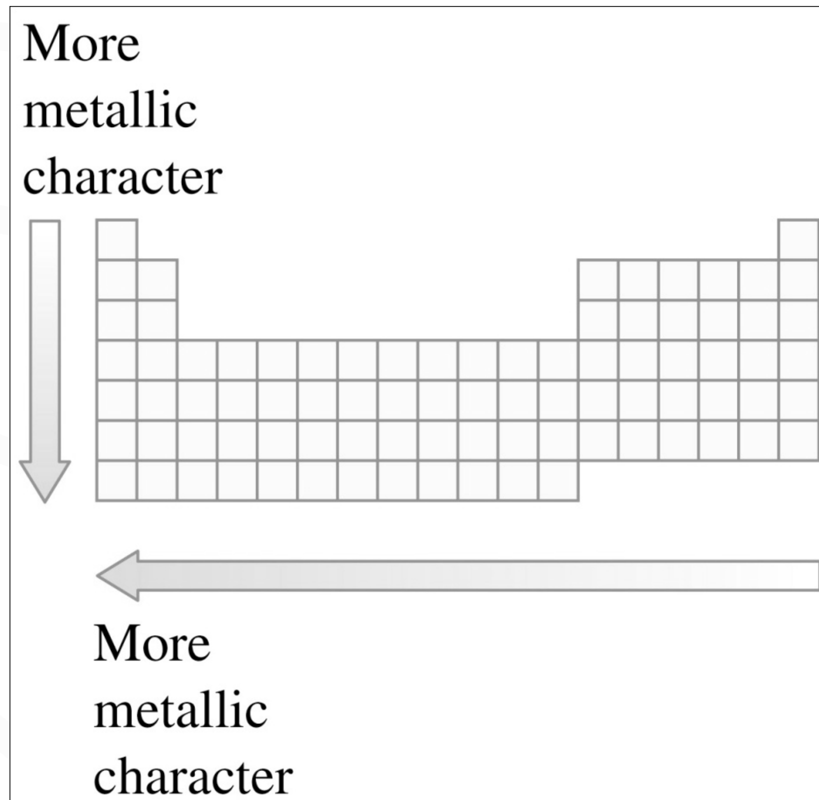
Metals

- ***Metals*** have a small number of electrons in their valence shells and tend to form ***positive*** ions.
  - For example, an aluminum atom loses its three valence electrons in forming Al^{3+}.
- All *s*-block elements (except H and He), all *d*- and *f*-block elements, and some *p*-block elements are metals.

Metallic character

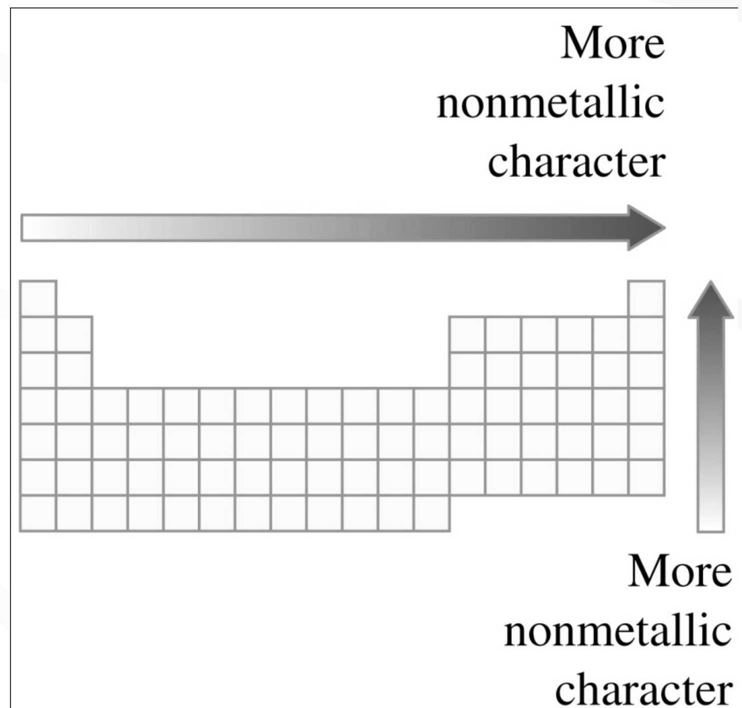
- Metallic character is related to atomic radius and ionization energy.

