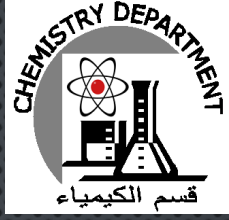
General Chemistry I

NAC 1101



Lecture 5

Periodic Properties of Elements

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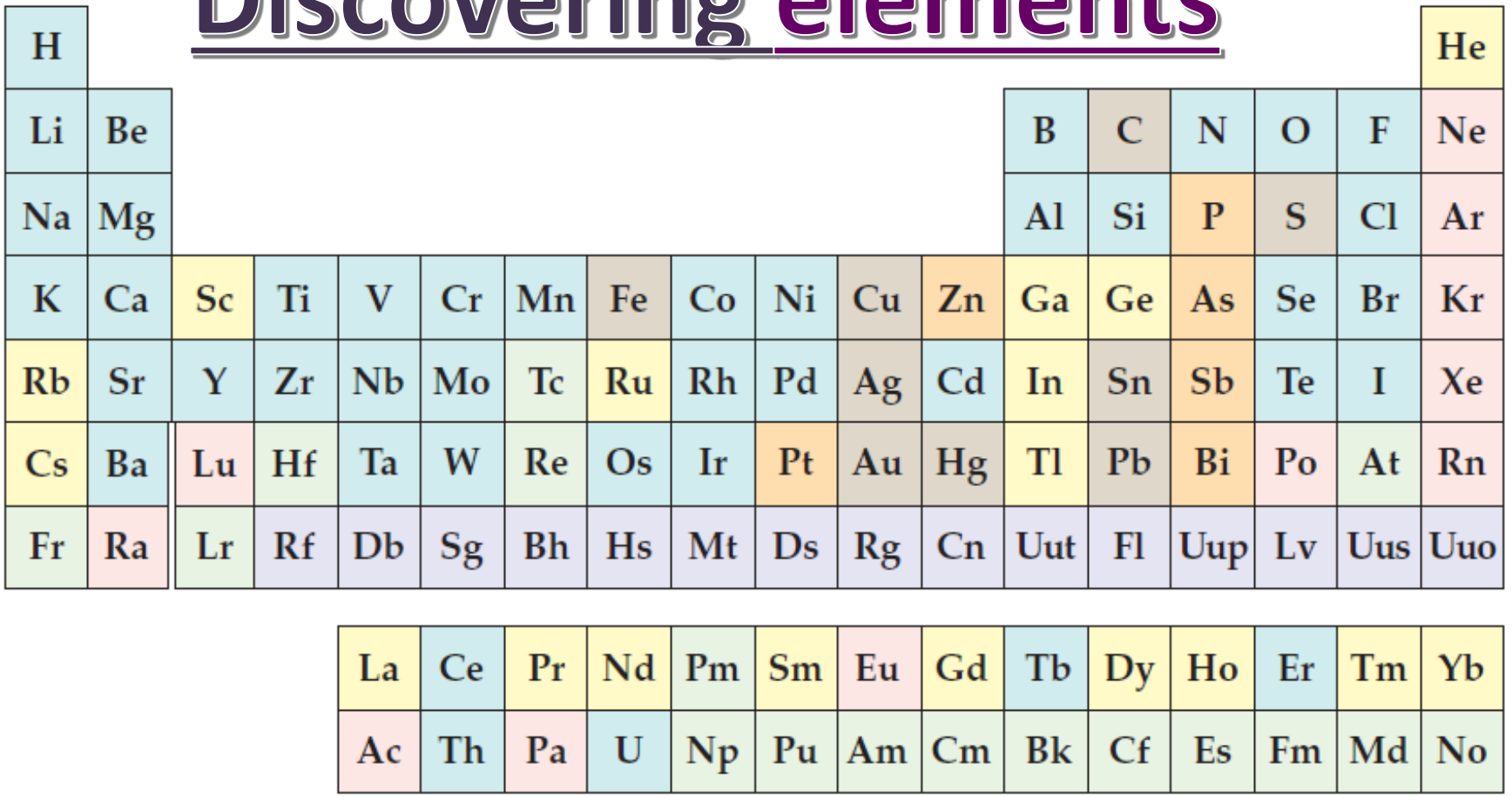
Outline

- Development of the Periodic Table
- Effective Nuclear Charge
- Sizes of Atoms and Ions
- Ionization Energy
- Electron Affinity

Discovering elements



Copper, silver, and gold have all been known since ancient times, whereas most of the other metals were not isolated until much later.

Timeline of Periodic Table

(1869) Dmitri Mendeleev and Lothar Meyer

- Arranged elements in order of increasing atomic weight (*atomic numbers were not discovered yet*) where similar chemical and physical properties recured periodically.

Mendeleev

left blank spaces in his table for elements he predicted their existence and properties as gallium (Ga) and germanium (Ge) which he named eka-aluminum ("under" aluminum) and eka-silicon ("under" silicon), respectively.

Comparison of Properties of Eka-Silicon Predicted by Mendeleev with Observed Properties of Germanium

Property	Mendeleev's Predictions for Eka-Silicon (made in 1871)	Observed Properties of Germanium (discovered in 1886)
Atomic weight	72	72.59
Density (g/cm^3)	5.5	5.35
Specific heat (J/g-K)	0.305	0.309
Melting point (°C)	High	947
Color	Dark gray	Grayish white
Formula of oxide	XO_2	GeO_2
Density of oxide (g/cm^3)	4.7	4.70
Formula of chloride	XCl_4	$GeCl_4$
Boiling point of chloride (°C)	A little under 100	84

(1913) Henry Moseley

- developed the concept of atomic numbers by bombarding different elements with high-energy electrons.
- He found that each element produced X-rays of a unique frequency that generally increased as the atomic mass increased.
- He arranged the X-rays frequencies in order by assigning a unique whole number, called an atomic number, to each element.
- He correctly identified the atomic number as the number of protons in the nucleus of the atom.

Clarity of previous Problems

- Concept of atomic number (AN) clarified some problems in the periodic table (PT) of Moseley's day, which was based on atomic weights (AW).
- The atomic weight of ${}^{39.948}_{18}Ar$ is greater than that of ${}^{39.0983}_{19}K$, yet the chemical and physical properties of Ar are much more like those of Ne and Kr than like those of Na and Rb. If elements are arranged in order of increasing AN, Ar and K appear in their correct places PT.
- Moseley's studies also identified "holes" in PT, which led to the discovery of new elements.

Effective Nuclear Charge

- Many properties of atoms depend on electron configuration and on how strongly the outer electrons in the atoms are attracted to the nucleus.

Coulomb's law $$F = \frac{q_1 q_2}{r^2}$$

The attractive force between an electron and the nucleus depends on the magnitude of the nuclear charge and on the average distance between the nucleus and the electron.

Understanding e-nucleus attraction in a hydrogen atom (1 e + 1 proton) is easy, in contrast to many-e atoms, that experience attraction of each e to nucleus and e-e repulsion.

