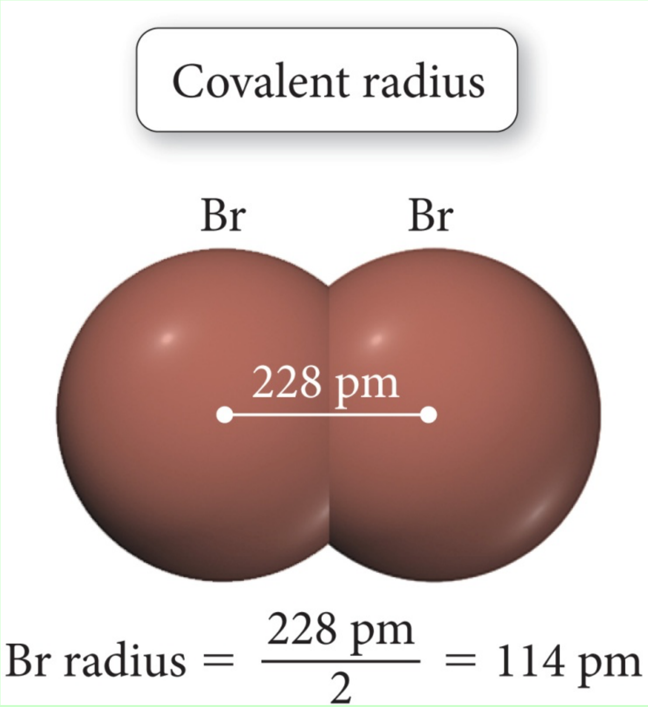
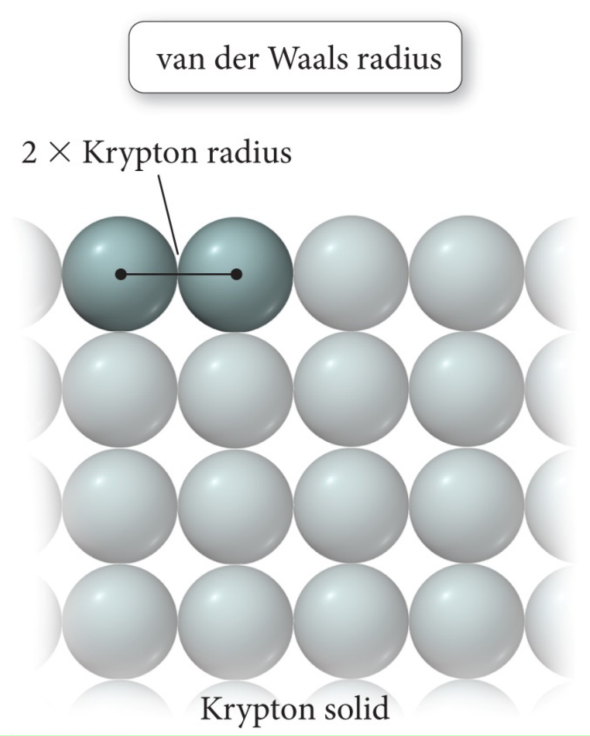
Atomic Structure and Periodicity

Trend in Atomic Radius – Main Group

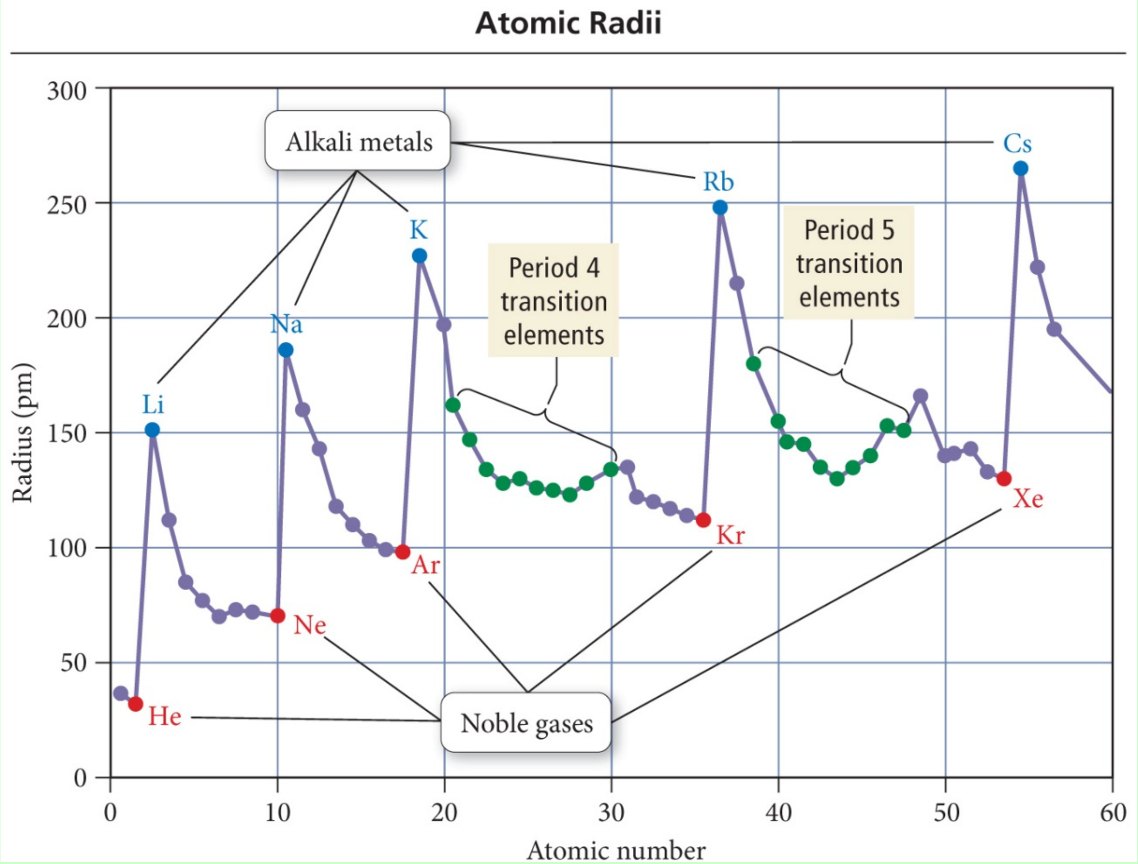
- There are several methods for measuring the radius of an atom, and they give slightly different numbers.
  - ✓ Van der Waals radius = nonbonding
  - ✓ Covalent radius = bonding radius
  - ✓ Atomic radius is an average radius of an atom based on measuring large numbers of elements and compounds.