- Metallic character generally ***increases*** from right to left across a period, and ***increases*** from top to bottom in a group.



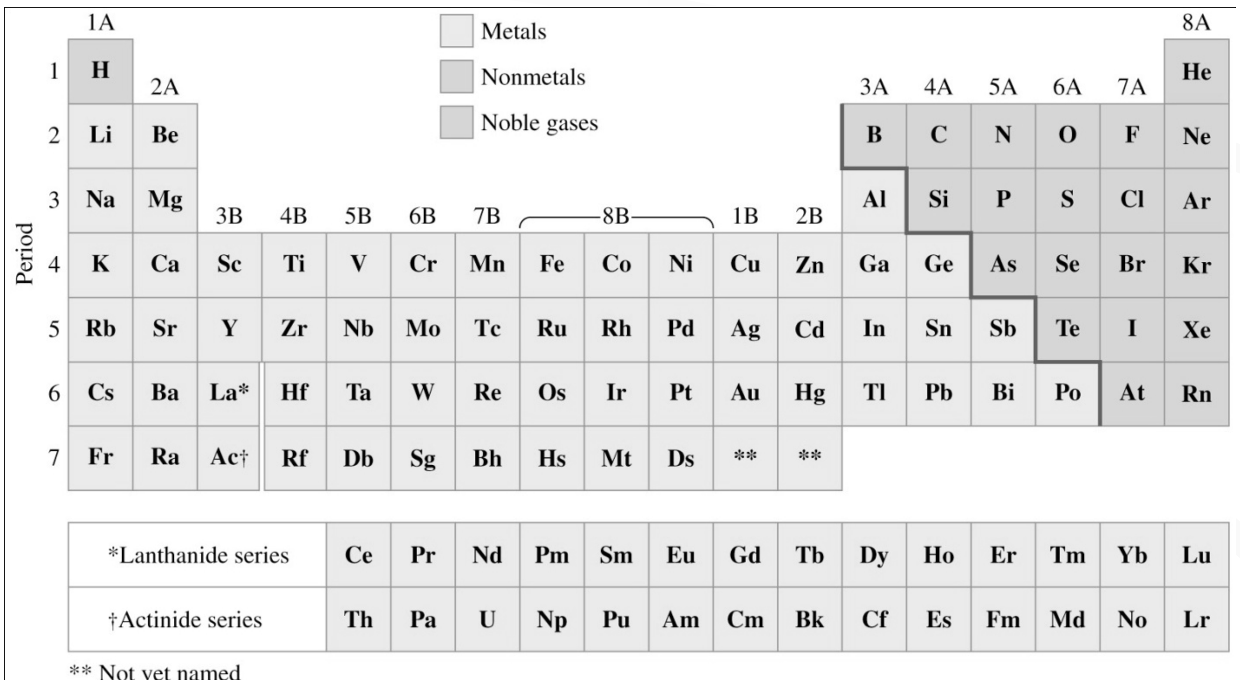
Nonmetals

- Atoms of a **nonmetal** generally have larger numbers of electrons in their valence shell than do metals.
- Many nonmetals tend to form negative ions.
- All nonmetals (except H and He) are *p*-block elements.
    - Nonmetallic character generally increases right-to-left and increases bottom-to-top on the periodic table (the opposite of metallic character).

