Announcement

- We will be trying out a new classroom over the next couple of weeks.

- **Lecture will be in Welch 2.110 starting next week**

CH 431: INORGANIC CHEMISTRY

Periodic Trends and Simple Bonding Theory

MFT Chapters 2 and 3

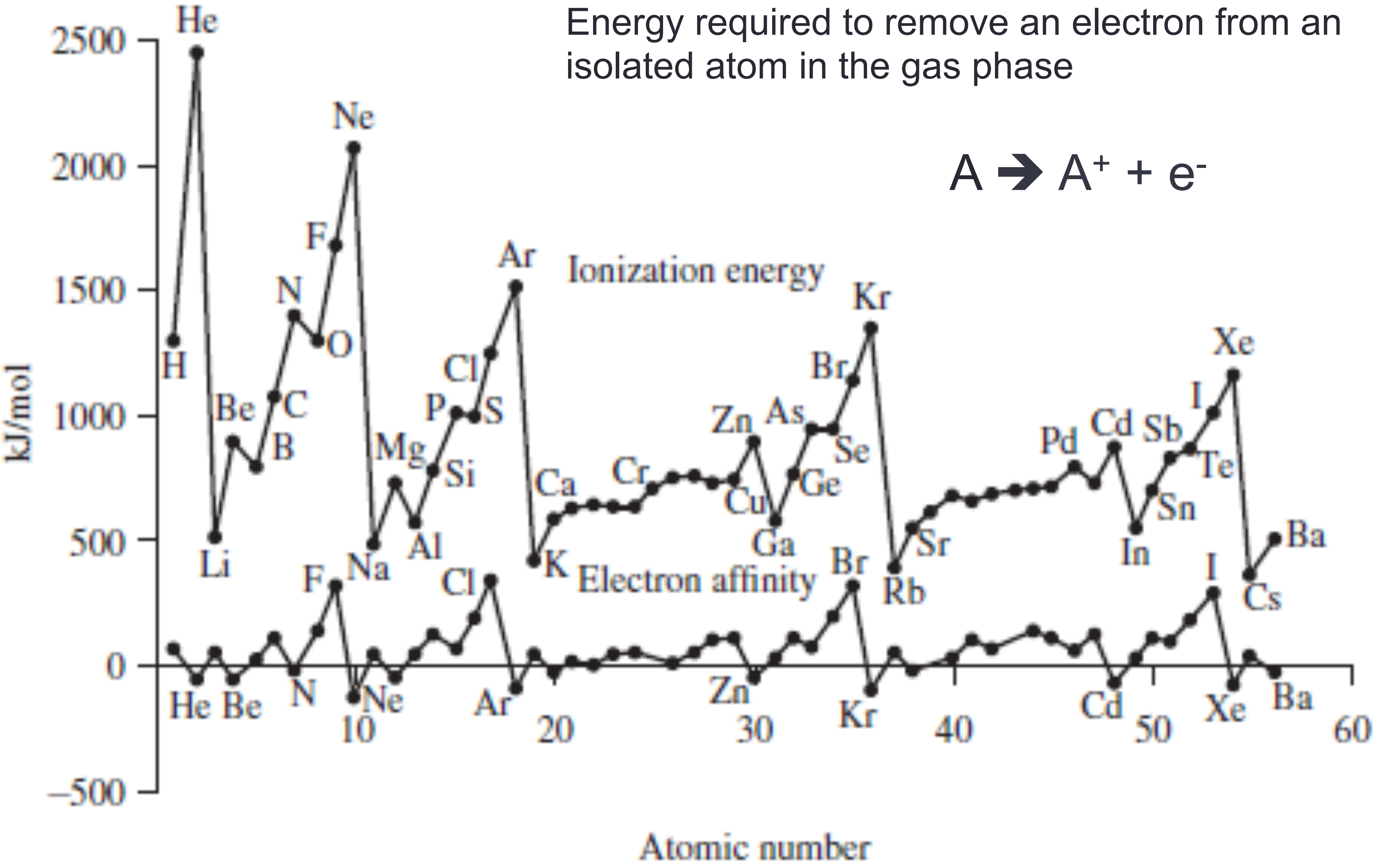
PERIODIC TRENDS

Periodic trends: shielding (Z_{eff})