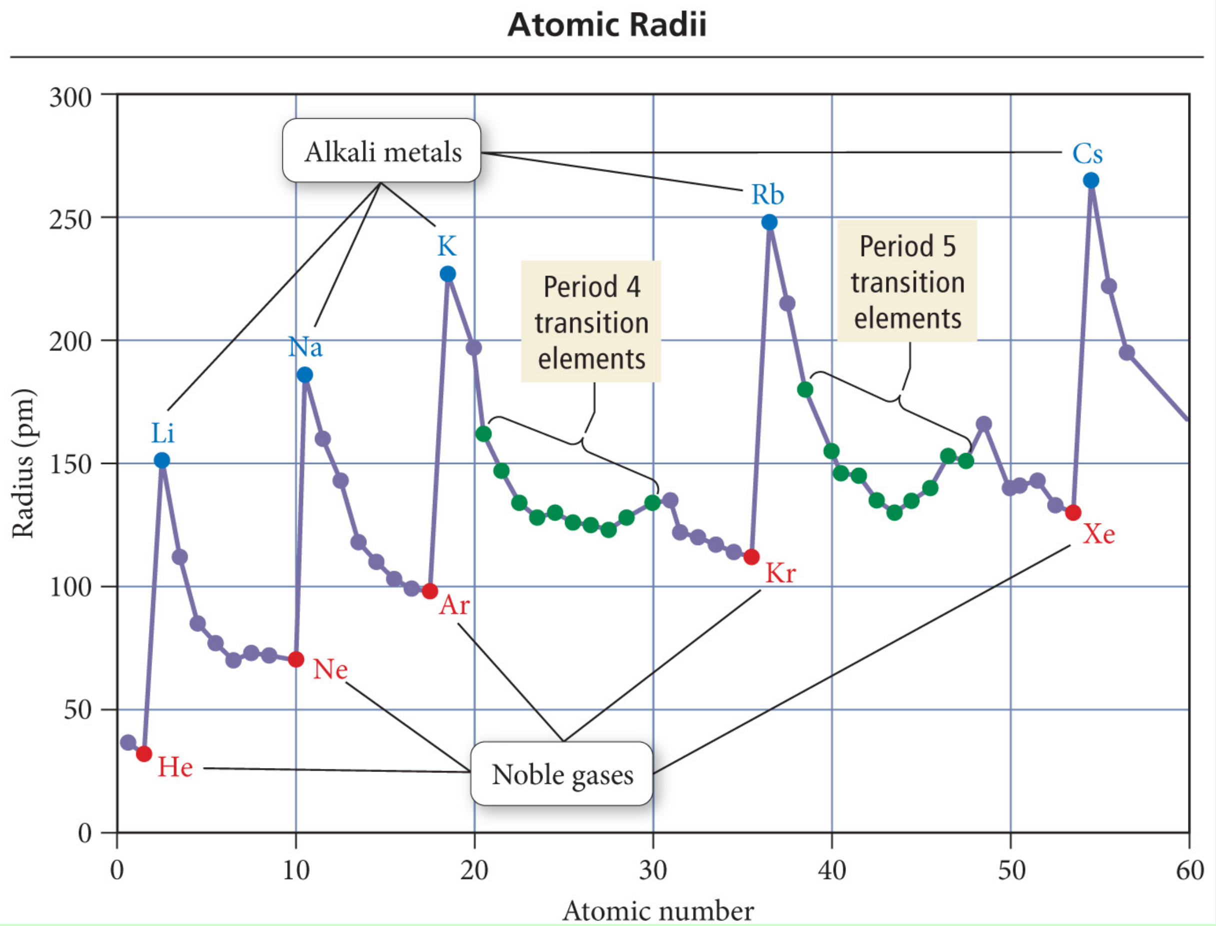
Trend in Atomic Radius – Main Group

- **Atomic radius decreases across period (left to right)**
  - ✓ Adding electrons to same valence shell
  - ✓ Effective nuclear charge increases
  - ✓ Valence shell held closer



Trend in Atomic Radius – Main Group

- Atomic radius increases down group
  - ✓ Valence shell farther from nucleus
  - ✓ Effective nuclear charge fairly close



Periodic Trends in Atomic Radius

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	$GeCl_4$

Quantum-Mechanical Explanation for the Group Trend in Atomic Radius

- The size of an atom is related to the distance the valence electrons are from the nucleus.

Quantum-Mechanical Explanation for the Group Trend in Atomic Radius

- The larger the orbital an electron is in, the farther its most probable distance will be from the nucleus, and the less attraction it will have for the nucleus.

Quantum-Mechanical Explanation for the Group Trend in Atomic Radius

- Traversing down a group adds a principal energy level.

Quantum-Mechanical Explanation for the Group Trend in Atomic Radius

- The larger the principal energy level an orbital is in, the larger its volume.

Quantum-Mechanical Explanation for the Group Trend in Atomic Radius

- Quantum-mechanics predicts the atoms should get larger down a column.

Quantum-Mechanical Explanation for the Period Trend in Atomic Radius

- The larger the effective nuclear charge an electron experiences, the stronger the attraction it will have for the nucleus.