Electron's Screening

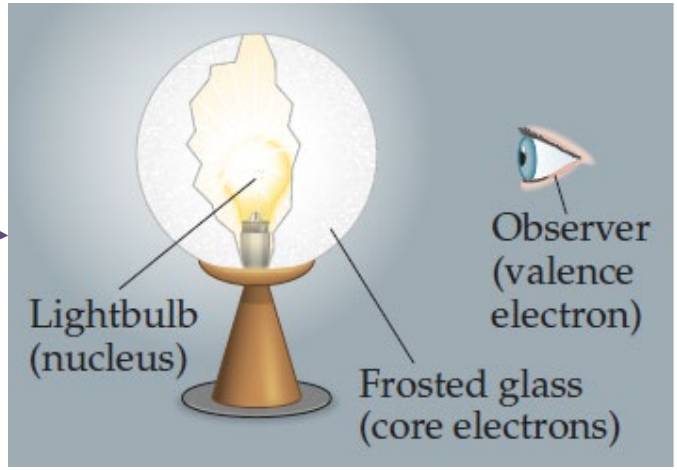
- refers to canceling some of e-nucleus attraction due to e-e repulsions in many-electron atoms.
- Each e experiences less attraction (screened by other es) than it would if the other electrons weren't there.

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

- Z_{eff}: effective nuclear charge,
- Z: actual nuclear charge
- S : a screening constant (a positive number)

$$Z_{eff} < Z$$

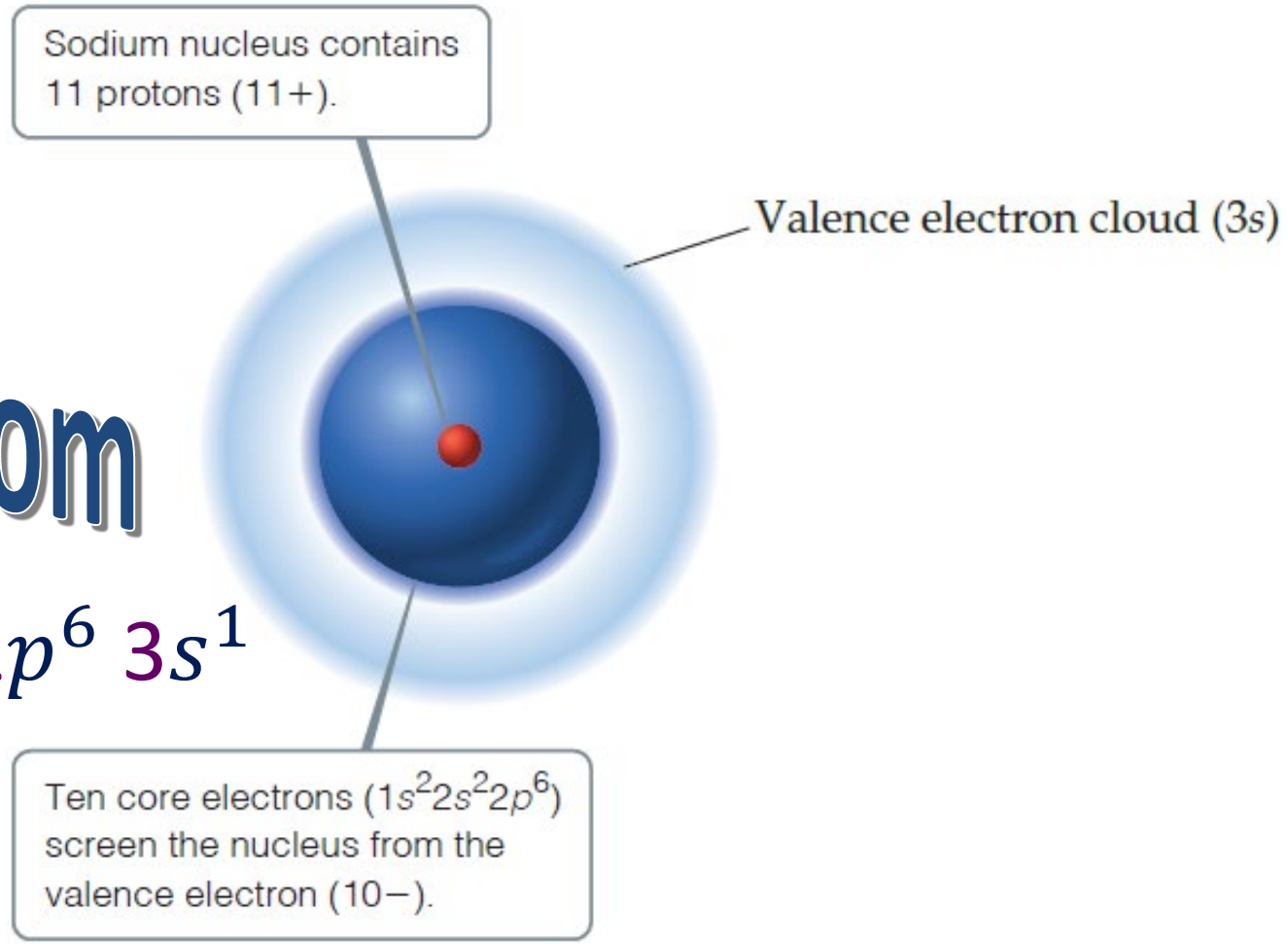
An analogy for effective nuclear charge.



Valence's Electron

- For a valence e, most of the shielding is due to the core electrons, which are much closer to the nucleus.
- As a result, for the valence electrons in an atom the value of S is usually close to the number of core electrons in the atom.
- es in the same valence shell do not screen one another very effectively, but they do affect the value of S slightly.

- Z = 11+, and there are 10 core es which screen Z "seen" by the $3s$ e.
- We expect S to equal 10 and the $3s$ e to experience $Z_{eff} = Z - S = 11 - 10 = 1+$.



