Chapter 9

The Periodic Table and some Atomic Properties

Remember the "orbital diagrams" from the previous chapter? They determine the magnetic properties of an atom.

Electron Spins and Magnetic Properties

- The spin quantum number m_s gives the electron the ability to interact with magnetic fields.
- The electron acts as a tiny magnet, and it aligns its spin so that there is an attractive force between the source of the magnetic field and the electron.

"Wait, what? I don't see anything about orbital diagrams, electron spin, and magnetic properties at the beginning of Ch. 9 of the textbook", you say?

The book discusses those <u>at the end of this chapter</u> (instead of the "Electrons in Atoms" chapter)

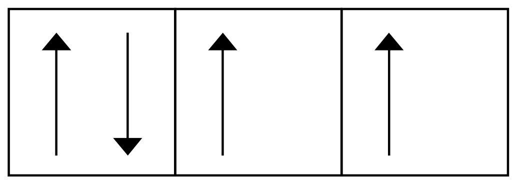
Not unreasonable, as this chapter is about "atomic properties", after all

But instead of discussing it at the end of the chapter like the book does, we will discuss it at the beginning

… before the orbital diagrams fade from our memory 😵‍💫

Paramagnetism

If an atom has one or more unpaired electrons (at least one orbital occupied by a single electron)



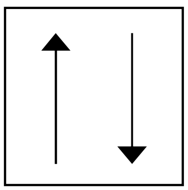
2 unpaired electrons

it is **attracted to a magnetic field**.

Then the atom is **paramagnetic**.

Diamagnetism

If all the electrons in an atom are paired (all orbitals are occupied by two electrons of opposite spins)



their spins cancel out, and the atom is **repelled by a magnetic field.**

Then the atom is **diamagnetic**.

Example

Determine if a gas-phase carbon atom is paramagnetic

Carbon: $1s^2 2s^2 2p^2$

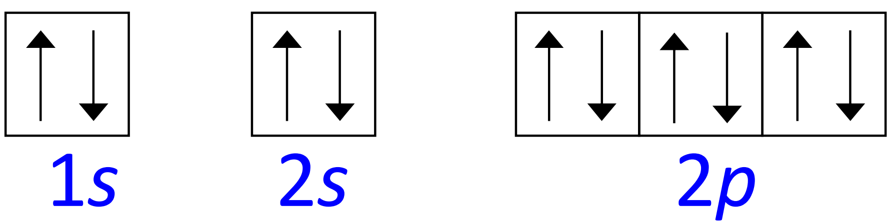
$1s$ $2s$ $2p$

Carbon has 2 unpaired electrons in 2p orbitals, therefore it is paramagnetic.

Example

Determine if atoms of neon gas is paramagnetic

Neon: $1s^2 2s^2 2p^6$



Neon has no unpaired electrons, therefore it is diamagnetic.

Electron configurations and paramagnetism/diamagnetism discussed here are for <u>isolated atoms</u>.

When bonded, even to another atom of the same element, electron configurations and the resulting paramagnetism/diamagnetism change.

Trends in the periodic table

We will study the periodic trends of the following:

- Ionization Energy
- Electron Affinity
- Atomic Radius

Trends in the periodic table

Why do we see trends?

- Trends across a period (left to right) can be explained by **increasing effective nuclear charge**
- Trends from top to bottom in a group can be explained by **increasing distance from the nucleus**

Ionization Energy

Energy required to remove an electron from a gaseous atom or ion.

$$X(g) \rightarrow X^{+}(g) + e^{-}$$

$$Mg(g) \rightarrow Mg^{+}(g) + e^{-} \qquad \Delta E = 735\ kJ$$

Ionization energy of Mg = 735 kJ/mol

Electron Affinity

- Energy change for an atom when it gets an electron

  $X(g) + e^{-} \rightarrow X^{-}(g)$

- e^{-} can only attach to an atom if ΔE for that process is negative (energy is released).

- If electron affinity is listed as a (+) value, it is the magnitude of the energy released.

- The extra electron is repelled by the electrons in the atom, but is attracted to the nucleus.
  - Usually favorable overall, releasing energy

Atomic Radius

- Atomic radius is the size of the largest occupied orbitals (which is in the valence shell) in an atom.
- As such, its precise value depends on how we define the "size" of the electron cloud in those orbitals.
- But the trends in the atomic radius don't depend on the specific definition used

To understand trends, we need to remember:

Protons in the nucleus are (+) charged

Electrons in the surrounding shells are (–) charged

Protons and electrons attract

Stronger attraction pulls electrons closer to the nucleus (smaller radius)

Stronger attraction makes it harder to remove an electron from the atom (larger ionization energy)

Stronger attraction makes it more favorable to add an electron to the atom (larger electron affinity)

The concept of “shielding”

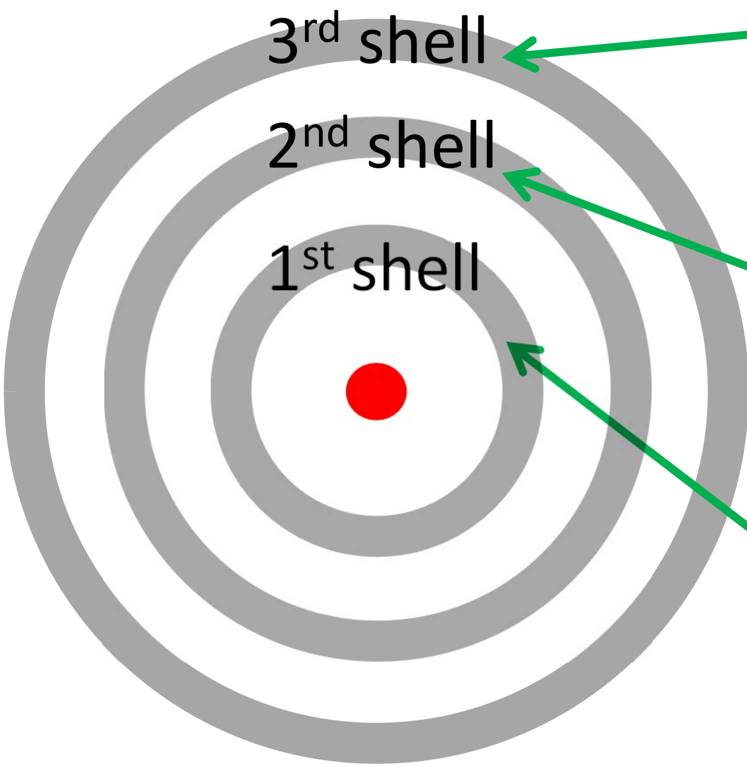
Other electrons in the same atom counteract the attractive force exerted by the nucleus on an electron, because electrons repel each other.

If an electron provides full shielding to another electron, it’s as if that second electron is feeling one less proton in the nucleus.

Each electron is “shielded” from the nucleus by other electrons to some extent.

The more of an electron’s “cloud” lies between the other electron and the nucleus, the more shielding it provides.

In order to shield another electron from the nuclear charge, an electron's cloud must lie between the nucleus and the other electron.