Quantum-Mechanical Explanation for the Period Trend in Atomic Radius

- The stronger the attraction the valence electrons have for the nucleus, the closer their average distance will be to the nucleus.

Quantum-Mechanical Explanation for the Period Trend in Atomic Radius

- Traversing across a period increases the effective nuclear charge on the valence electrons.

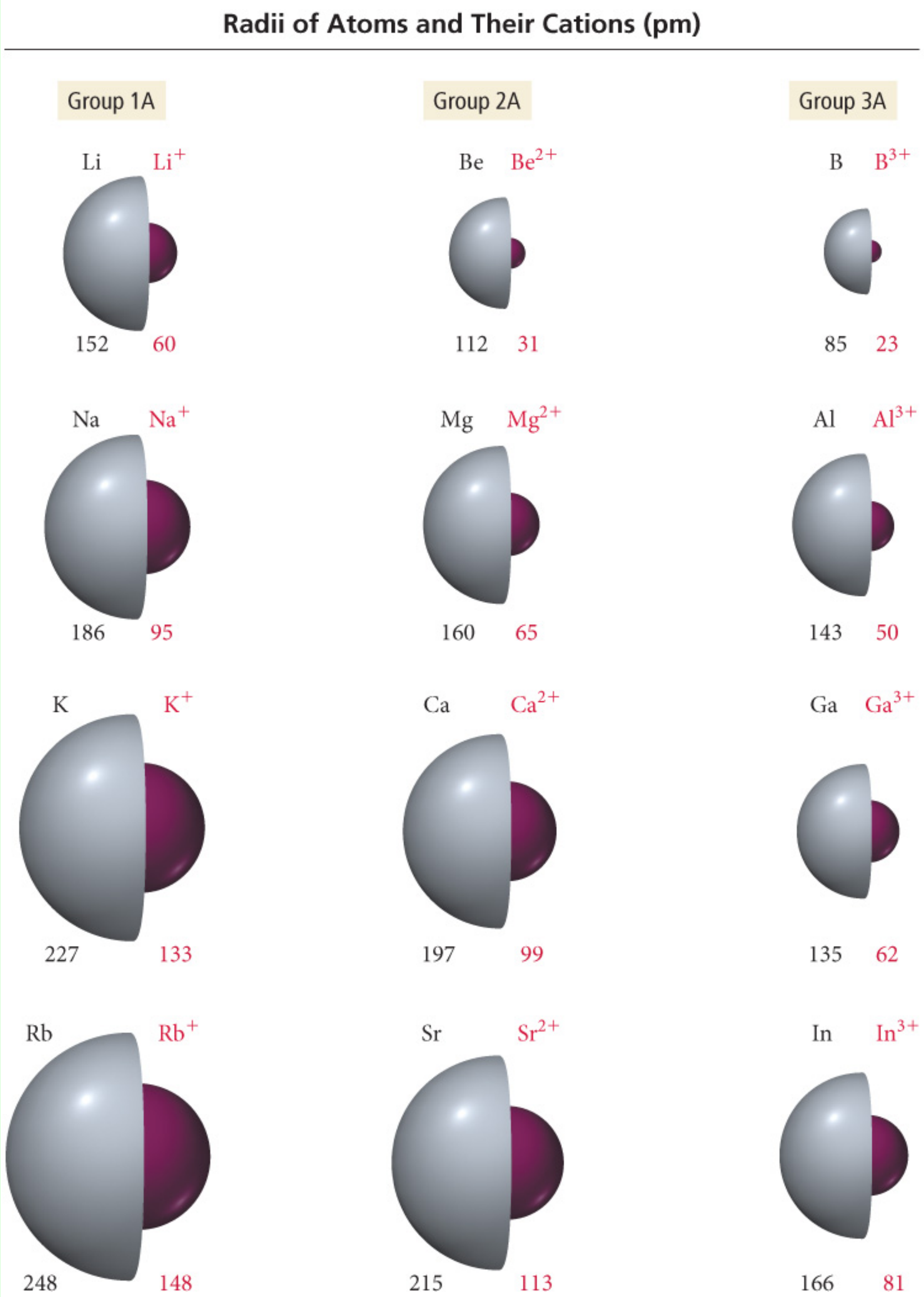
Quantum-Mechanical Explanation for the Period Trend in Atomic Radius

- Quantum-mechanics predicts the atoms should get smaller across a period.