- In multi-electron atoms, each electron acts as a shield for electrons farther from the nucleus
- This reduces the attraction between the nucleus and more distant electrons
- Inner orbitals shield outer orbitals, electrons in outer orbitals experience Z_{eff} instead of Z

- Z increases across a period, the inner electrons remain constant, so the Z_{eff} gets bigger

Periodic trends: ionization energy



Energy required to remove an electron from an isolated atom in the gas phase

$$A \rightarrow A^{+} + e^{-}$$

Periodic trends: ionization energy

- Generally, across a period the ionization energy increases, due to increased nuclear charge (Z/Z_{eff})
- Examples of breaks in this trend
  - Be to B: switch from s block to p block, 2s slightly shields 2p electrons
  - N to O: N is $2p^3$ with one electron in each p orbital, O is $2p^4$ and has one orbital with two electrons: e-e repulsion makes this electron easier to remove

- Down a group: ionization energy decreases since going to new ‘n’ values (different energy levels) as you go down. This effect is smaller in magnitude than the effect of going across a period.

Periodic trends: Atomic size

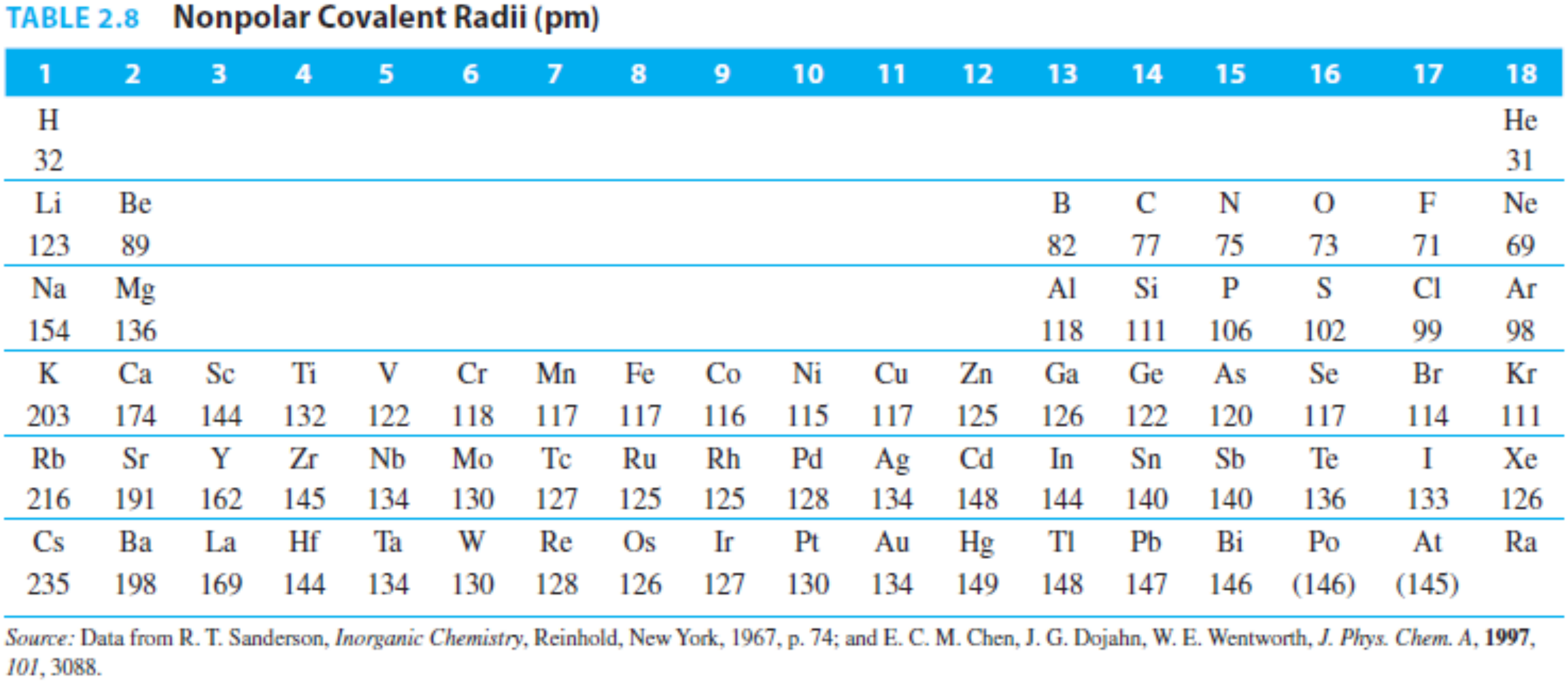


TABLE 2.8 **Nonpolar Covalent Radii (pm)**

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
H																	He
32																	31
Li	Be											B	C	N	O	F	Ne
123	89											82	77	75	73	71	69
Na	Mg											Al	Si	P	S	Cl	Ar
154	136											118	111	106	102	99	98
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
203	174	144	132	122	118	117	117	116	115	117	125	126	122	120	117	114	111
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
216	191	162	145	134	130	127	125	125	128	134	148	144	140	140	136	133	126
Cs	Ba	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Ra
235	198	169	144	134	130	128	126	127	130	134	149	148	147	146	(146)	(145)	

Source: Data from R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, 1967, p. 74; and E. C. M. Chen, J. G. Dojahn, W. E. Wentworth, *J. Phys. Chem. A*, **1997**, *101*, 3088.