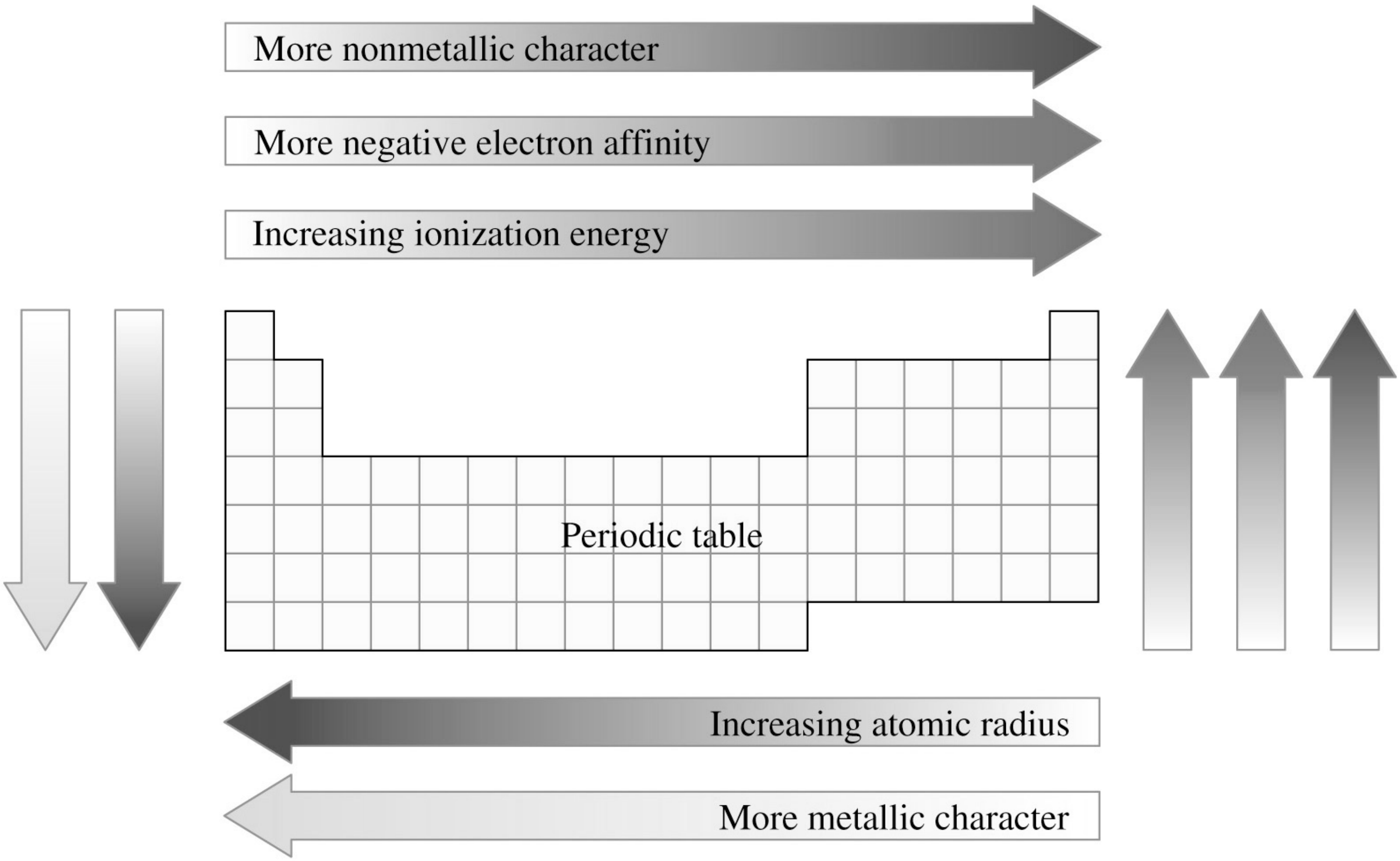


Metalloids

- A heavy stepped diagonal line separates metals from nonmetals; some elements along this line are called **metalloids**.
- Metalloids have properties of both metals and nonmetals.