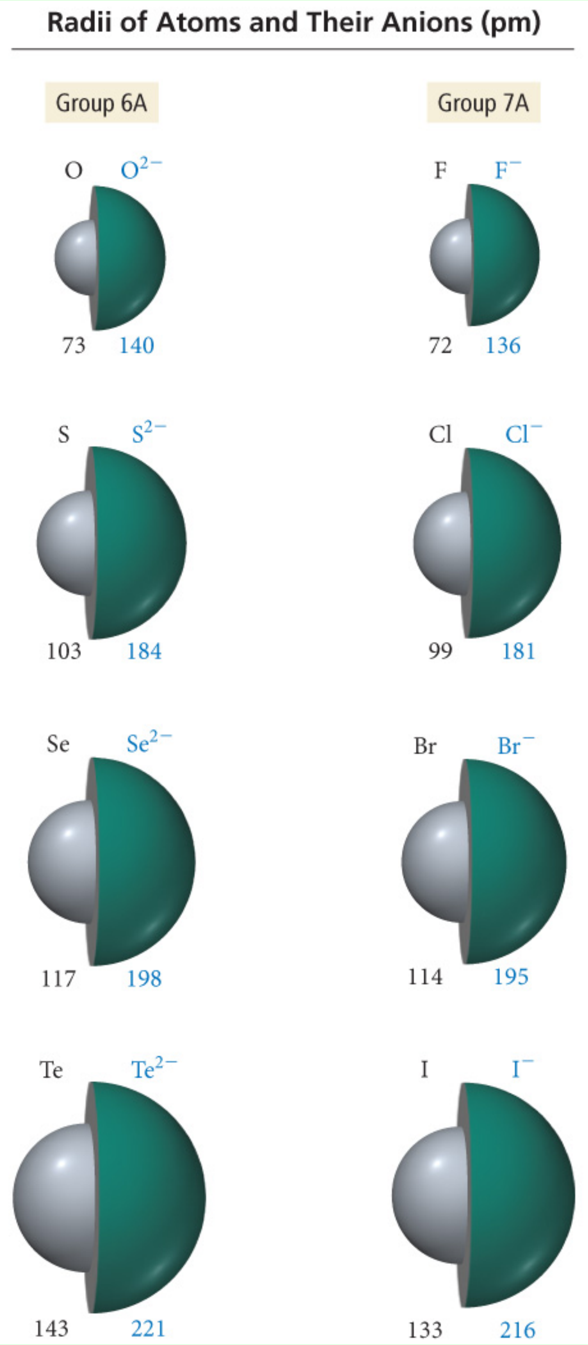
Trends in Ionic Radius

- Ions in the same group have the same charge.
- Ion size increases down the column.
  - Higher valence shell, larger
- Cations are smaller than neutral atoms; anions are larger than neutral atoms.
- Cations are smaller than anions.
  - Except Rb^+ and Cs^+ bigger or same size as F^- and O^{2-}.
- Larger positive charge = smaller cation
  - For isoelectronic species
  - Isoelectronic = same electron configuration
- Larger negative charge = larger anion
  - For isoelectronic species

Periodic Trends in Ionic Radius



Periodic Trends in Ionic Radius



Ionization Energy (IE)

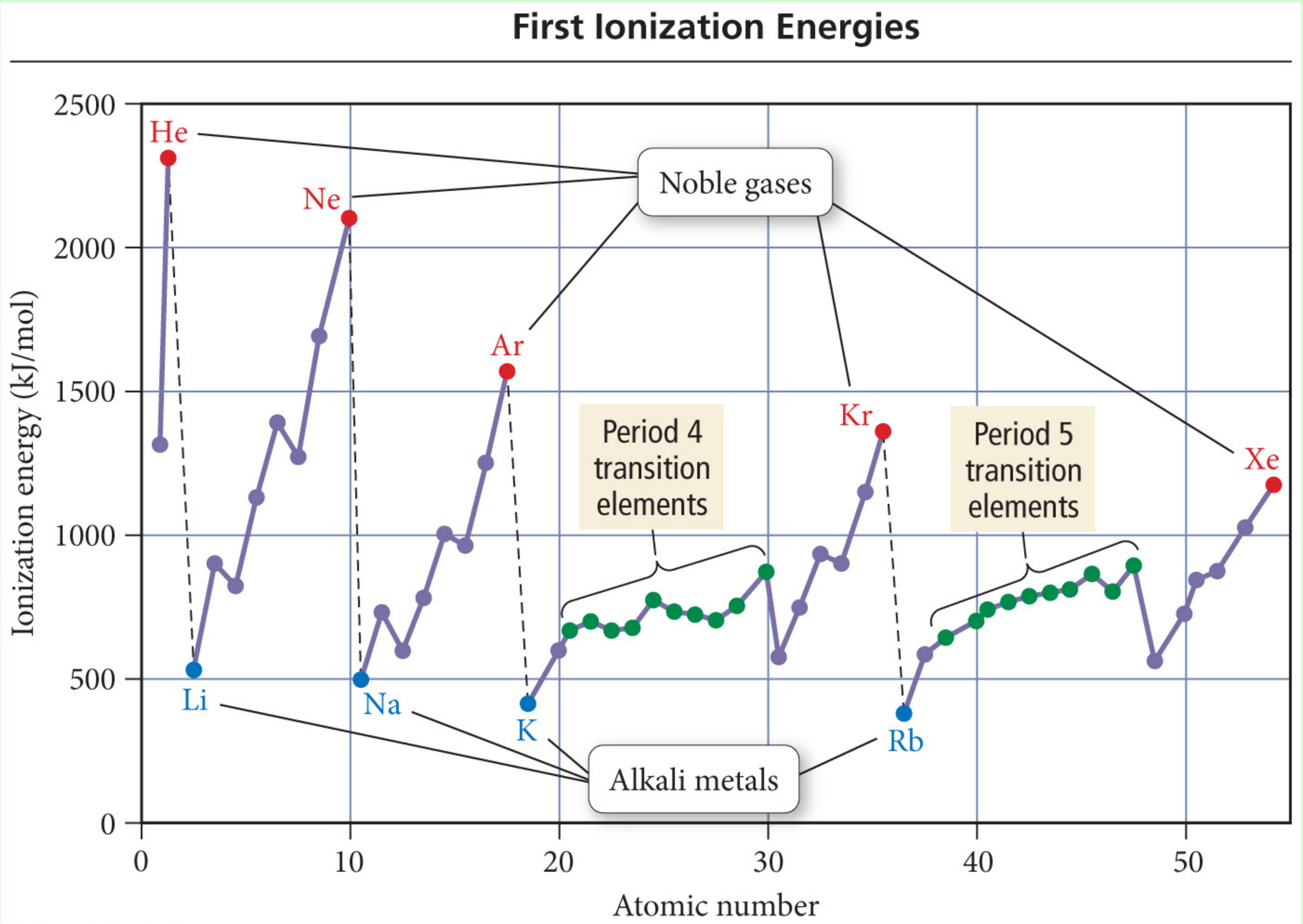
- Minimum energy needed to remove an electron from an atom or ion
  - ✓ Gas state
  - ✓ Endothermic process
  - ✓ Valence electron easiest to remove, lowest IE
  - ✓ $M(g) + IE_1 \rightarrow M^{1+}(g) + 1\ e^-$
  - ✓ $M^{+1}(g) + IE_2 \rightarrow M^{2+}(g) + 1\ e^-$
    - ➢ First ionization energy = energy to remove electron from neutral atom, second IE = energy to remove from 1+ ion, etc.