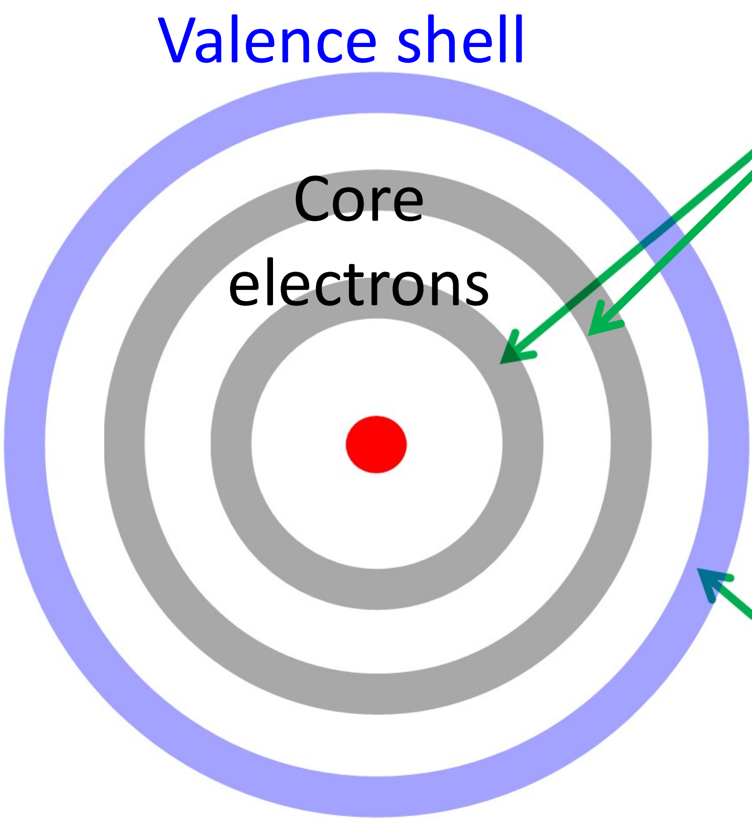


- Is shielded by the 1st and 2nd shells
- Does not shield the 1st and 2nd shells

- Shields the 3rd shell from the nucleus
- Does not shield the 1st shell
- Is shielded by the 1st shell

- Almost completely exposed to the nuclear charge
- Not shielded by the outer electrons
- Shields 2nd and 3rd shells (cancels the effect of two protons)

"Shielding" of the valence electrons



Shells closer to the nucleus ("core electrons") almost completely shield the valence electrons from the protons that came with the core electrons.

e.g. the valence electron of Na (Z=11) feels very little of the 10 protons that came with the 10 core electrons.

Valence electrons are partially shielded by other valence electrons.

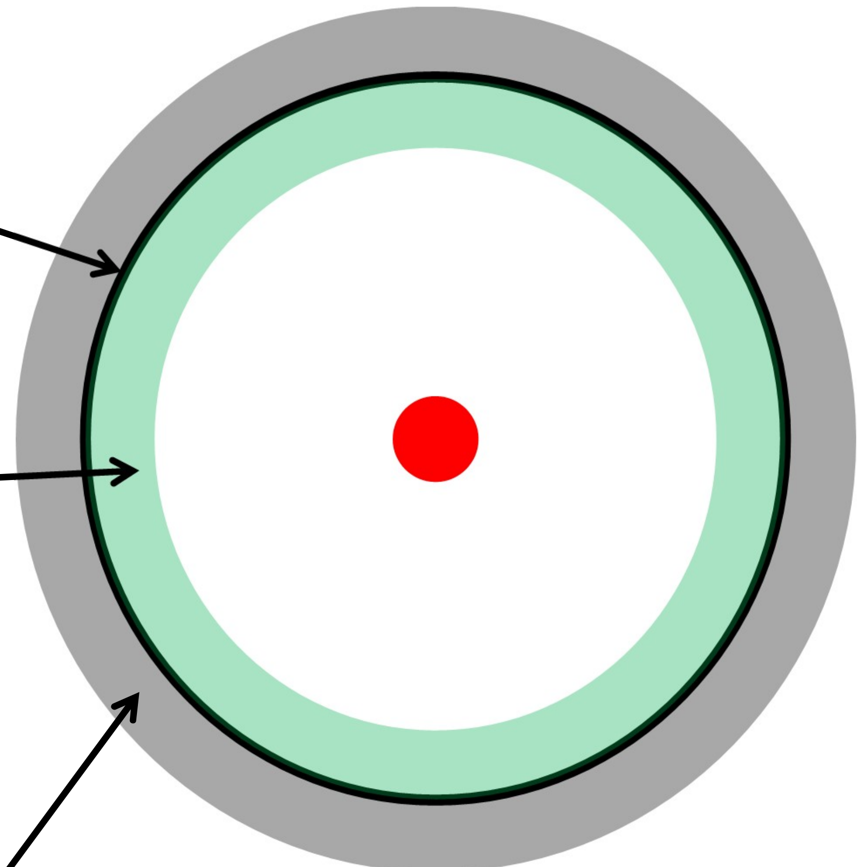
They do **<u>partially</u> feel** the protons that were added when other valence electrons were added to build the atom.

Understanding the "partial shielding" of the valence electrons by other valence electrons

For a given electron in a shell:

- Only a part (about a third) of other valence electrons' "cloud" is closer to the nucleus than the given electron
- That part provides "shielding" — like the core electrons do

- Part of the other electrons' cloud is farther out
- That part provides no shielding



Vertical trends in the periodic table

Understood in terms of:

- Distance from the nucleus, and
- "Core" electrons completely canceling the effect of an equal number of protons in the nucleus
    - ➢ Outermost shell's distance from the nucleus won't be affected much by the protons that came with the earlier, "core" electrons
- Each time we go down in the periodic table, a new valence shell starts getting populated
- The valence shell is the farthest from the nucleus

Vertical trends in the periodic table

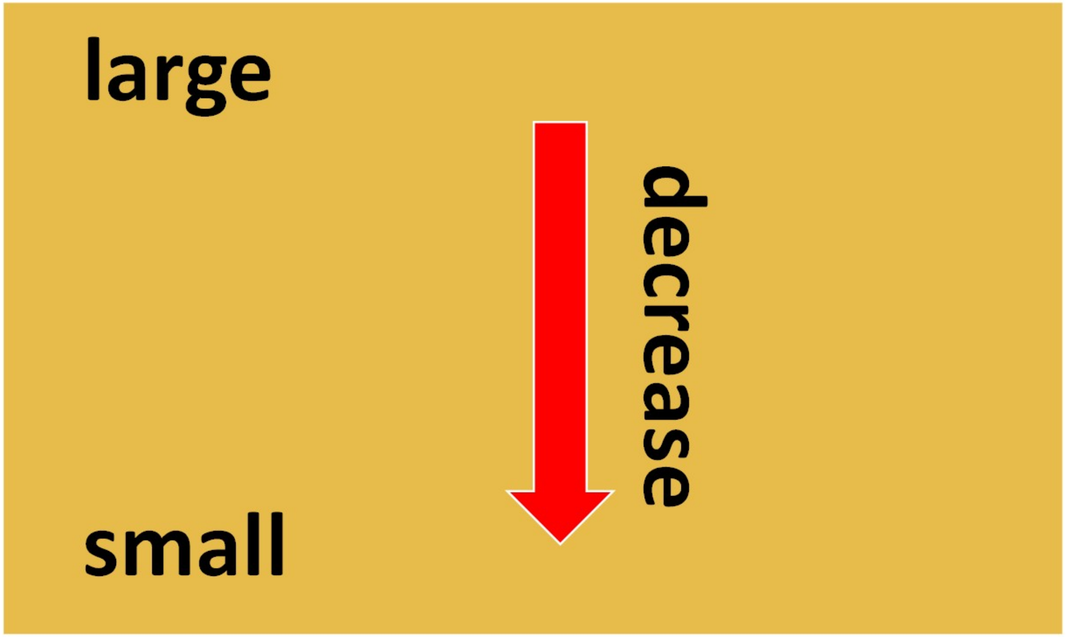
Going downward in a group:

- Atomic size is determined by the farthest shell. So it gets larger as we travel down the periodic table in a given group

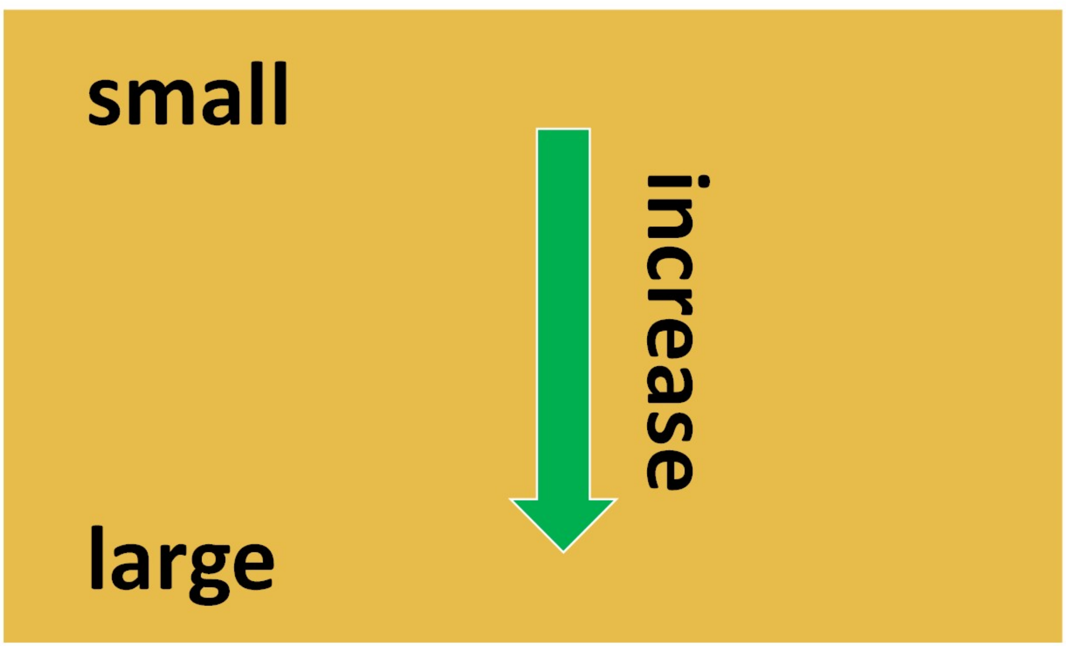
- Removing an electron from a farther-out shell costs less energy (smaller plus-minus attraction)
  - ➢smaller ionization energy

- Adding an electron to farther-out shells releases less energy (smaller plus-minus attraction)
  - ➢ smaller electron affinity

Vertical trends in the Periodic Table



Ionization Energy
Electron Affinity



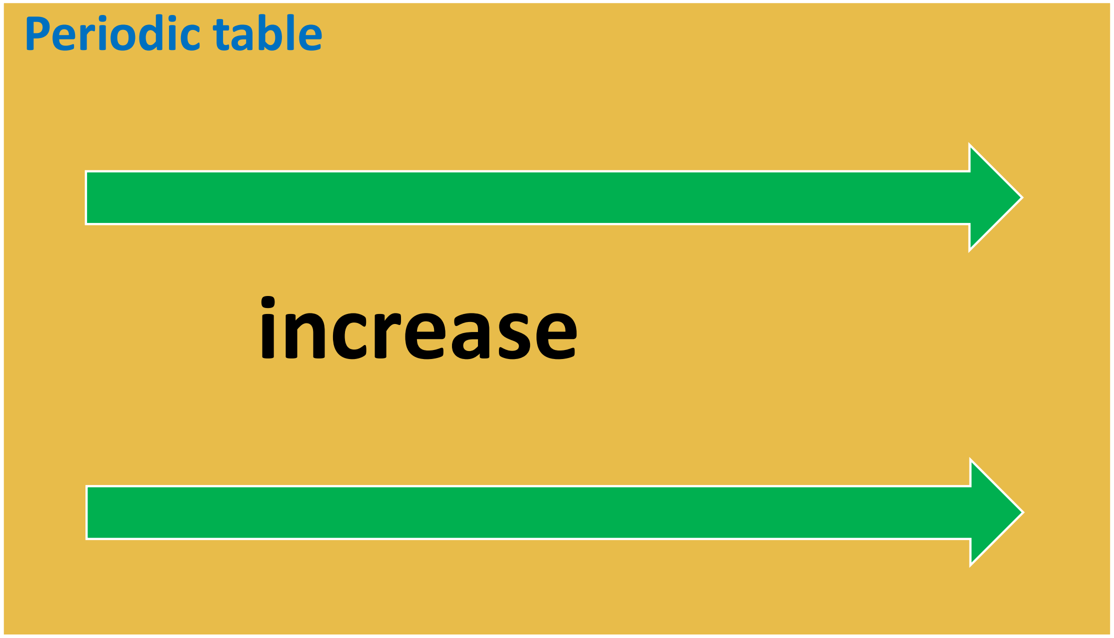
Atomic Radius

Horizontal trends in the periodic table

All horizontal trends are explained by this:

Incomplete shielding by electrons in the valence shell leads to **increasing effective nuclear charge** felt by each of them as we go from left to right across a period.

Effective nuclear charge



Understanding “increasing effective nuclear charge”

Across a period, each new atom adds a proton in the nucleus and an electron in the valence shell.

But the added electron does not fully cancel the effect of the accompanying proton on the other valence electrons.

As more valence electrons are added (going across a period), more of those “only partially shielded protons” are added with them.

Increasing number of “only partially shielded protons” lead to **increasing effective nuclear charge**.

Increasing effective nuclear charge explains all horizontal trends. Across a period:

<u>Atomic radius decreases</u>

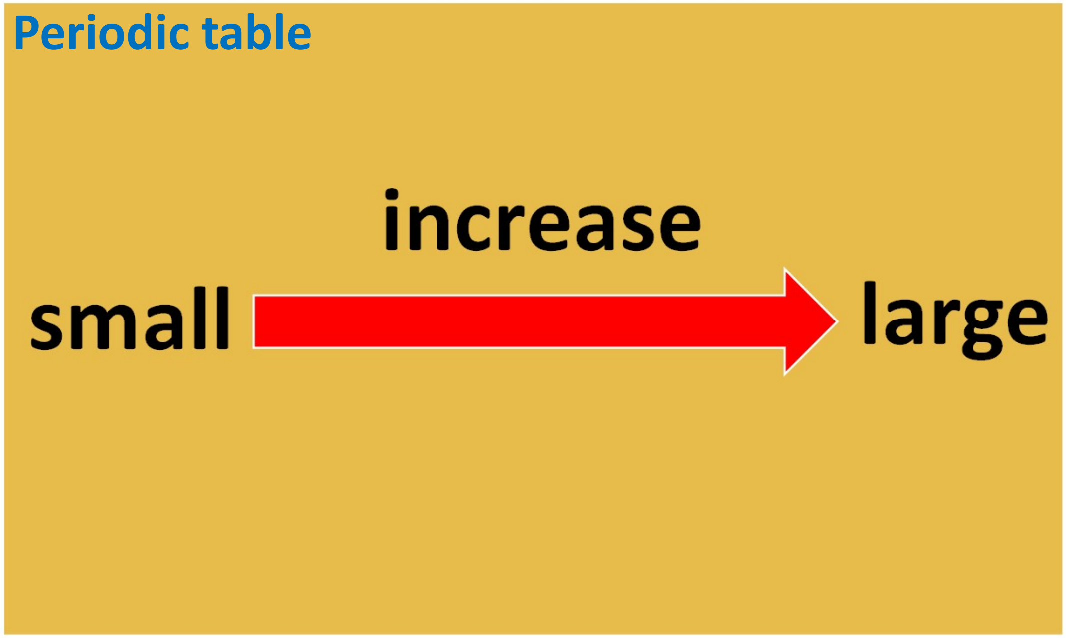
- Stronger attraction by the nucleus pulls the valence electrons closer and closer