Summary of trends



The noble gases

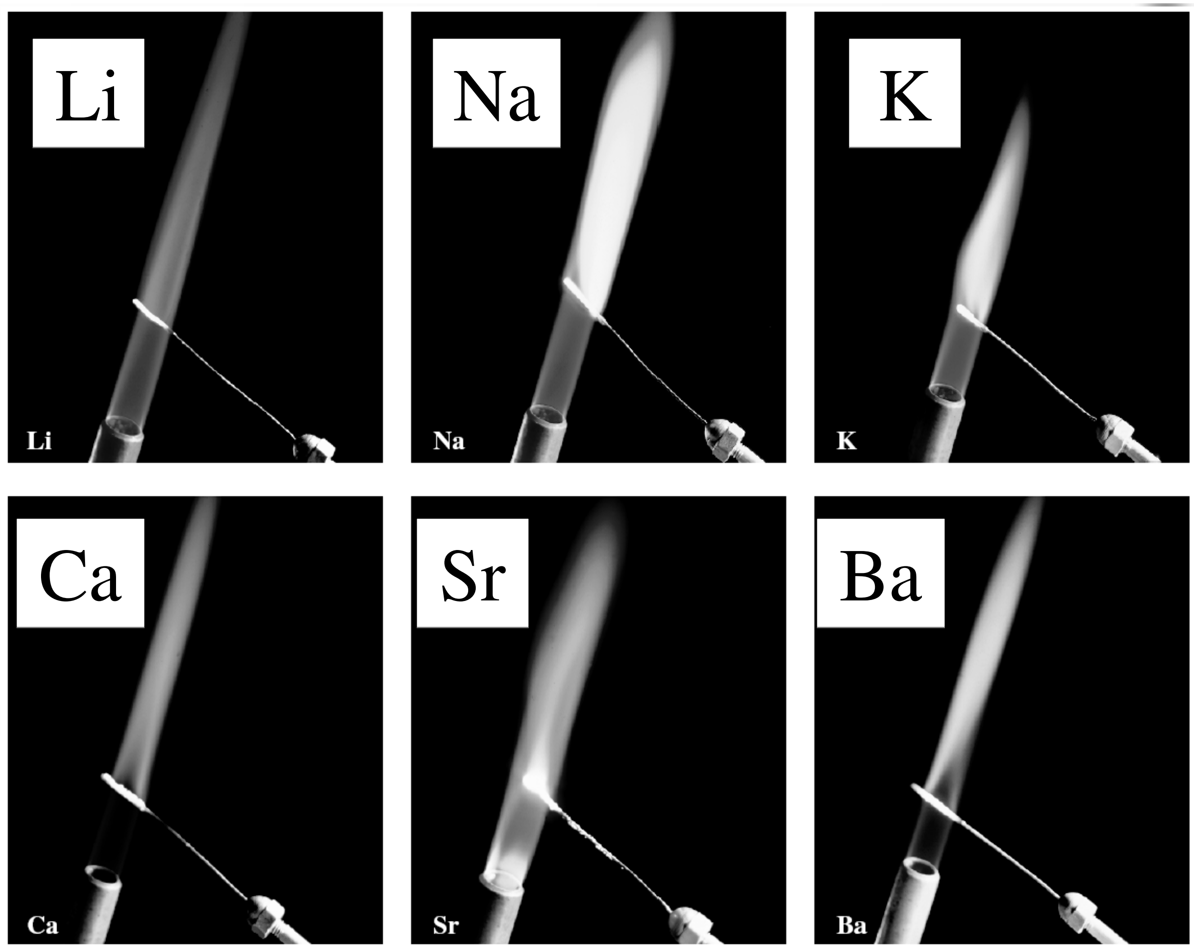
- The **noble gases** are on the far right of the periodic table between the highly active nonmetals of Group 7A and the very reactive alkali metals Group 1A.
- The noble gases rarely enter into chemical reactions because of their stable electron configurations.
- However, a few compounds of noble gases (except for He and Ne) have been made.

Other trends- flame color

Atoms emit energy when electrons drop from higher to lower energy states.

Elements with low **first ionization energies** can be excited in a Bunsen burner flame, and often emit in the visible region of the spectrum.

Elements with high values of IE_1 usually require higher temperatures for emission, and the emitted light is in the UV region of the spectrum.