Sodium atom

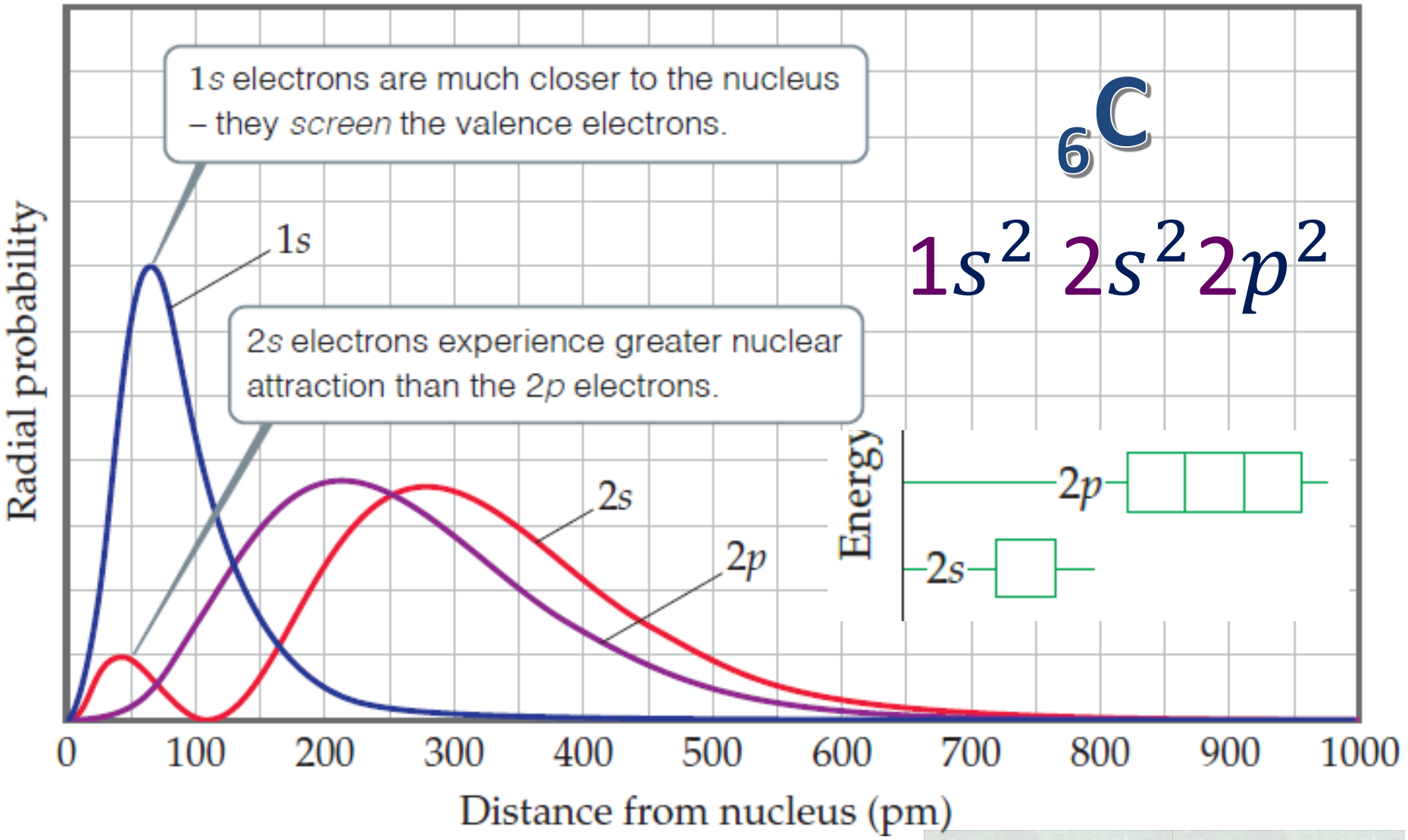
$_{11}$Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$

It is more complicated

- Because $3s$ e has a small probability of being very close to the nucleus, in the region occupied by the core es.

- Thus, this e experiences a greater net attraction than the simple $S = 10$. The actual $Z_{eff} = 2.5 +$ for $3s$ e in Na & S changes from 10 to 8.5

Electron's Screening & Undegeneracy



$_{6}C$

$1s^2\ 2s^2 2p^2$

2s es are less screened than 2p es

(ns < np < nd in E)

Trends in Valene e's Z_{eff}

Z_{eff} increases from left to right across any period of the periodic table.

- Although the number of core es stays the same across the period, the number of protons increases.
- The valence es added to counterbalance the increasing nuclear charge screen one another ineffectively, thus, Z_{eff} increases steadily.

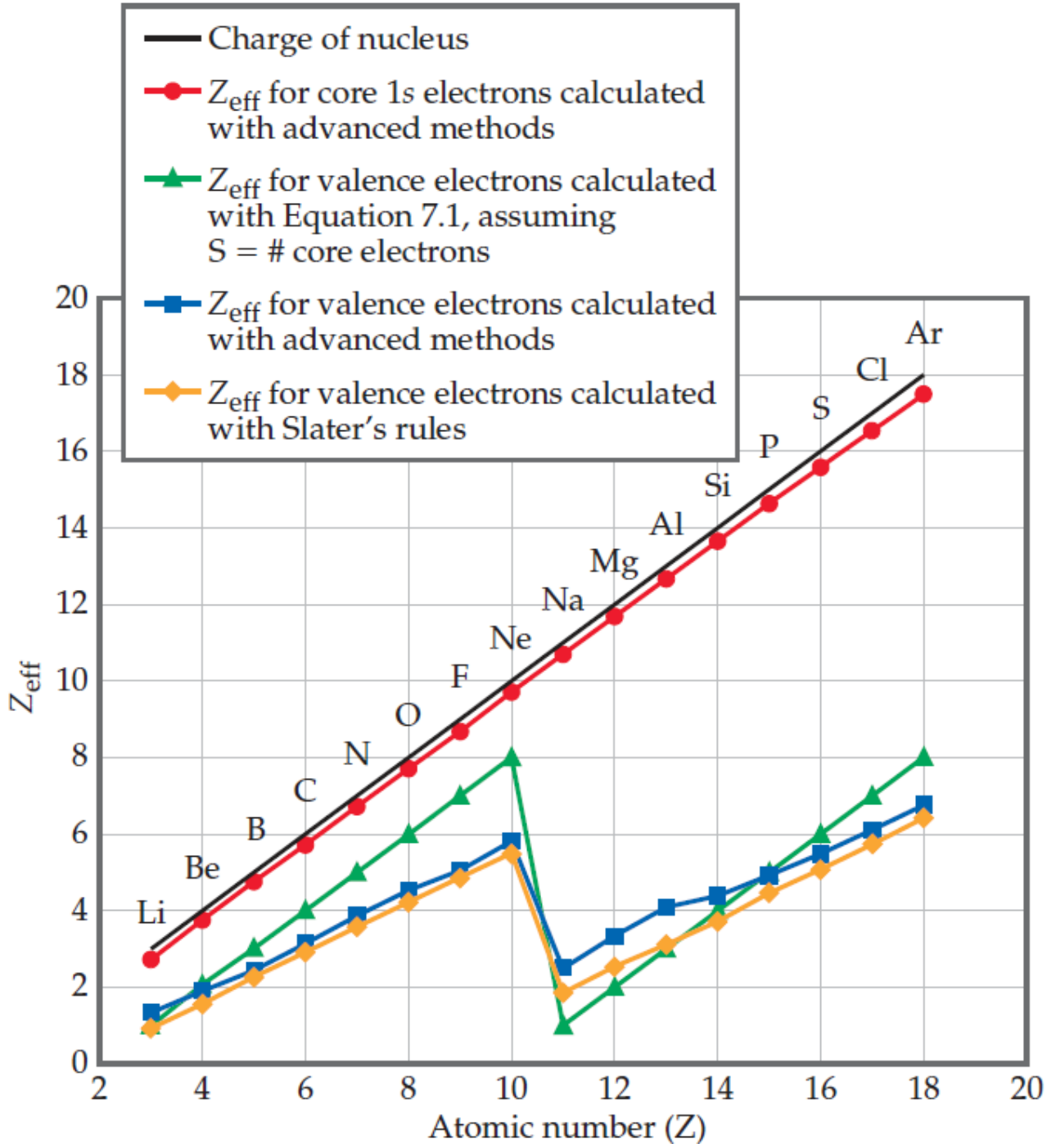
- For $_3$Li the two core es ($1s^2$) screen the $2s$ valence e from the 3+ nucleus efficiently. Consequently, the valence e experiences $Z_{eff} \approx 3 - 2 = 1+$.