Ionization Energy: the energy required to remove an electron from an atom

- Increases for successive electrons taken from the same atom
- Tends to increase across a period

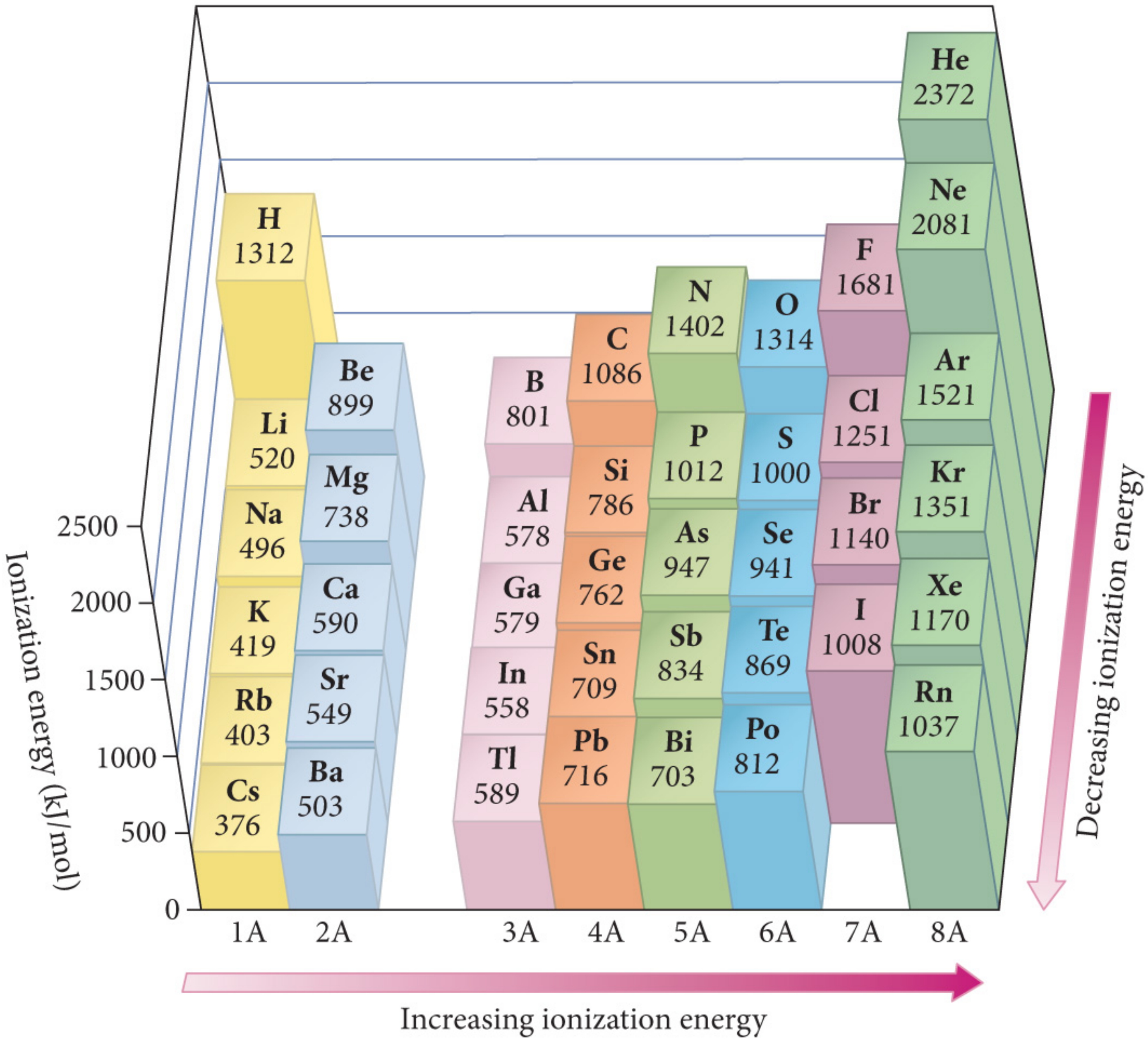
  - Electrons in the same quantum level do not shield as effectively as electrons in inner levels, ↑ protons, ↑ Energy required
  - Irregularities at half filled and filled sublevels due to extra repulsion of electrons paired in orbitals, making them easier to remove

- Tends to decrease down a group
  - Outer electrons are farther from the Nucleus, more shielding effect



First Ionization Energies
Ionization energy (kJ/mol)
2500
2000
1500
1000
500
0
0
10
20
30
40
50
Atomic number
He
Ne
Ar
Kr
Xe
Noble gases
Li
Na
K
Rb
Alkali metals
Period 4 transition elements
Period 5 transition elements

Trends in First Ionization Energy



Quantum-Mechanical Explanation for the Trends in First Ionization Energy

- The strength of attraction is related to the most probable distance the valence electrons are from the nucleus and the effective nuclear charge the valence electrons experience.

Quantum-Mechanical Explanation for the Trends in First Ionization Energy

- The larger the orbital an electron is in, the farther its most probable distance will be from the nucleus and the less attraction it will have for the nucleus.

Quantum-Mechanical Explanation for the Trends in First Ionization Energy

- Quantum-mechanics predicts the atom's first ionization energy should get lower down a column.

Quantum-Mechanical Explanation for the Trends in First Ionization Energy

- Traversing across a period increases the effective nuclear charge on the valence electrons.

Quantum-Mechanical Explanation for the Trends in First Ionization Energy

- Quantum-mechanics predicts the atom’s first ionization energy should get larger across a period.