<u>Ionization energy increases</u>

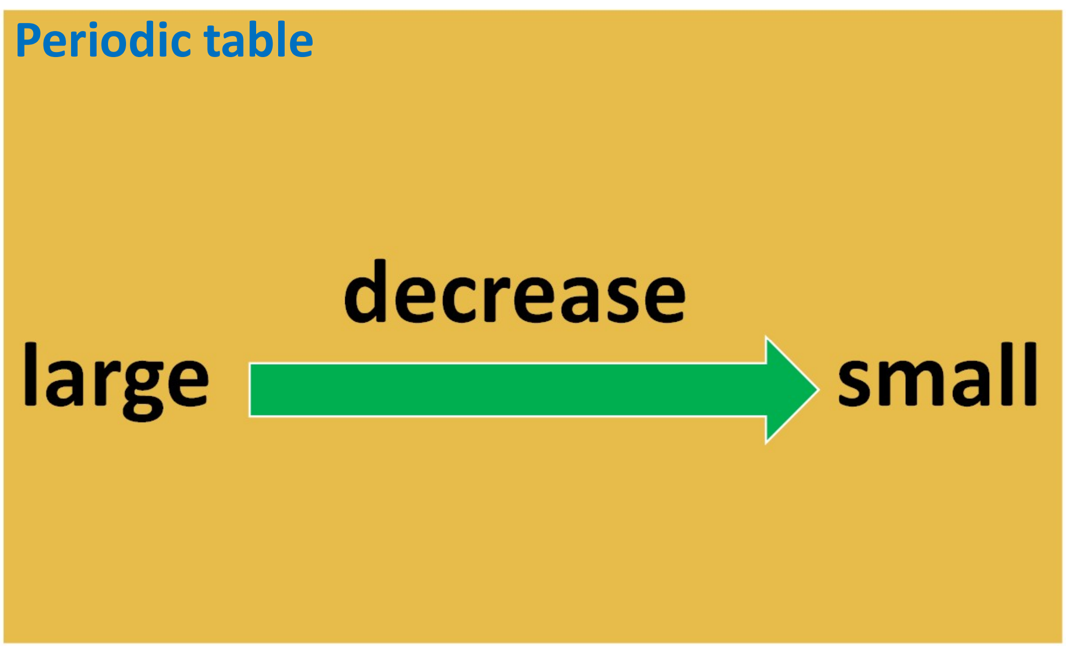
- Stronger attraction by the nucleus raises the energy cost of removing an electron

<u>Electron affinity increases</u>

- Stronger attraction by the nucleus makes the energy of the added electron lower, releasing more energy