- For ${}_4\mathrm{Be}$ ($1s^2 2s^2$), Z_{eff} experienced by each valence e is larger because here the two core $1s$ es screen a 4+ nucleus, and each $2s$ electron only partially screens the other. Consequently, $Z_{eff} \approx 4 - 2 = 2$ that is experienced by each $2s$ electron.

Trends in Valene e's Z_{eff}

Going down a column, Z_{eff} experienced by valence electrons changes far less than it does across a period.

- A simple estimate for S would expect same Z_{eff} for the valence electrons in lithium ($Z_{eff} = 3 - 2 = 1+$) and sodium ($Z_{eff} = 11 - 10 = 1+$).
- However, Z_{eff} increases slightly as we go down a column because the more diffuse core electron cloud is less able to screen the valence es from the nuclear charge.
- In the case of the alkali metals, Z_{eff} increases from $1.3+$ for Li, to $2.5+$ for Na, to $3.5+$ for K.

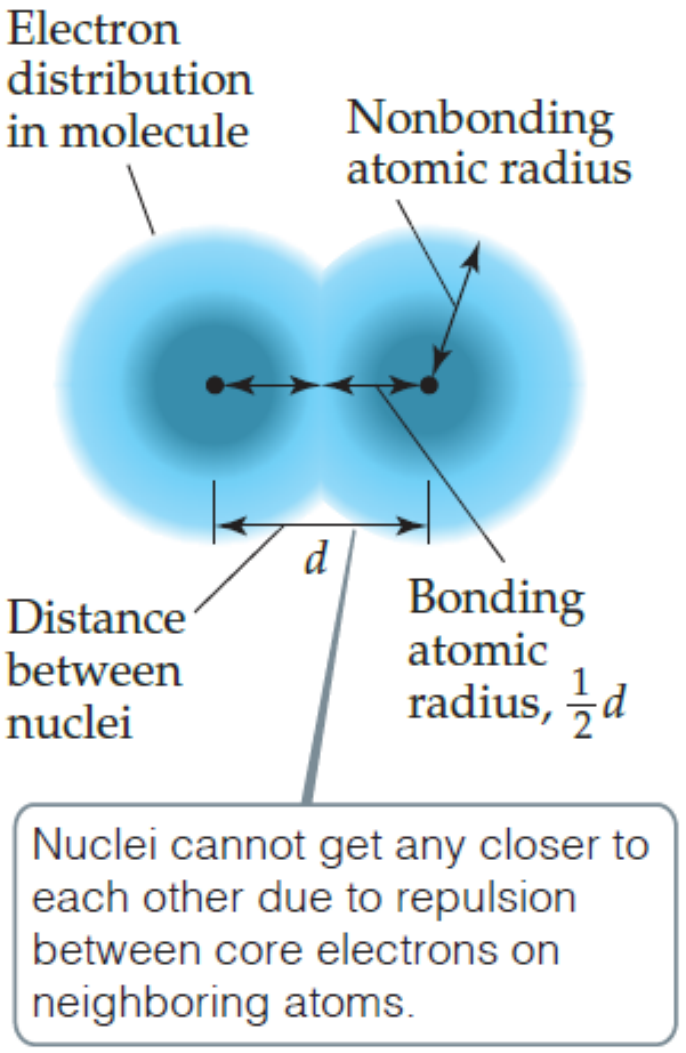


- Variations in Z_{eff} for Period 2 and Period 3 elements.
- Across periods, Z_{eff} felt by innermost 1*s* e increases (red circles) closely as the increase in Z (black line) because these es are not screened much.

Sizes of atoms & ions

- It is tempting to think of atoms as hard, spherical objects. According to the quantum mechanical model, however, atoms do not have sharply defined boundaries at which the electron distribution becomes zero.

We can define atomic size in several ways, based on the distances between atoms in various situations.



2 colliding Ar atoms

Distance between nuclei of 2 bonded atoms

- Atomic radius is defined based on the distance between the nuclei when two atoms are bonded to each other.
- The shortest distance separating the two nuclei during such collisions is **TWICE** the radii of atoms.
- The *bonding atomic radius* (also known as the covalent radius) for any atom in a molecule is equal to half of the bond distance, d, and is smaller than the *nonbonding atomic (van der Waals) radius*.
- Unless otherwise noted, we mean *bonding atomic radius* when we speak of the "size" of an atom.

Periodic Trends in Atomic Radii

Within each group, bonding atomic radius tends to increase from top to bottom.

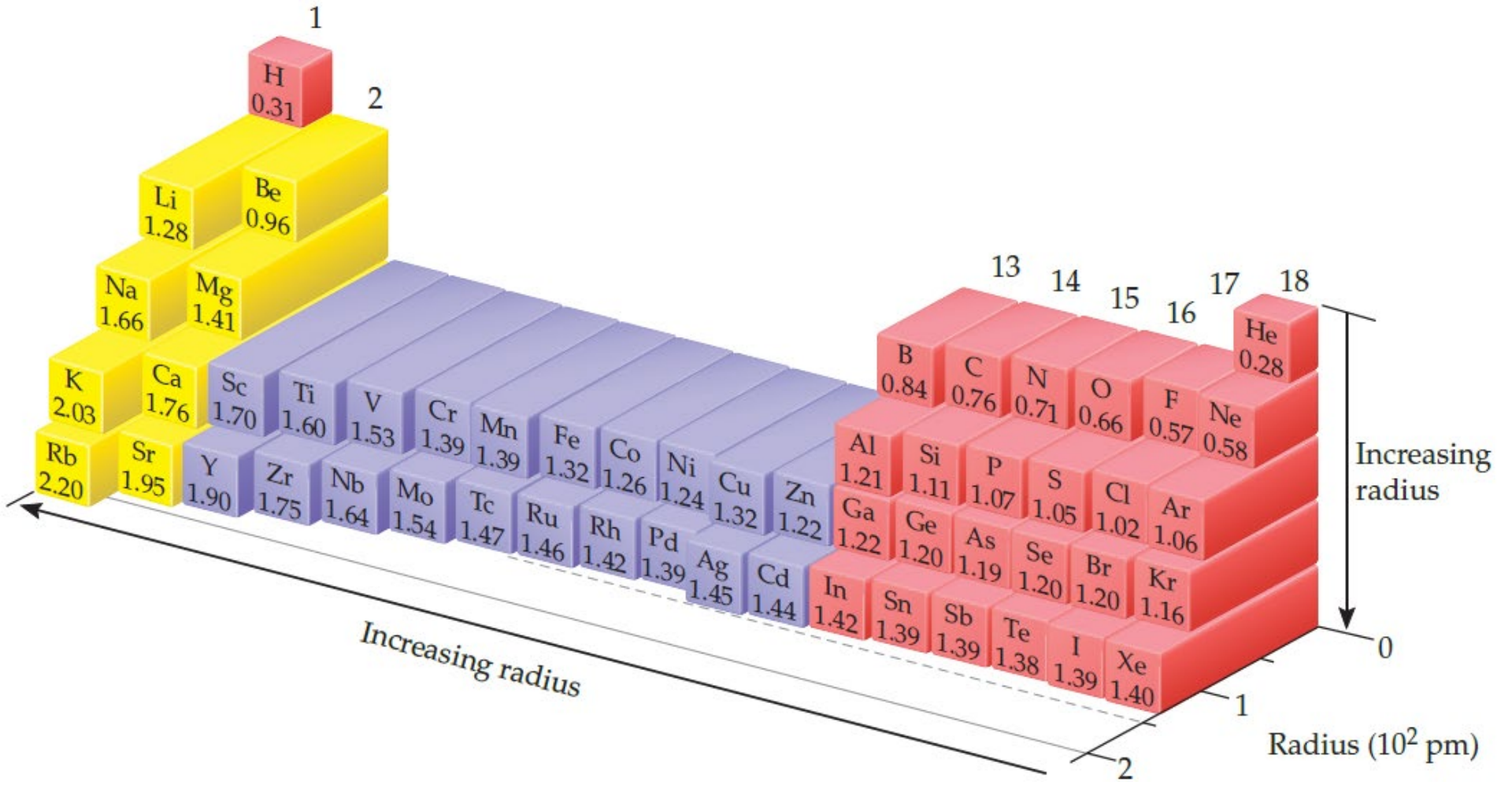
- This results primarily from the increase in the principal quantum number (n) of the outer es.
- As we go down a column, the outer es have a greater probability of being farther from the nucleus, causing the atomic radius to increase.