Trends in Second and Successive Ionization Energies

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

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

Core electrons

Electron Affinity

- Energy is released when an neutral atom gains an electron. **CHANGE in ENERGY**
  - ✓ Gas state
  - ✓ $M(g) + 1e^{-} \rightarrow M^{1-}(g) + EA$
- Electron affinity is defined as exothermic (−), but may actually be endothermic (+).
  - ✓ Some alkali earth metals and all noble gases are endothermic. Why?
- The more energy that is released, the larger the electron affinity.
  - ✓ The more negative the number, the larger the EA.

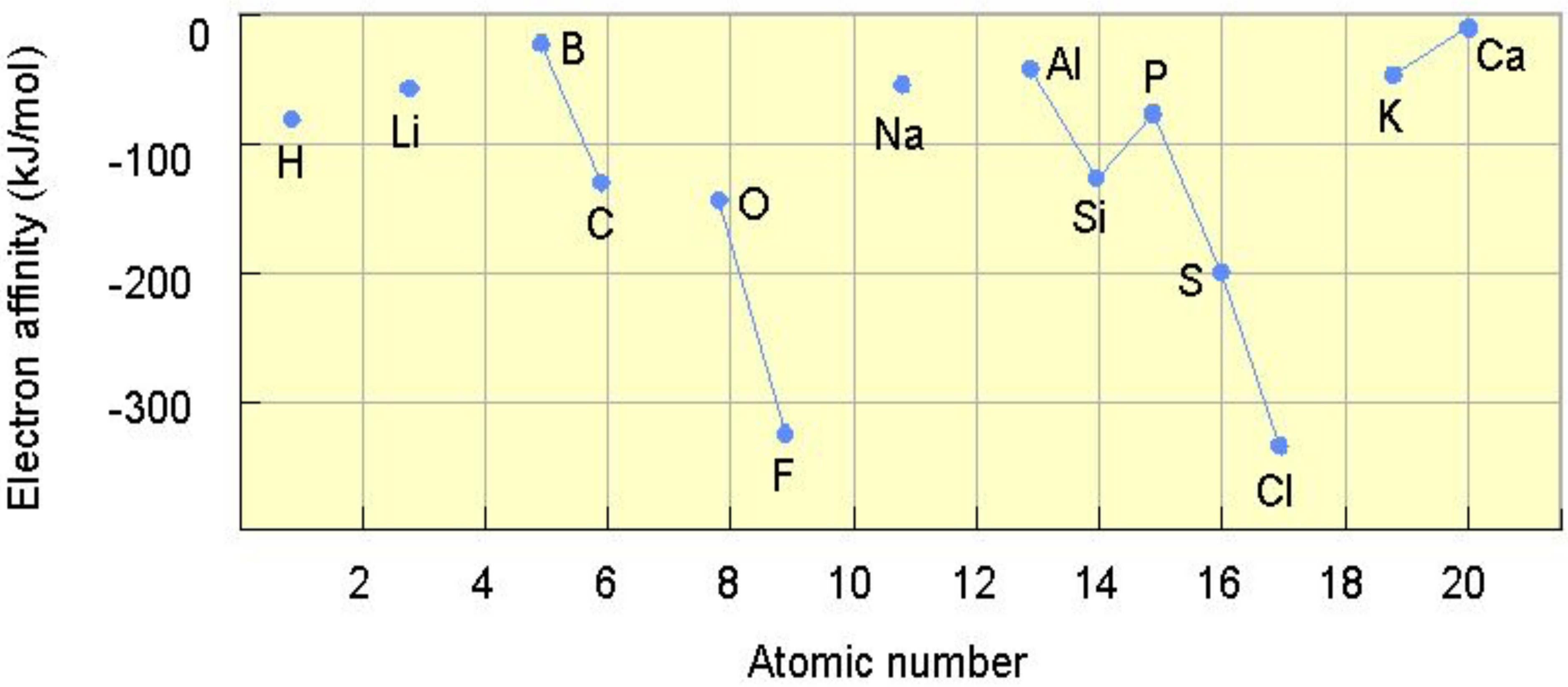
Trends in Electron Affinity

- Alkali metals decrease electron affinity down the column.
  - But not all groups do
  - Generally irregular increase in EA from second period to third period
- "Generally" increases across period
  - Becomes more negative from left to right
  - Not absolute
  - Group 5A generally lower EA than expected because extra electron must pair
  - Groups 2A and 8A generally very low EA because added electron goes into higher energy level or sublevel
- Highest EA in any 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