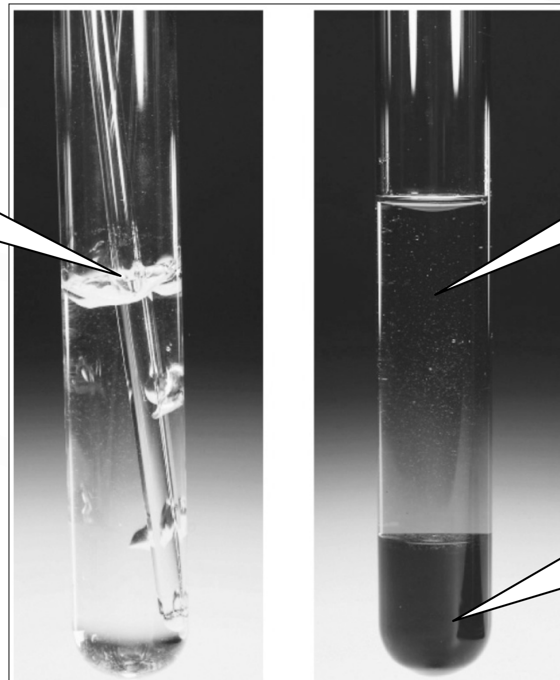


Oxidizing and reducing agents revisited

- The halogens (Group 7A) are good oxidizing agents.
- Halogens have a high affinity for electrons, and their oxidizing power generally varies with electron affinity.

When Cl_2 is bubbled into a solution containing colorless iodide ions …

… the chlorine oxidizes I^- to I_2, because EA_1 for Cl_2 is greater than EA_1 for I_2.



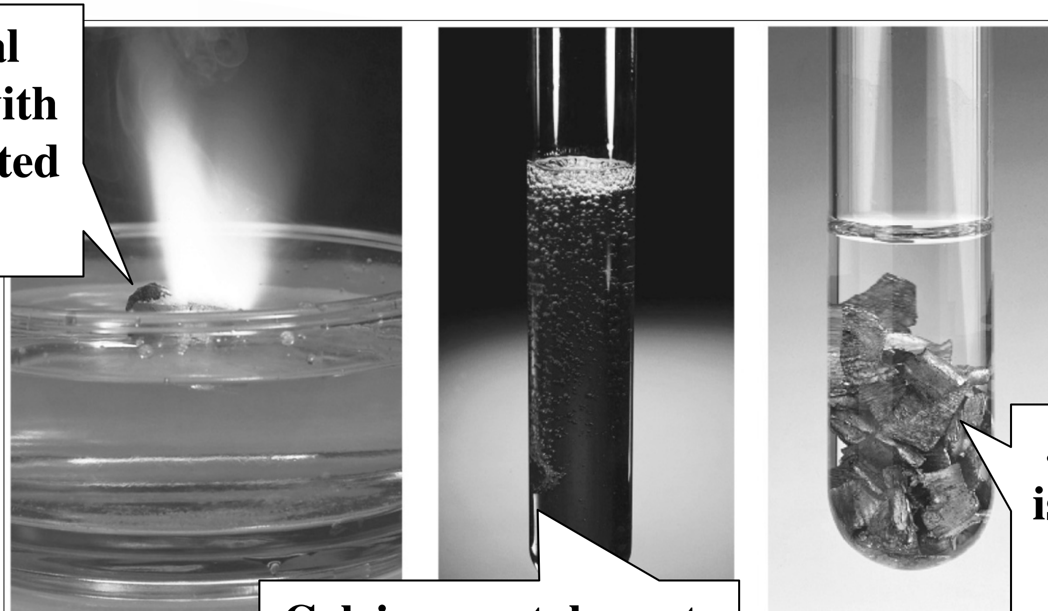
(a) **(b)**

Displaced I_2 is brown in aqueous solution …

… but dissolves in CCl_4 to give a purple solution.

Oxidizing and reducing agents revisited (cont'd)

- The *s*-block elements are very strong reducing agents.
- All the IA metals and the heavier IIA metals will displace H_2 from water, in part because of their low values of IE_1.
- A low IE_1 means that the metal easily gives up its electron(s) to hydrogen in water, forming hydrogen gas.



(a) (c)