Periodic Trends in Atomic Radii

Within each period, bonding atomic radius tends to decrease from left to right.

- There are some minor exceptions, such as for Cl to Ar or As to Se).
- The major factor influencing this trend is the increase in Z_{eff} across a period that steadily draws the valence es closer to the nucleus, causing the bonding atomic radius to decrease.

Trends in bonding atomic radii for Periods 1-5

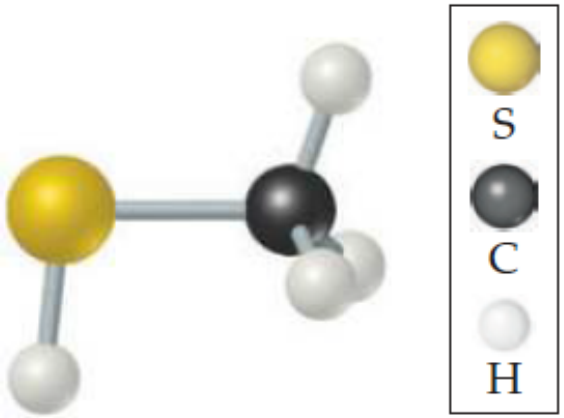


Exercise

- Natural gas used in home heating and cooking is odorless. Because natural gas leaks pose the danger of explosion or suffocation, various smelly substances are added to the gas to allow detection of a leak. One such substance is methyl mercaptan, CH_3SH. Use previous figure to predict the lengths of the C–S, C –H, and S –H bonds in this molecule.

Answer

- C –S bond length = bonding atomic radius of C + bonding atomic radius of S = 76 pm + 105 pm = 181 pm
- C –H bond length = 76 pm + 31 pm = 107 pm
- S –H bond length = 105 pm + 31 pm = 136 pm



Methyl mercaptan

Periodic Trends in Ionic Radii

- Ionic radii can also be determined from interatomic distances in ionic compounds.

- The size of an ion also depends on its nuclear charge (Z), the number of es it possesses, and the orbitals in which the valence es reside.

When a cation is formed:

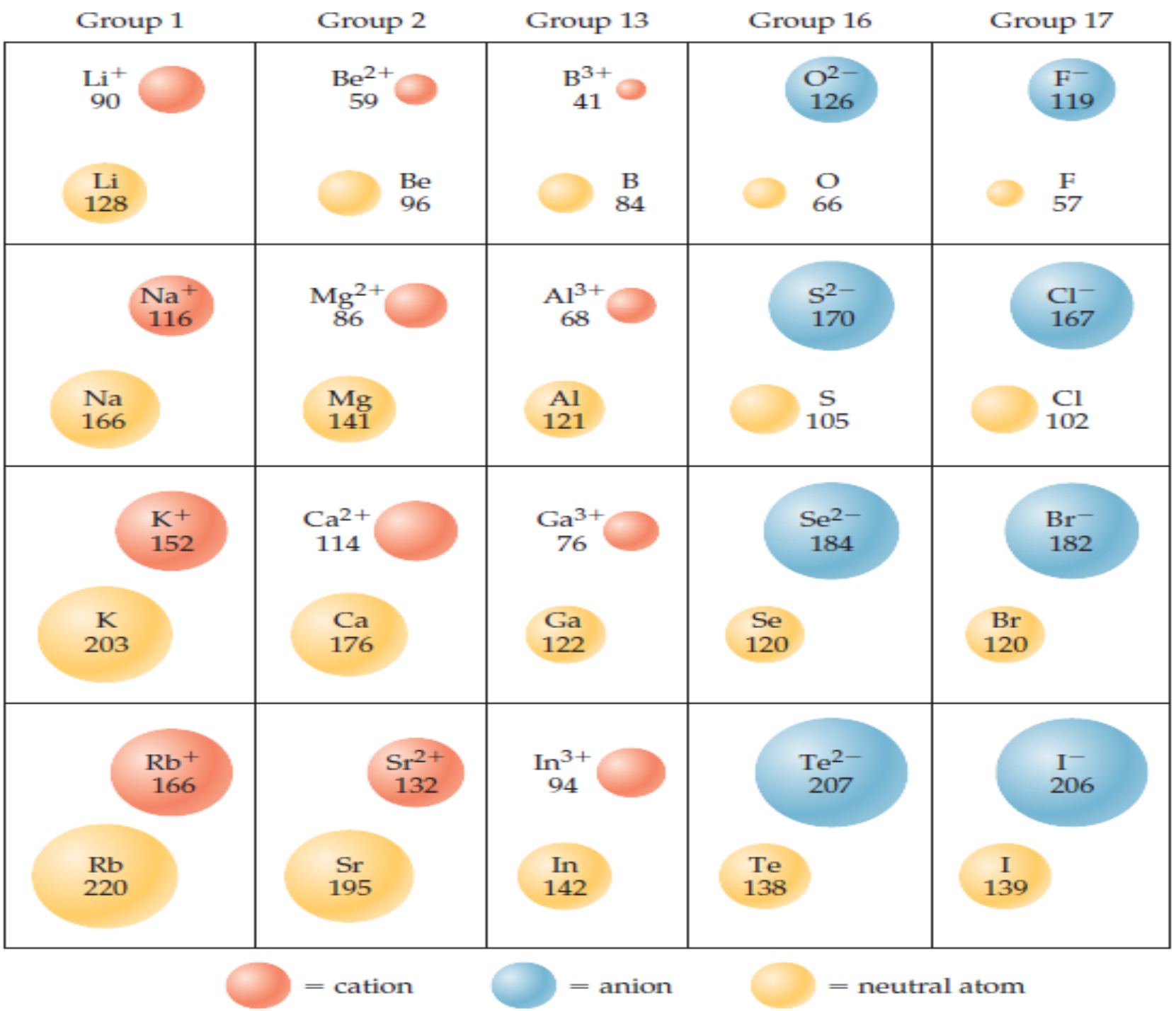
- es are removed from the occupied atomic orbitals that are the most spatially extended from the nucleus.
- the number of e–e repulsions is reduced.