Table of Electron Affinities

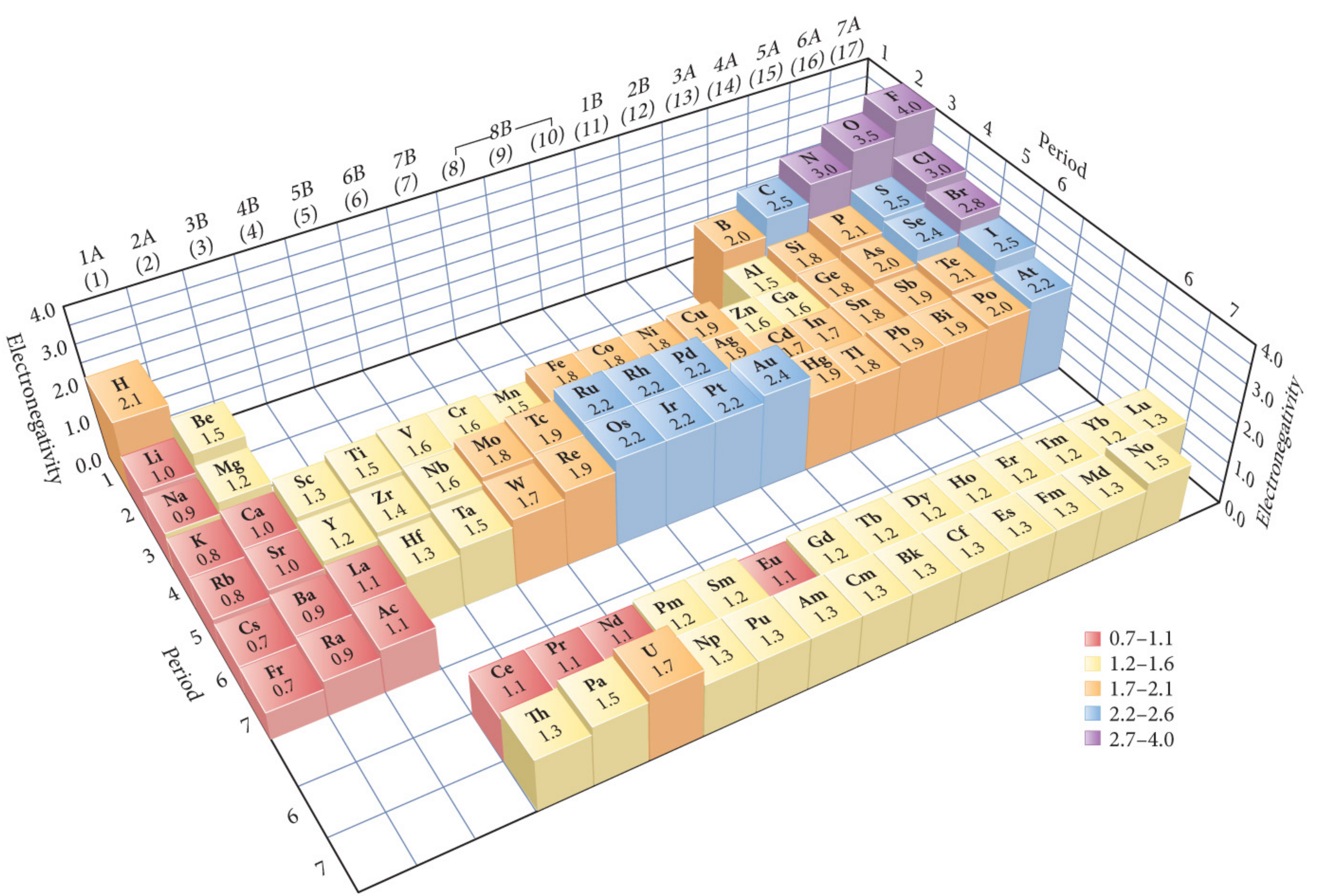


Electronegativity

- The ability of an atom to attract bonding electrons to itself is called **electronegativity**.
- Increases across period (left to right) and decreases down group (top to bottom)
  - Fluorine is the most electronegative element.
  - Francium is the least electronegative element.
  - Noble gas atoms are not assigned values.
  - Opposite of atomic size trend.
- The larger the difference in electronegativity, the more polar the bond.
  - Negative end toward more electronegative atom.