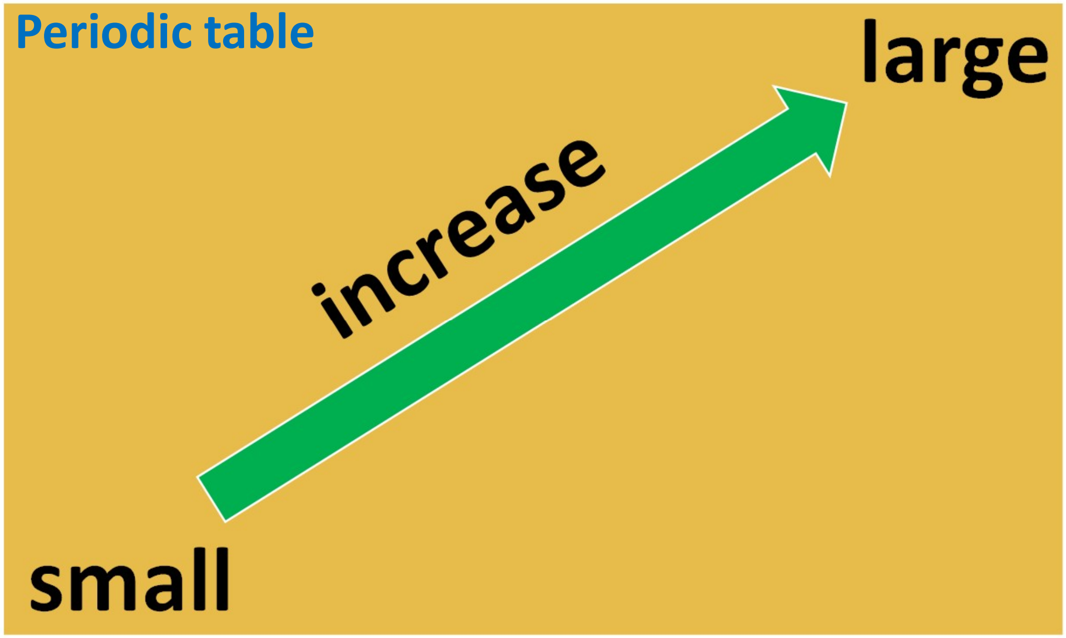


Ionization Energy
Electron Affinity

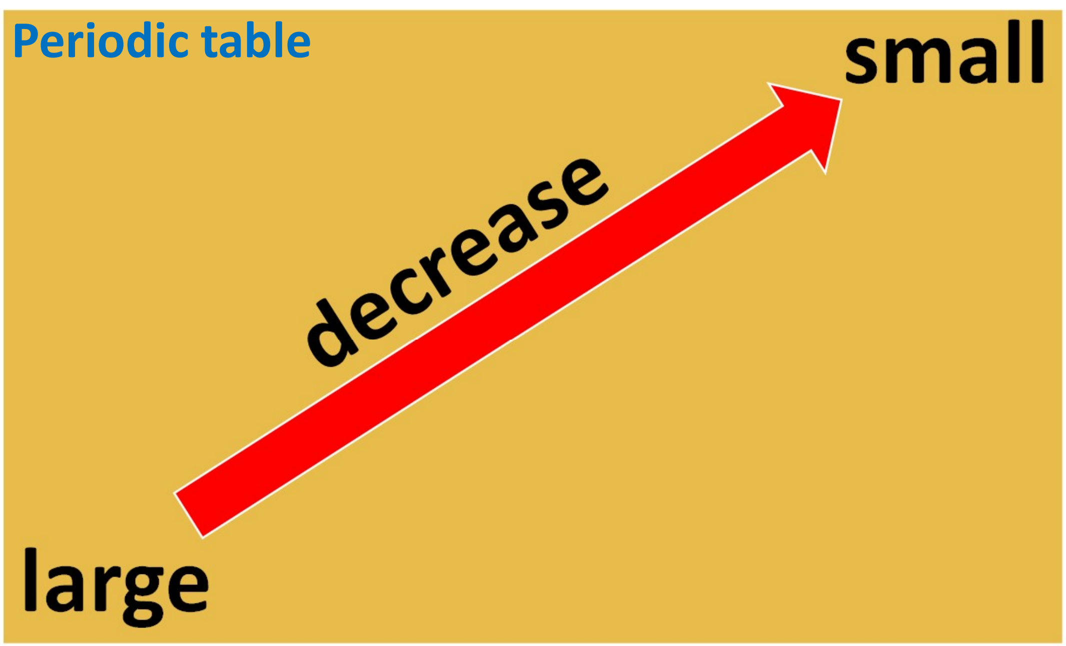


Atomic Radius

Overall trends in the Periodic Table

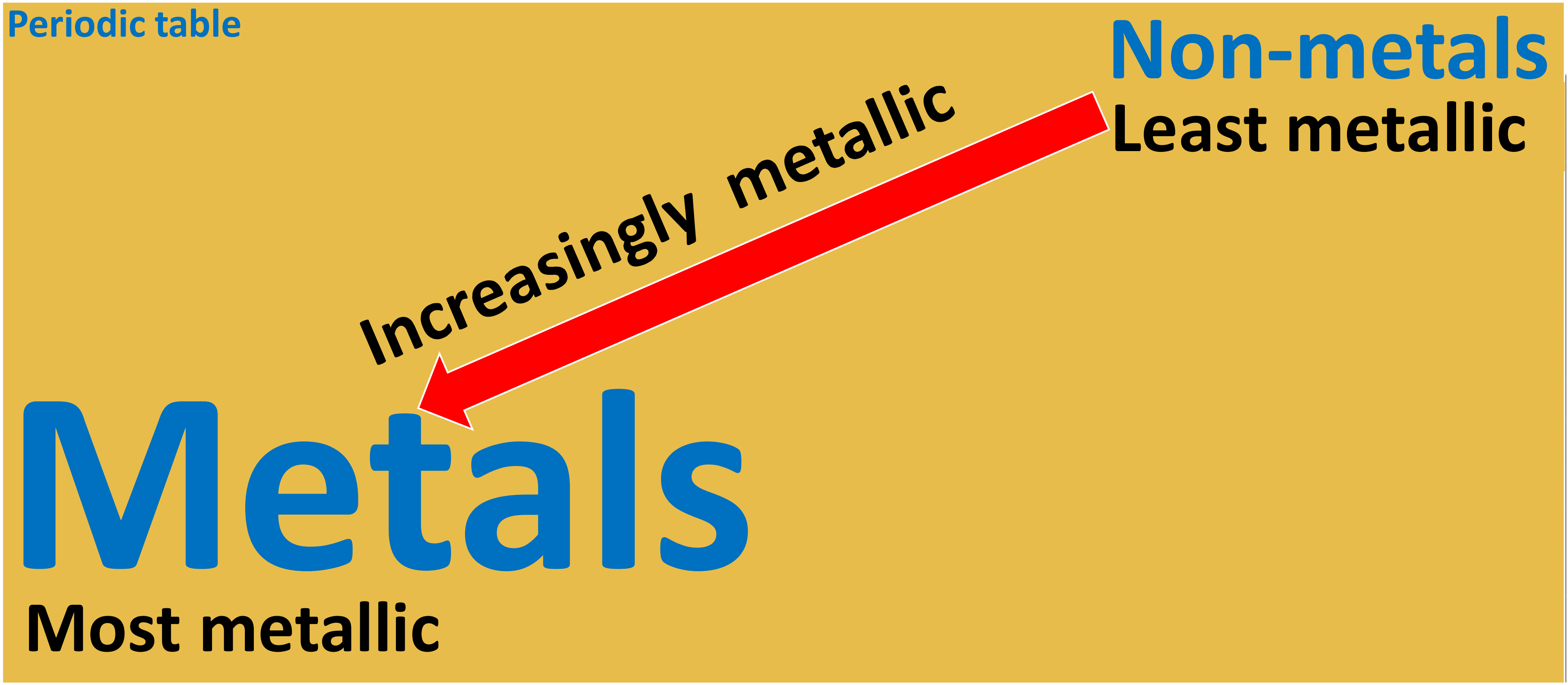


Ionization Energy
Electron Affinity



Atomic Radius

Low ionization energy (low cost for electron removal), and low electron affinity (low “reward” for accepting an electron) leads to metallic character



“Metallic character”

Metals form cations (low energy cost to remove electrons)

- All of their chemistry is defined by this!

Valence shell electrons are “loose” enough to jump between metal atoms where they are more stable being (still weakly) attracted to the nuclei of numerous metal atoms.

- Metals conduct electricity

The “loose”, conducting electrons form a glue-like non-specific, non-directional bonding between metal atoms.

- Because there are no specific bonds to break, metal atoms easily slide around
- Therefore metals tend to be easy to push and pull into shape (malleable and ductile)

Using metallic character to remember trends

We can remember the periodic trends by simply remembering where the metals are in the periodic table, and one of the most prominent features of metals: they conduct electricity

Metals conduct electricity because their valence electrons are “loose”

Using metallic character to remember trends

Electrons being "loose" means they are not strongly bound to the atom.

That means the energy cost to remove an electron from a "more metallic" atom must be lower (lower ionization energy), and less energy will be released by adding an electron (small electron affinity).

Also, a "loose" valence shell, weakly attracted by the nucleus, will not be "squeezed" smaller. It will be larger than the less metallic elements.

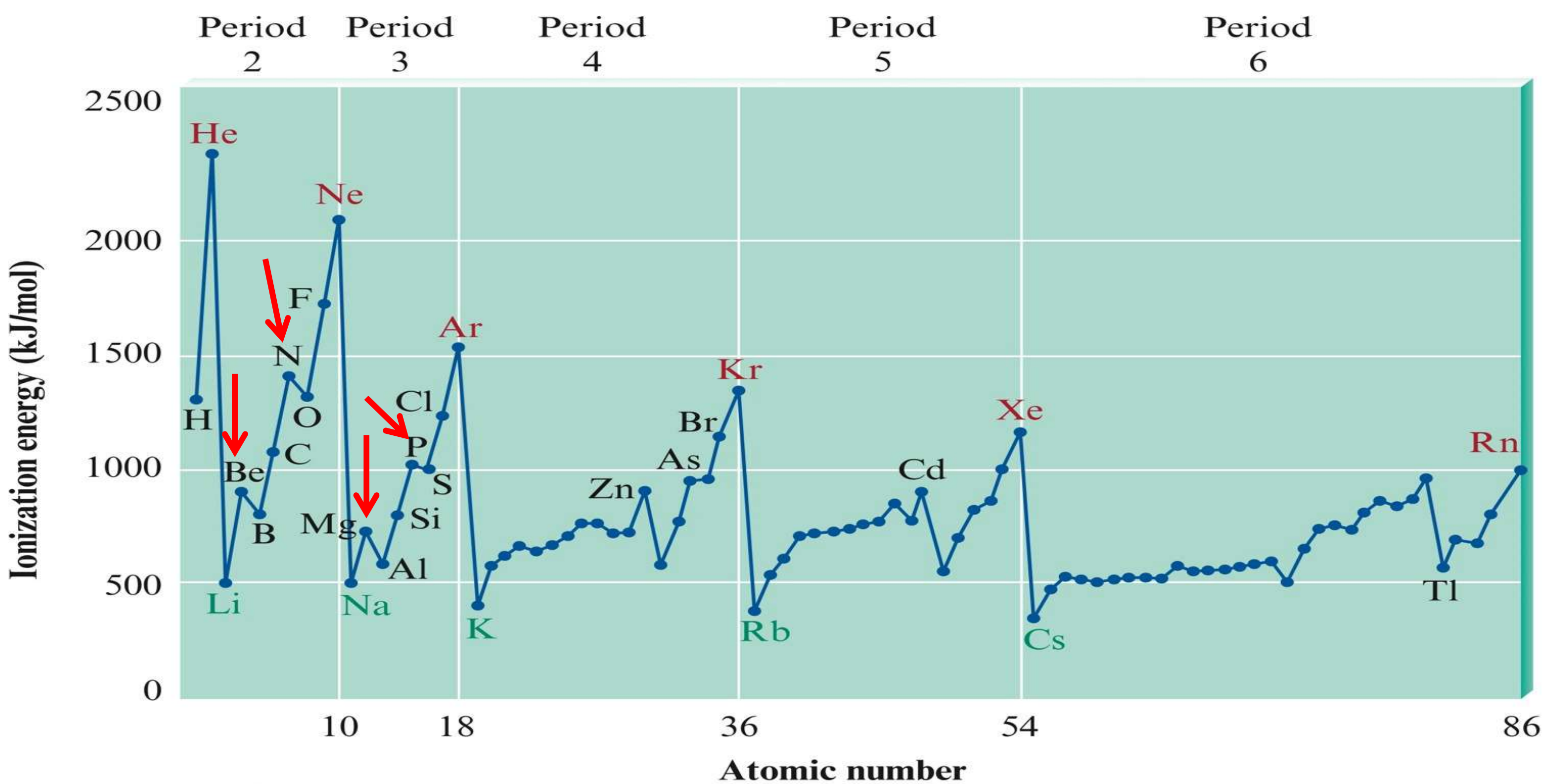
In the next few slides, we will take a closer look at the three properties (ionization energy, electron affinity, atomic radius) whose periodic trends we considered.