Cations are smaller than their parent atoms

When an anion is formed:

- When es are added to an atom to form an anion, the increased e–e repulsions cause the electrons to spread out more in space.

Anions are larger than their parent atoms.


Group 1
Group 2
Group 13
Group 16
Group 17
Li+ 90
Li 128
Be2+ 59
Be 96
B3+ 41
B 84
O2− 126
O 66
F− 119
F 57
Na+ 116
Na 166
Mg2+ 86
Mg 141
Al3+ 68
Al 121
S2− 170
S 105
Cl− 167
Cl 102
K+ 152
K 203
Ca2+ 114
Ca 176
Ga3+ 76
Ga 122
Se2− 184
Se 120
Br− 182
Br 120
Rb+ 166
Rb 220
Sr2+ 132
Sr 195
In3+ 94
In 142
Te2− 207
Te 138
I− 206
I 139
= cation
= anion
= neutral atom

For isoelectronic ions

Isoelectronic ions= ions carrying the same charge, e.g., O^{2-}, F^{-}, Na^{+}, Mg^{2+}, and Al^{3+} (all have 10 es)

Ionic radius increases on moving down a column in PT, i.e., with increasing the principal quantum number of the outermost occupied orbital of an ion.

- list members in order of increasing atomic number; therefore, the nuclear charge increases as we move through the series.
- Because the number of es remains constant, ionic radius decreases with increasing nuclear charge as es are more strongly attracted to the nucleus.

Increasing nuclear charge ⟶

8 protons	9 protons	11 protons	12 protons	13 protons
10 electrons	10 electrons	10 electrons	10 electrons	10 electrons
O^{2-}	F^-	Na^+	Mg^{2+}	Al^{3+}
126 pm	119 pm	116 pm	86 pm	68 pm

Decreasing ionic radius ⟶

Exercise

- Arrange Mg^{2+} , Ca^{2+} , and Ca in order of decreasing radius.

Answer

- Cations are smaller than their parent atoms, and so $Ca^{2+} < Ca$.
- Because Ca is below Mg in Group 2, Ca^{2+} is larger than Mg^{2+}.
- Consequently, $Ca > Ca^{2+} > Mg^{2+}$.

Ionization Energy

is the minimum energy required to remove an electron from the ground state of the isolated gaseous atom or ion.

- If the electron in an H atom is excited from n = 1 (the ground state) to n = ∞ (the electron is completely removed from the atom), it means it is ionized.

All ionization energies for atoms are positive: Energy must be absorbed to remove an electron.

Ionization Energy vs. Work Function

Feature	Ionization Energy	Work Function
System	Isolated, gaseous atom	Surface of a bulk solid
Electrons	Outermost shell e	Delocalized e from the surface
Energy, same element	higher	lower
Reason	e is more strongly bound to a single nucleus	es are attracted to multiple nuclei and are shielded by other electrons

1st Ionization Energy, I_1

the energy needed to remove the first electron from a neutral atom.

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

2nd Ionization Energy, I_2

the energy needed to remove the second electron from an atom, and so forth, I_3, etc.

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

Variations in Successive Ionization Energies

- IEs for a given element increase as successive es are removed: $I_1 < I_2 < I_3$, and so forth, because with each successive removal, an e is being pulled away from an increasingly positive ion, requiring increasingly more energy.

Inner shell electrons

- IE increases sharply when an inner-shell e is removed.
  - For $_{14}$Si: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2$, IEs increase steadily from 786 to 4356 kJ/mol for the four es in the $3s$ and $3p$ subshells.
  - Removal of the fifth e, which comes from the $2p$ subshell, requires **16091** kJ/mol because this e is much closer to nucleus than the four n = 3 es, and experiences a much greater Z_{eff}.

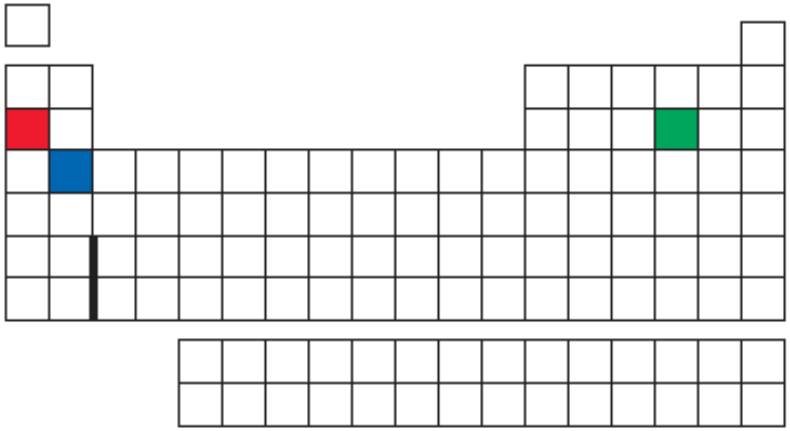
only outermost es are involved in the sharing and transfer of electrons that give rise to chemical bonding and reactions.

TABLE 7.2 Successive Values of Ionization Energies, *I*, for the Elements Sodium to Argon (kJ/mol)

Element	I_1	I_2	I_3	I_4	I_5	I_6	I_7
Na	496	4562					
Mg	738	1451	7733		(inner-shell electrons)		
Al	578	1817	2745	11577			
Si	786	1577	3232	4356	16091		
P	1012	1907	2914	4964	6274	21267	
S	1000	2252	3357	4556	7004	8496	27107
Cl	1251	2298	3822	5159	6542	9362	11018
Ar	1521	2666	3931	5771	7238	8781	11995

Exercise

- Three elements are indicated in the periodic table in the margin. Which one has the largest second ionization energy?