Electronegativity Scale

Trends in Electronegativity

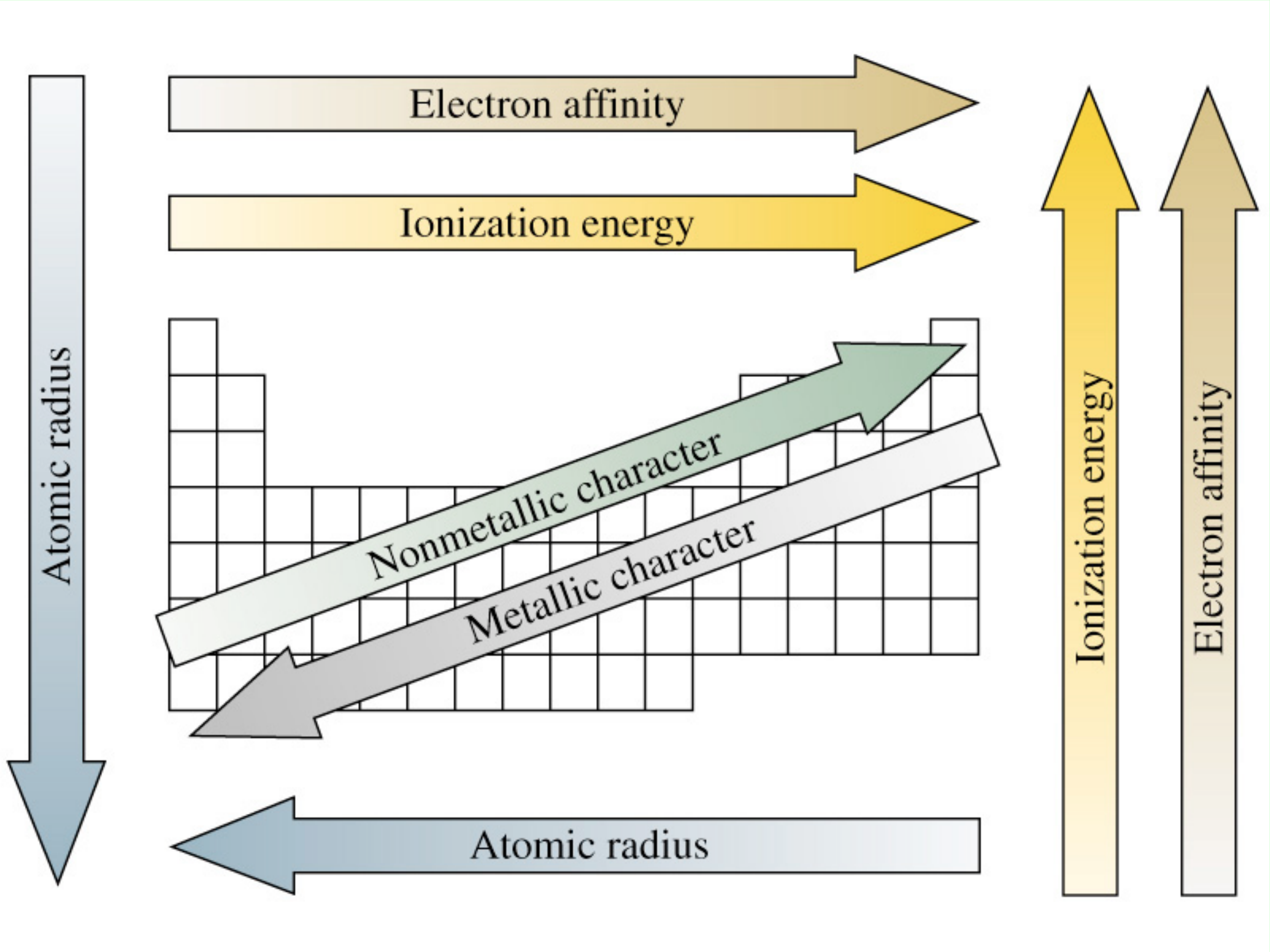


Electronegativity Difference and Bond Type

- If the difference in electronegativity between bonded atoms is 0, the bond is **pure covalent**.
  - Equal sharing
- If the difference in electronegativity between bonded atoms is 0.1 to 0.4, the bond is **nonpolar covalent**.
- If the difference in electronegativity between bonded atoms is 0.5 to 1.9, the bond is **polar covalent**.
- If difference in electronegativity between bonded atoms is larger than or equal to 2.0, the bond is **"100%" ionic**.

Summary of Periodic Trends

In the locker



Bond Polarity

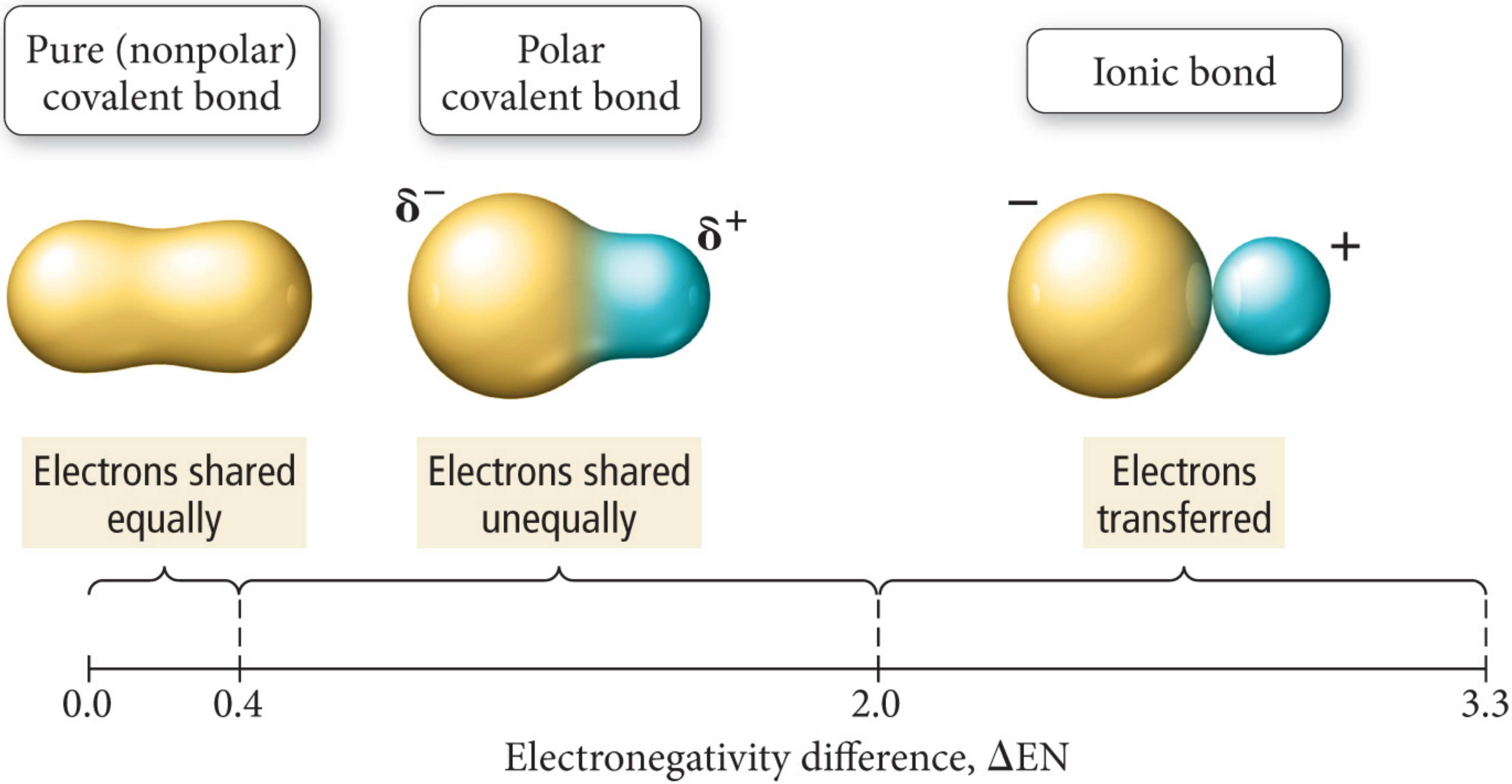
TABLE 9.1 The Effect of Electronegativity Difference on Bond Type

Electronegativity Difference (ΔEN)	Bond Type	Example
Small (0–0.4)	Covalent	Cl_2
Intermediate (0.4–2.0)	Polar covalent	HCl
Large (2.0+)	Ionic	NaCl

Bond Dipole Moments

- **Dipole moment**, μ, is a measure of bond polarity.
  - A dipole is a material with a + and − end.
  - it is directly proportional to the size of the partial charges and **directly** proportional to the distance between them.
    - $\mu = (q)(r)$
    - Not Coulomb's law
    - Measured in Debyes, D
- Generally, the more electrons two atoms share and the larger the atoms are, the larger the dipole moment.

The Continuum of Bond Types



Magnetic Properties of Transition Metal Atoms and 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

Magnetic Properties of Transition Metal Atoms and Ions

- 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