Ionization energy trends have "bumps"

Atoms with **filled or half-filled subshells** appear to have anomalously high ionization energies (**more stable than the atoms on their left or right**)

-- Half-filled or filled subshells are relatively stable

-- It takes more energy to pry away an electron



Second, third, etc. ionization energies for an element can tell us how many valence electrons it has

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	495	4560					
Mg	735	1445	7730	Core electrons*			
Al	580	1815	2740	11,600			
Si	780	1575	3220	4350	16,100		
P	1060	1890	2905	4950	6270	21,200	
S	1005	2260	3375	4565	6950	8490	27,000
Cl	1255	2295	3850	5160	6560	9360	11,000
Ar	1527	2665	3945	5770	7230	8780	12,000

- From the **jump** in successive ionization energies, we can tell when we are **starting to dig into the lower shell**, having to lift the electron from a lower level.
- So we can tell which periodic table group the atom belongs to.

"Ionization energy" can refer to removing an electron from entities other than a neutral atom

$X^{+}(g) \rightarrow X^{2+}(g) + e^{-}$

1st IE of X^{+}
2nd IE of X
3rd IE of X^{-}

$X^{-}(g) \rightarrow X(g) + e^{-}$

1st IE of X^{-}
2nd IE of X^{2-}

etc.

More on Electron Affinity

- Adding an e^- to an atom is <u>not</u> the reverse of removing an electron from a neutral atom.
- Removing an e^- from an atom creates a charge separation that always requires energy (ionization energy)
- But adding an e^- to a neutral atom (electron affinity) doesn't combine or separate charges.

More on Electron Affinity (cont.)

Some elements don’t have an EA because the ΔE for adding an e^{-} is (+). The element cannot form an anion in vacuum because there is no barrier to simply spitting out the added electron in order to attain a lower energy (basically the e^{-} bounces off the atom)

Electron Affinity trends have many exceptions

Atoms with filled subshells (Group 2, 12, 18) have anomalously small (or zero) electron affinities

- Added electron has to go to a higher-energy subshell

Atoms with half-filled subshells (Groups 7, 15) have anomalously small (or zero) electron affinities

- Configuration with added electron lacks the stabilization of the half-filled subshell

Second period elements have smaller (or zero)EA than the element below them, violating the trend

- Their small size makes it more difficult to squeeze in an extra electron

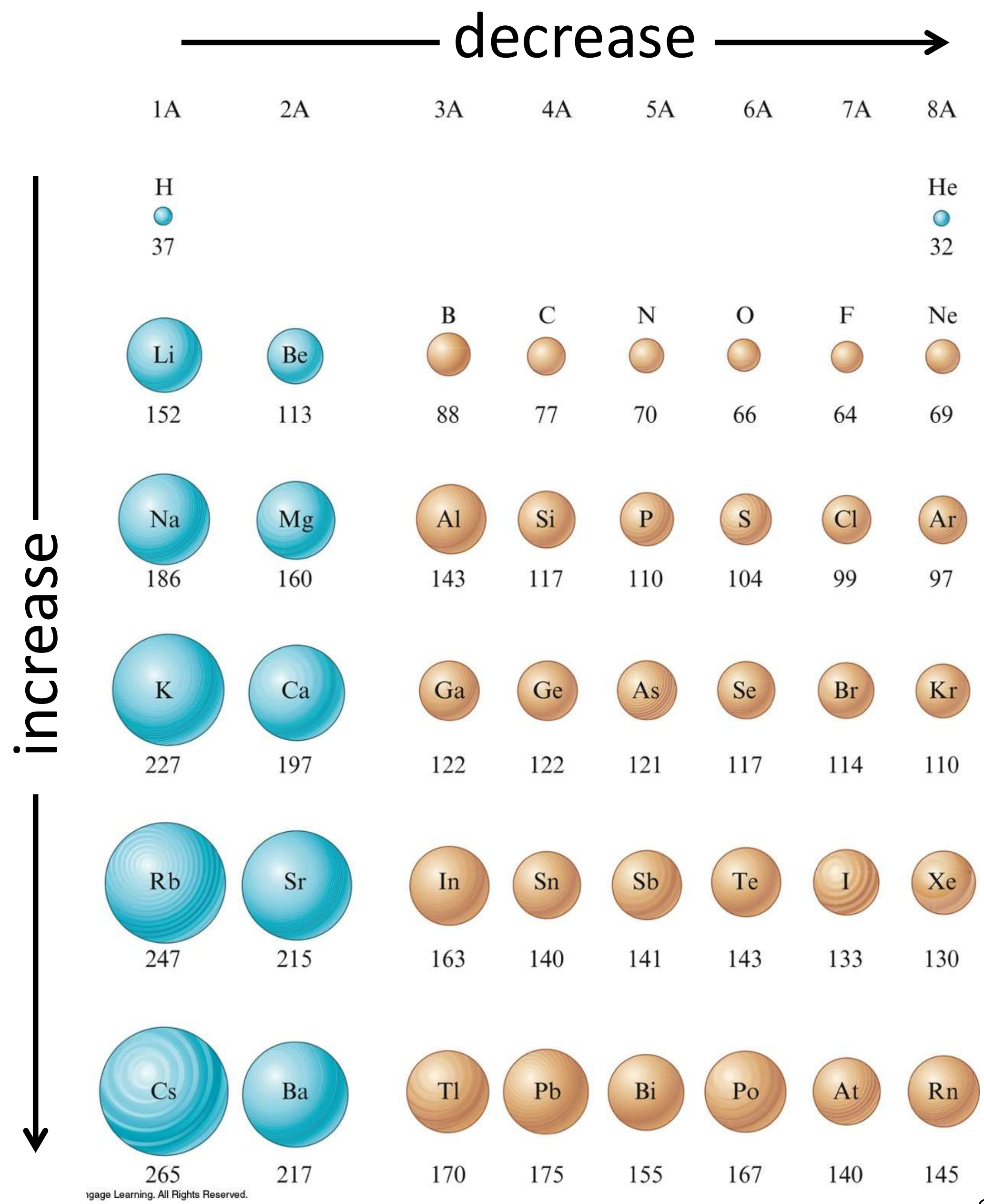
Electron Affinity trends have many exceptions