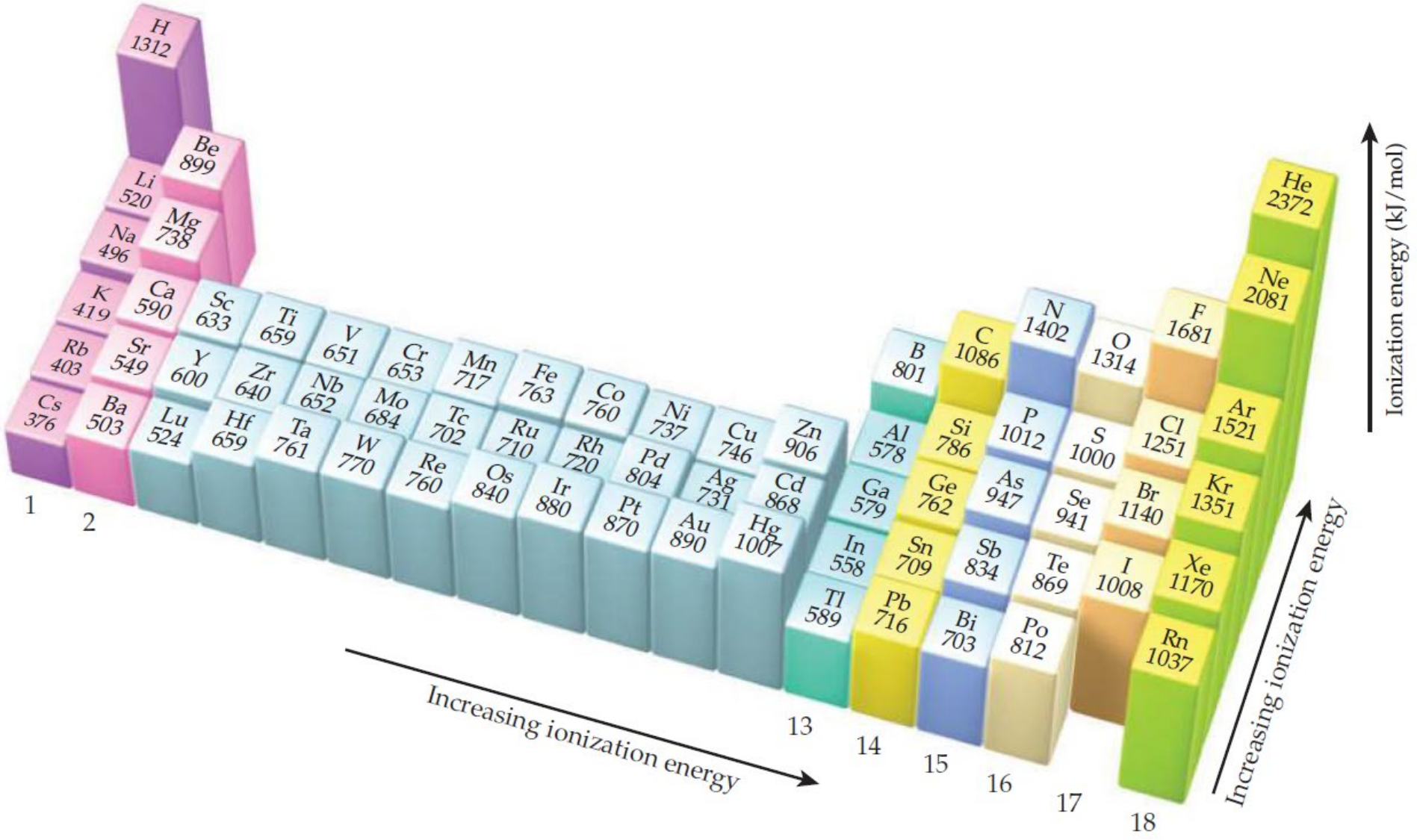
Answer

- The red box represents Na, which has one valence e. I_2 of Na is associated with the removal of a core e.
- The other elements, S (green) and Ca (blue), have two or more valence es.
- Thus, Na should have the largest I_2.

Periodic Trends in I_1

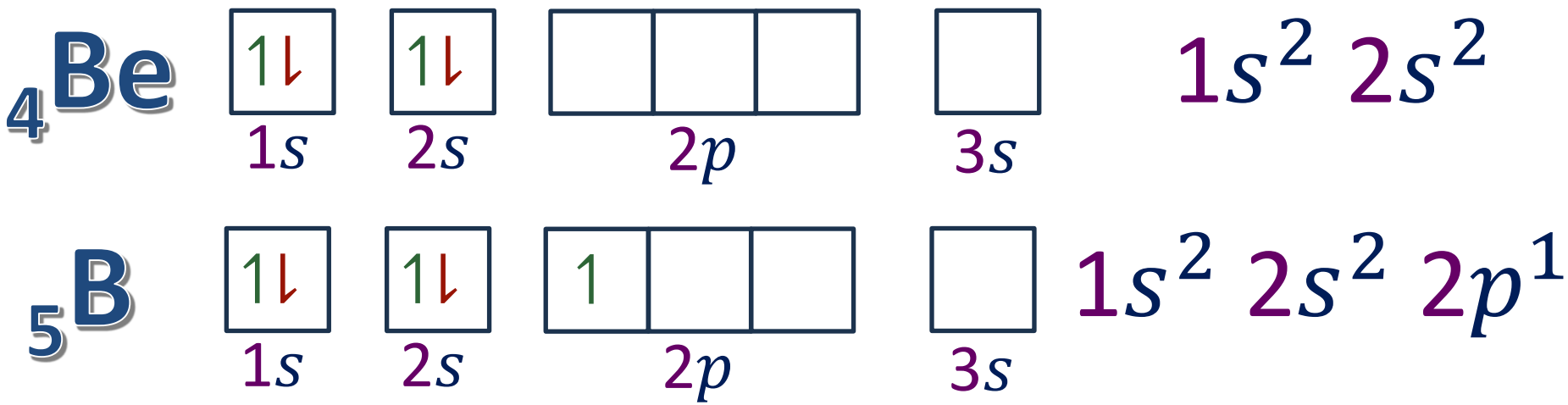
- I_1 generally increases from left to right across a period.
  - The alkali metals show the lowest I_1 in each period, and the noble gases show the highest.
  - There are slight irregularities in this trend.
- I_1 generally decreases down any column in PT.
  - I_1 of the noble gases follow the order He > Ne > Ar > Kr > Xe.
- The s- and p-block elements show a larger range of I_1 values than do the transition metal elements.
  - Generally, the I_1 of the transition metals increase slowly from left to right in a period.
  - The f-block metals also show only a small variation in the values of I_1 .