≥0 kJ/mol — −348.6 kJ/mol

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** −72.8																	**He** ≥0
2	**Li** −59.6	**Be** ≥0											**B** −27.0	**C** −121.8	**N** ≥0	**O** −141.0	**F** −328.2	**Ne** ≥0
3	**Na** −52.9	**Mg** ≥0											**Al** −41.8	**Si** −134.1	**P** −72.0	**S** −200.4	**Cl** −348.6	**Ar** ≥0
4	**K** −48.4	**Ca** −2.4	**Sc** −18	**Ti** −8	**V** −51	**Cr** −65.2	**Mn** ≥0	**Fe** −15	**Co** −64.0	**Ni** −111.7	**Cu** −119.2	**Zn** ≥0	**Ga** −40	**Ge** −118.9	**As** −78	**Se** −195.0	**Br** −324.5	**Kr** ≥0
5	**Rb** −46.9	**Sr** −5.0	**Y** −30	**Zr** −41	**Nb** −86	**Mo** −72.1	**Tc** −60	**Ru** −101.0	**Rh** −110.3	**Pd** −54.2	**Ag** −125.9	**Cd** ≥0	**In** −39	**Sn** −107.3	**Sb** −101.1	**Te** −190.2	**I** −295.2	**Xe** ≥0
6	**Cs** −45.5	**Ba** −14.0	**La** −45	**Hf** ≥0	**Ta** −31	**W** −79	**Re** −20	**Os** −104.0	**Ir** −150.9	**Pt** −205.0	**Au** −222.7	**Hg** ≥0	**Tl** −37	**Pb** −35	**Bi** −90.9	**Po** −180	**At** −270	**Rn** ≥0
7	Fr	Ra	Ac	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Uub	Uut	Uuq	Uup			
Lanthanides 6				Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu	
Actinides 7				Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr	

From chem.libretexts.org/Bookshelves/General_Chemistry/Map%3A_Chemistry_-_The_Central_Science_(Brown_et_al.)/07._Periodic_Properties_of_the_Elements/7.5%3A_Electron_Affinities

Atomic Radii trends of the main group elements have no serious exceptions



Practice

Which of the following elements has the smallest atomic radius?

a) P

b) Cl

c) S

d) Na

e) Si

All in the same Period,
Cl is the rightmost

1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)									

Practice

Which of the following elements has the highest ionization energy?

a) Li

b) Na

c) K

d) Rb

e) Cs

All in the same group,
Li is the topmost

1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 16.00	9 F 19.00	10 Ne 20.179
11 Na 22.99	12 Mg 24.30											13 Al 26.98	14 Si 28.09	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.10	20 Ca 40.08	21 Sc 44.96	22 Ti 47.87	23 V 50.94	24 Cr 52.00	25 Mn 54.938	26 Fe 55.85	27 Co 58.93	28 Ni 58.69	29 Cu 63.55	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.92	34 Se 78.96	35 Br 79.90	36 Kr 83.80
37 Rb 85.47	38 Sr 87.62	39 Y 88.91	40 Zr 91.22	41 Nb 92.91	42 Mo 95.94	43 Tc (98)	44 Ru 101.1	45 Rh 102.91	46 Pd 106.42	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.71	51 Sb 121.75	52 Te 127.60	53 I 126.91	54 Xe 131.29
55 Cs 132.91	56 Ba 137.33	57 *La 138.91	72 Hf 178.49	73 Ta 180.95	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.2	78 Pt 195.08	79 Au 196.97	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.02	89 †Ac 227.03	104 Rf (261)	105 Db (262)	106 Sg (263)	107 Bh (262)	108 Hs (265)	109 Mt (266)									

Practice

Which of the following elements has the smallest ionization energy?

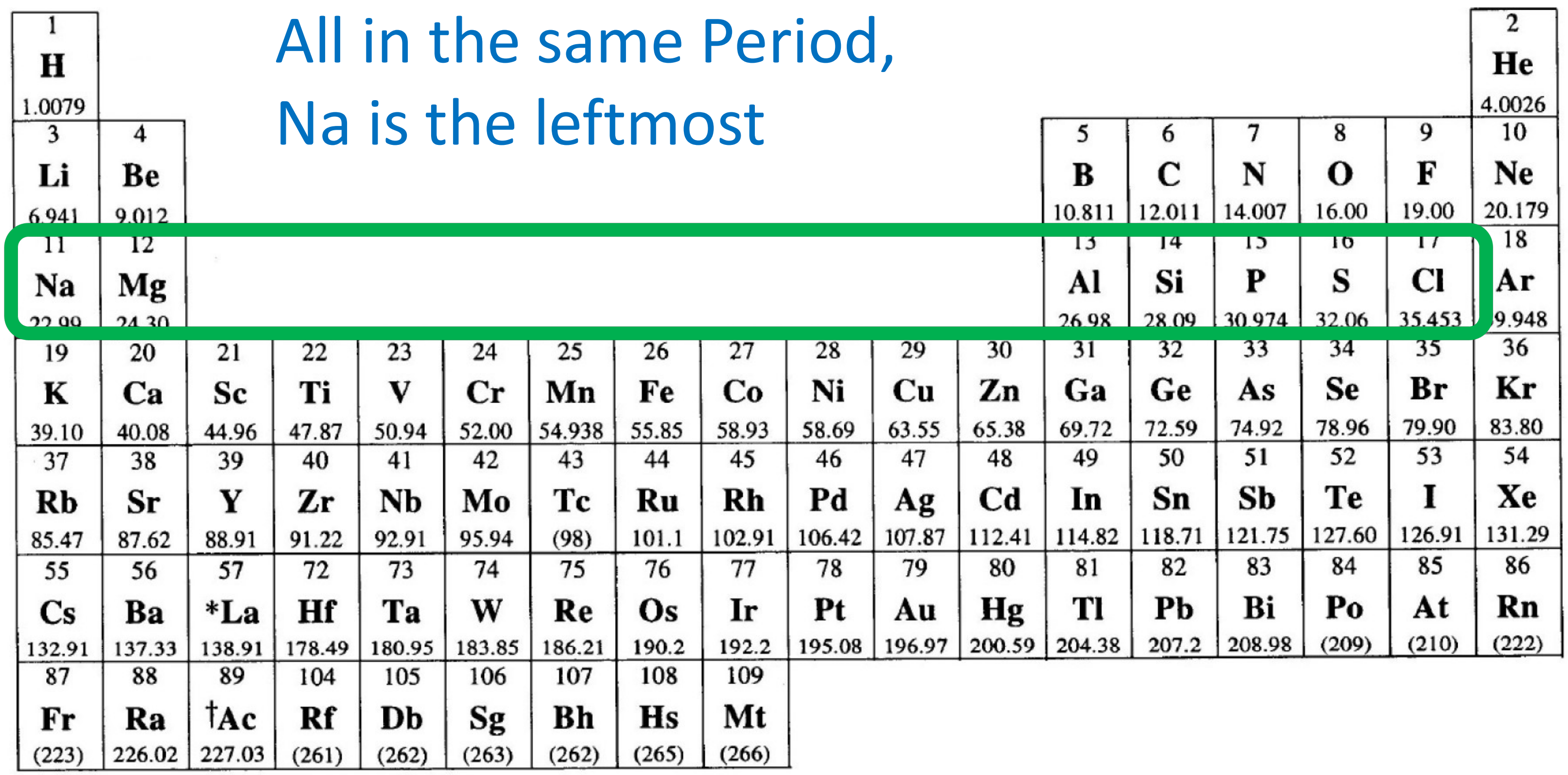
a) P

b) Cl

c) S

d) Na

e) Si



All in the same Period,
Na is the leftmost

Isoelectronic Series

A series of ions/atoms containing the same number of electrons.