Periodic Trends in I_1



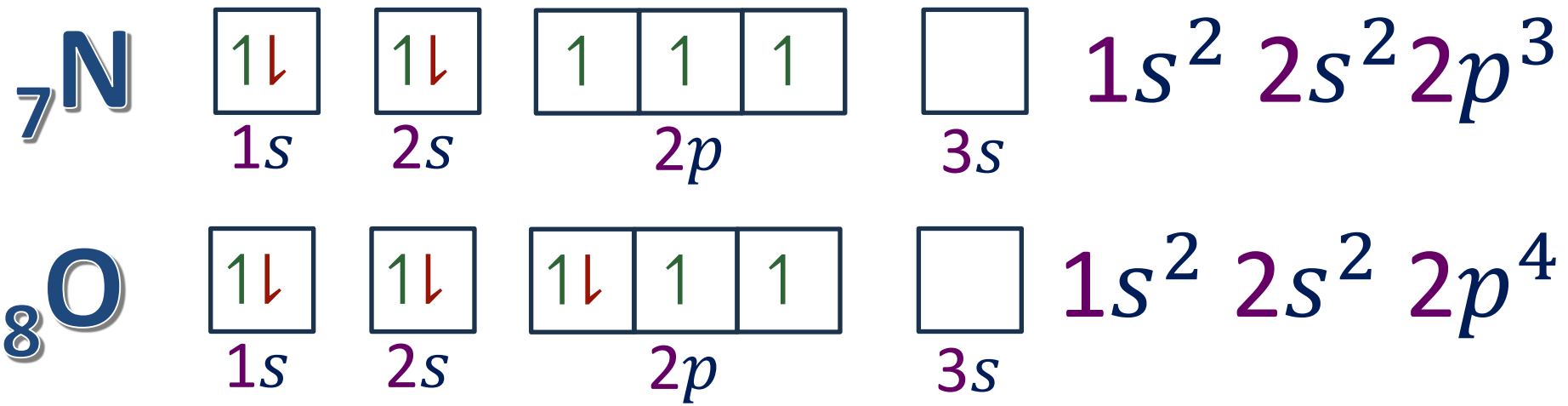
- In general, smaller atoms have higher I_1 .
- The same factors that influence atomic size also influence ionization energies.
- The energy needed to remove an e from the outermost occupied shell depends on both the Z_{eff} and the average distance of the e from the nucleus.
- Either increasing Z_{eff} or decreasing the distance from the nucleus increases the attraction between the e and the nucleus, and it becomes more difficult to remove the e, and, thus, I_1 increases.
- Across a period, there is both an increase in Z_{eff} and a decrease in atomic radius, causing the I_1 to increase.
- Down a column, the atomic radius increases, while Z_{eff} increases only gradually. The increase in radius dominates, so the attraction between the nucleus and e decreases, causing the I_1 to decrease.

Irregularity



- The decrease in I_1 from beryllium to boron occurs because the third valence e of B must occupy the $2p$ subshell, which is empty for Be. Recall that the $2p$ subshell is at a higher energy than the $2s$ subshell.

Irregularity



- The slight decrease in I_1 when moving from nitrogen to oxygen is the result of the repulsion of paired es in the p^4 configuration.
  - Remember that according to Hund's rule, each e in the p^3 configuration resides in a different p orbital, which minimizes the e–e repulsion among the three $2p$ electrons.

Electron Configurations of Ions

- When es are removed from an atom to form a cation, they are always removed first from the occupied orbitals having the largest principal quantum number, n.

$$Li(1s^2\ 2s^1) \rightarrow Li^+(1s^2) + e^-$$

$$Fe([Ar]4s^2\ 3d^6) \rightarrow Fe^{2+}([Ar]\ 3d^6) + 2e^-$$

$$Fe^{2+}([Ar]\ 3d^6) \rightarrow Fe^{3+}([Ar]\ 3d^5) + e^-$$

Filling vs. Removing es

- It may seem odd that $4s$ es are removed before $3d$ es in forming transition-metal cations, as we fill $4s$ first.
- On filling es, we add both an e to an orbital and a proton to the nucleus to change the identity of the element.
- In ionization, we do not reverse this process because no protons are being removed.
- Ca and Ti^{2+} have 20 es, but a Ti^{2+} ion has more protons than a Ca atom (22 vs. 20). That changes the relative energy levels of the orbitals enough that the two species have different electron configurations: Ca ($[Ar]4s^2$) and Ti^{2+} ($[Ar]\ 3d^2$).

Electron Configurations of Ions

- If there is more than one occupied subshell for a given value of n, the es are first removed from the orbital with the highest value of l.
- A tin atom loses its $5p$ es before its $5s$ es.

$$Sn([Kr]5s^2\ 4d^{10}\ 5p^2)$$

$$\rightarrow Sn^{2+}([Kr]5s^2\ 4d^{10}\ ) + 2e^-$$

$$\rightarrow Sn^{4+}([Kr]\ 4d^{10}\ ) + 4e^-$$

Addition of es to form anions

- es added to an atom to form an anion are added to the empty or partially filled orbital having the lowest value of n.

- An e added to a fluorine atom to form the F^- ion goes into the one remaining vacancy in the $2p$ subshell.

$$F(1s^2 2s^2 2p^5) + e^- \rightarrow F^-(1s^2 2s^2 2p^6)$$

Electron Affinity, EA

The energy change that occurs when an electron is added to a gaseous atom

- It measures the attraction, or affinity, of the atom for the added electron.
- For most atoms, energy is released when an e is added.
- Addition of an e to Cl atom is accompanied by an energy change of –349 kJ/mol (=EA).

$$Cl\,(g)([\mathrm{Ne}]\,3s^2 3p^5) + e^-$$

$$\rightarrow Cl^-(g)([\mathrm{Ne}]\,3s^2 3p^6) \quad EA = -349\ kJ/mol$$

- The greater the attraction between an atom and an added e, the more negative the atom's EA.
- For some elements, such as the noble gases, the electron affinity has a positive value, meaning that the anion is higher in energy than are the separated atom and electron:

$$Ar\,(g) + e^- \rightarrow Ar^-(g) \quad EA > 0$$

$$[Ne]3s^2\,3p^6 \qquad [Ne]3s^2\,3p^6\,4s^1$$

EA is positive means that an e will not attach itself to an Ar atom; in other words, the Ar^- ion is unstable and does not form.

Periodic Trends in EA

1												18
H −73	2											He > 0
Li −60	Be > 0											Ne > 0
Na −53	Mg > 0											Ar > 0
K −48	Ca −2											Kr > 0
Rb −7	Sr −5											Xe > 0

13	14	15	16	17
B −27	C −122	N > 0	O −141	F −328
Al −43	Si −134	P −72	S −200	Cl −349
Ga −30	Ge −119	As −78	Se −195	Br −325
In −30	Sn −107	Sb −103	Te −190	I −295

EA in kJ/mol for selected s- and p-block elements

- Trends are not as evident as they are for I.
- Halogens (are one e shy of a filled p subshell) have the most negative EA. By gaining an e, they form stable anions of noble-gas configuration.

- Addition of an e to a noble gas requires that the e resides in a higher-energy subshell that is empty in the atom that is energetically unfavorable, hence, EA is highly positive.

$_{4}$Be: [He] $2s^2$

$_{12}$Mg: [Ne] $3s^2$

- EA of Be and Mg are positive for the same reason; the added electron would reside in a previously empty p subshell that is higher in energy.

Group 15 elements have half-filled p subshells,

$_7$N: [He] $2s^2\ 2p^3$

14	15	16
C −122	N > 0	O −141
Si −134	P −72	S −200
Ge −119	As −78	Se −195
Sn −107	Sb −103	Te −190

- The added e must be put in an orbital that is already occupied, resulting in larger e–e repulsions.

- Consequently, these elements have EA that are either positive (N) or less negative than those of their neighbors to the left (P, As, Sb).

- Recall the discontinuity in the trends in I_1 for the same reason.

- EAs do not change greatly down a group.
- As we proceed from F (added electron goes into a $2p$ orbital) to I (added electron goes into a $5p$ orbital), the average distance between the added e and the nucleus steadily increases, causing the e–nucleus attraction to decrease.
- Yet, the orbital that holds the outermost e is increasingly spread out, so that as we proceed from F to I, the e–e repulsions are also reduced.
- As a result, the reduction in the e–nucleus attraction is counterbalanced by the reduction in e–e repulsions.


Thank You