For example:

O^{2-}, F^{-}, Ne, Na^{+}, Mg^{2+}, Al^{3+}

Consider what happens to the number of electrons when we form the ions above, and how they would compare with Ne.

Now think of other isoelectronic series. Write a few of them.

Practice:

Choose an alkali metal, an alkaline earth metal, a noble gas, and a halogen so that they constitute an isoelectronic series when the metals and halogen are written as their most stable ions.

- What is the electron configuration for each species?
- Determine the number of electrons for each species.
- Determine the number of protons for each species.

One example could be:

Cl^{-}, Ar, K^{+}, Ca^{2+}

- The electron configuration for each species is $1s^2 2s^2 2p^6 3s^2 3p^6$.
- The number of electrons for each species is 18.
- Cl^{-} has 17 protons, Ar has 18 protons, K^{+} has 19 protons, Ca^{2+} has 20 protons

Why think about isoelectronic series?

Same number and configuration of electrons

Increasing number of protons (increasing nuclear charge)

We can easily guess how their sizes vary!

For example:

	O^{2-}	F^{-}	Ne	Na^{+}	Mg^{2+}	Al^{3+}	all have 10 electrons
Z:	8	9	10	11	12	13	

Increasing nuclear charge

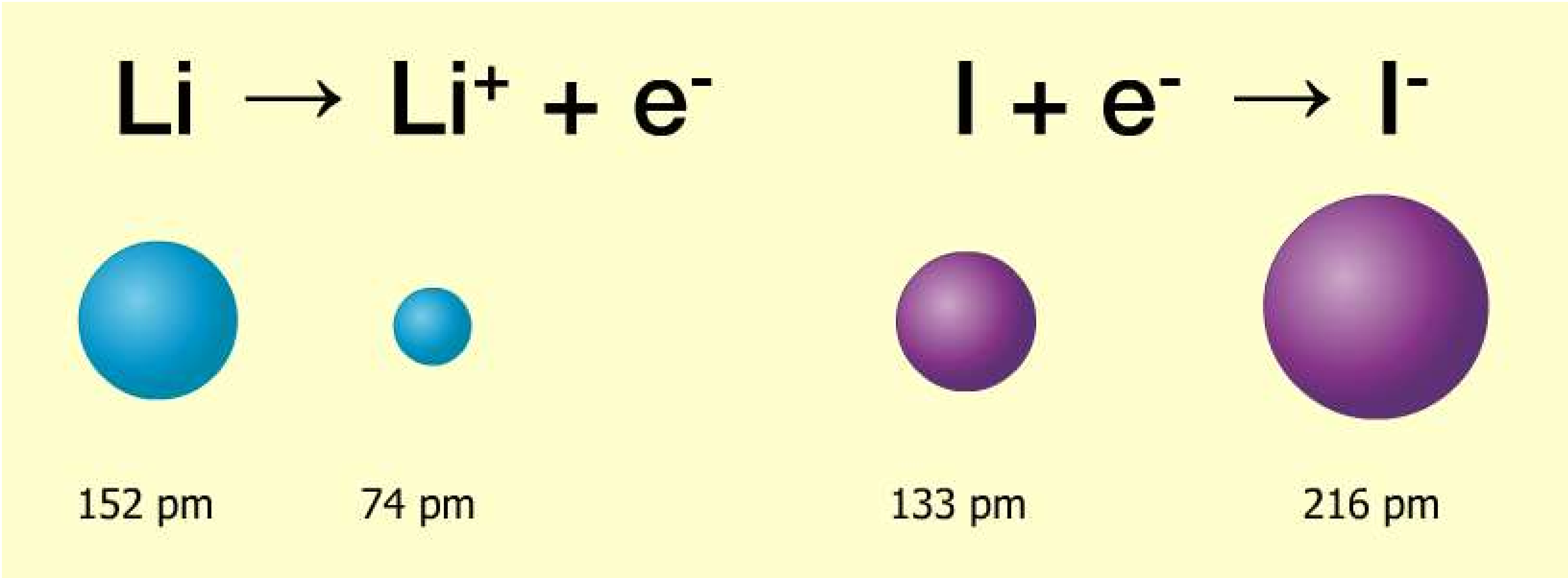
Decreasing radius

We will be considering the energetics of ionic bonds and ionic compounds later, and ion sizes are important in that regard.

So, understanding isoelectronic series helps.

But we need to study the periodic trends of ionic radii more directly as well.

Ionic Radii



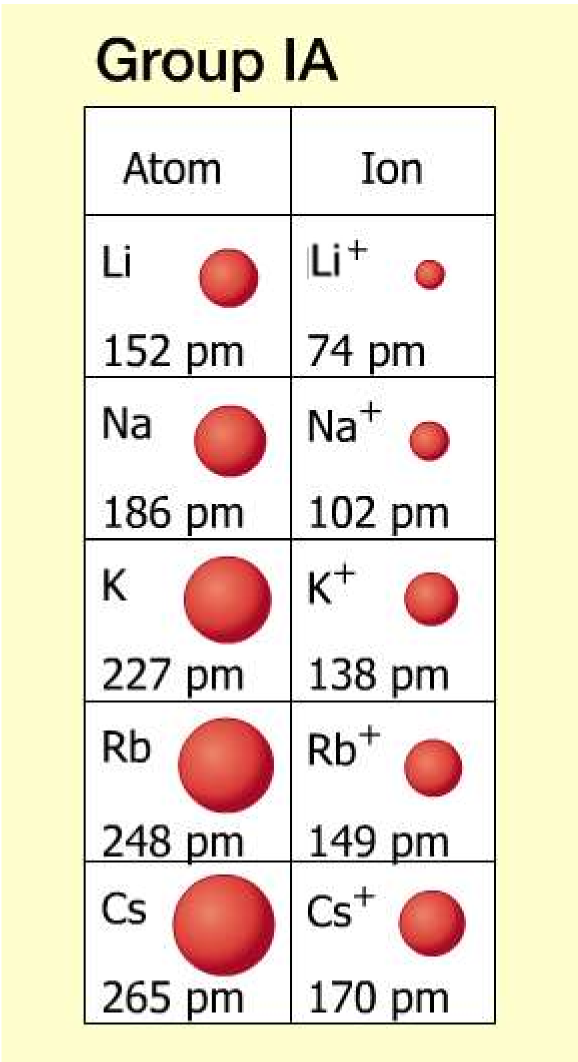
Cations are smaller than the parent atom

- because the valence shell is lost

Anions are larger than the parent atom

- because the extra electron-electron repulsion makes the valence shell puff up

Ionic Radii



- Ionic radius increases as we go down in a group,
  - Just like the atomic radius for the neutral atoms of elements
- Each period has one more shell than the previous one, making the ion larger than the one above it in the same group
  - Just like the atomic radius for the neutral atoms of elements

Ionic Radii

Period 3

Atom	Na 186 pm	Mg 160 pm	Al 143 pm	P 110 pm	S 103 pm	Cl 99 pm
Ion	Na^{+} 102 pm	Mg^{2+} 72 pm	Al^{3+} 53 pm	P^{3-} 212 pm	S^{2-} 184 pm	Cl^{-} 181 pm

isoelectronic ($10\ e^{-}$) — Isoelectronic ($18\ e^{-}$)

Considering cations and anions **separately**:

- Ionic radius decreases across a period
- There is a big jump in ionic radius between the last metal cation in the period and the first non-metal anion