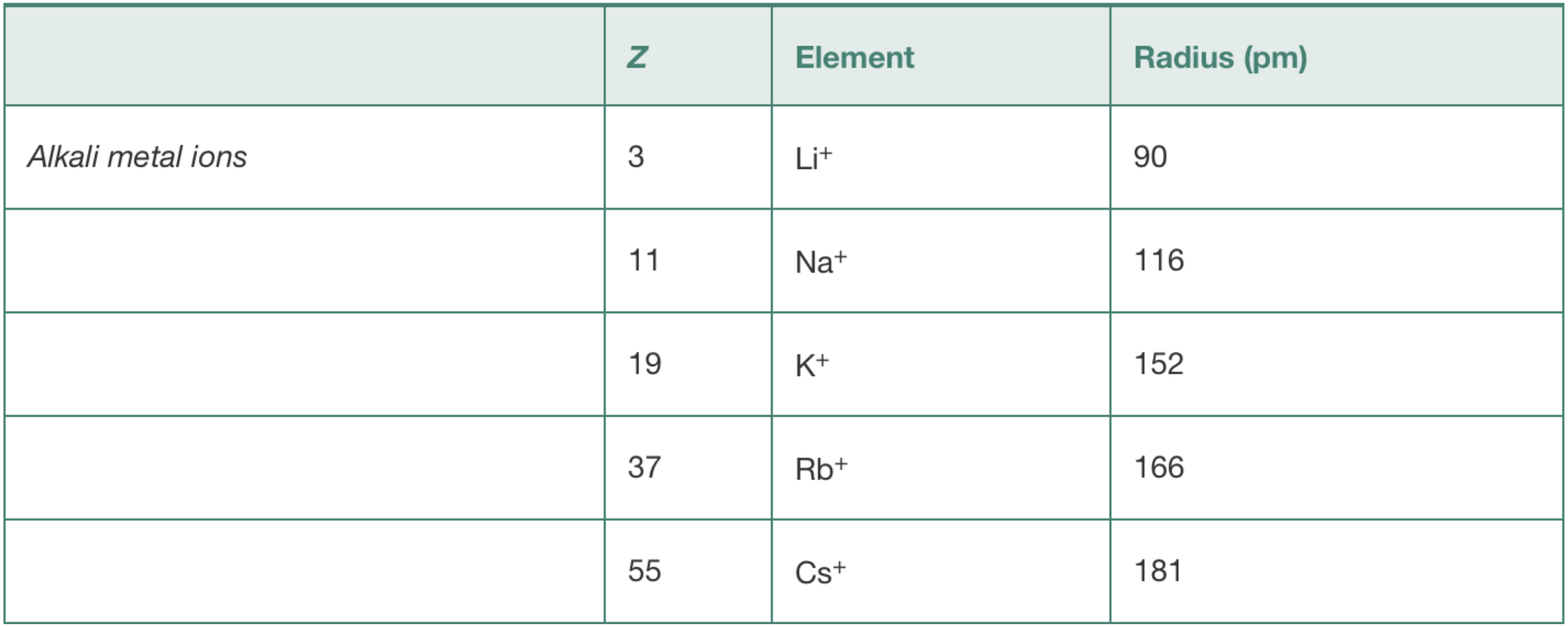
Periodic trends: Atomic size

- As nuclear charge increases (as you go across a periodic table), electrons are pulled towards the nucleus
- At the same time, as nuclear charge increases, so does the number of electrons. More electrons equals more repulsion
- The balance of these two things results in a gradual decrease in atomic size as you go across a period

- Atomic size increases as you go down a group: orbitals of higher energies (‘n’ values) are being occupied

Periodic trends: ionic radius

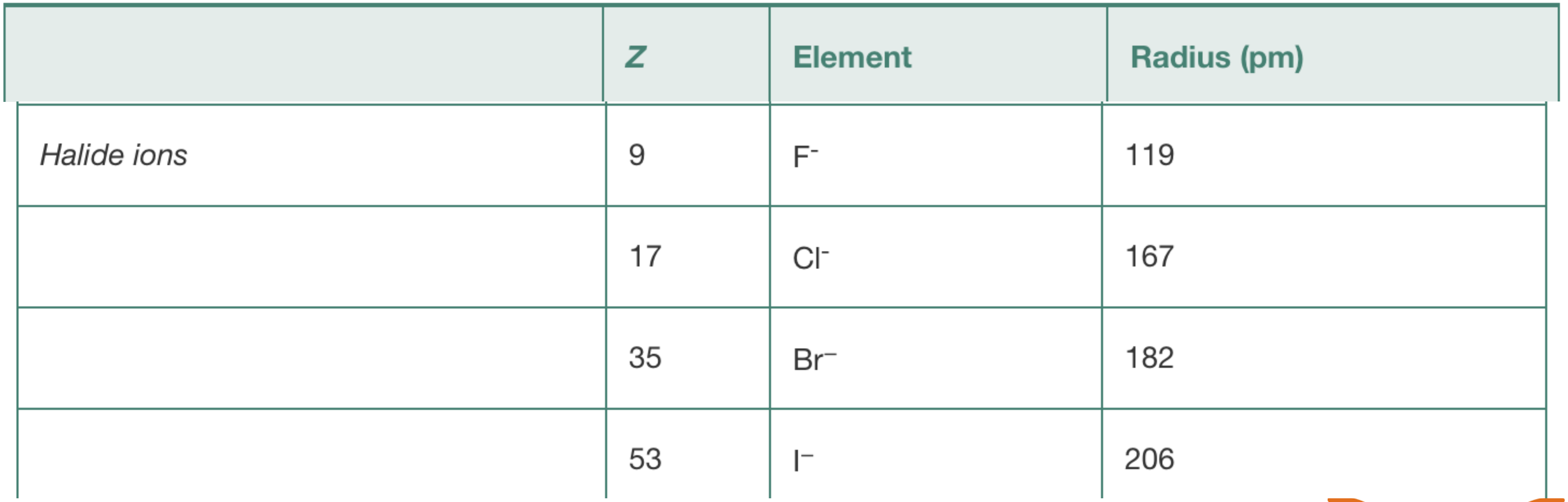
- Ionic radius is more tricky since different elements have different preferred ionic states
- When comparing ions of the same charge, ionic size increases as you go down a group (n gets larger)



	Z	**Element**	**Radius (pm)**
Alkali metal ions	3	Li$^+$	90
	11	Na$^+$	116
	19	K$^+$	152
	37	Rb$^+$	166
	55	Cs$^+$	181

Periodic trends: ionic radius

- Ionic radius is more tricky since different elements have different preferred ionic states
- When comparing ions of the same charge, ionic size increases as you go down a group (n gets larger)



	Z	Element	Radius (pm)
Halide ions	9	F^-	119
	17	Cl^-	167
	35	Br^-	182
	53	I^-	206

Periodic trends: ionic radius

- When comparing ions with the same number of total electrons, generally most positively charge ion is smallest, most negatively charges ion is largest (electron-electron repulsion increases)

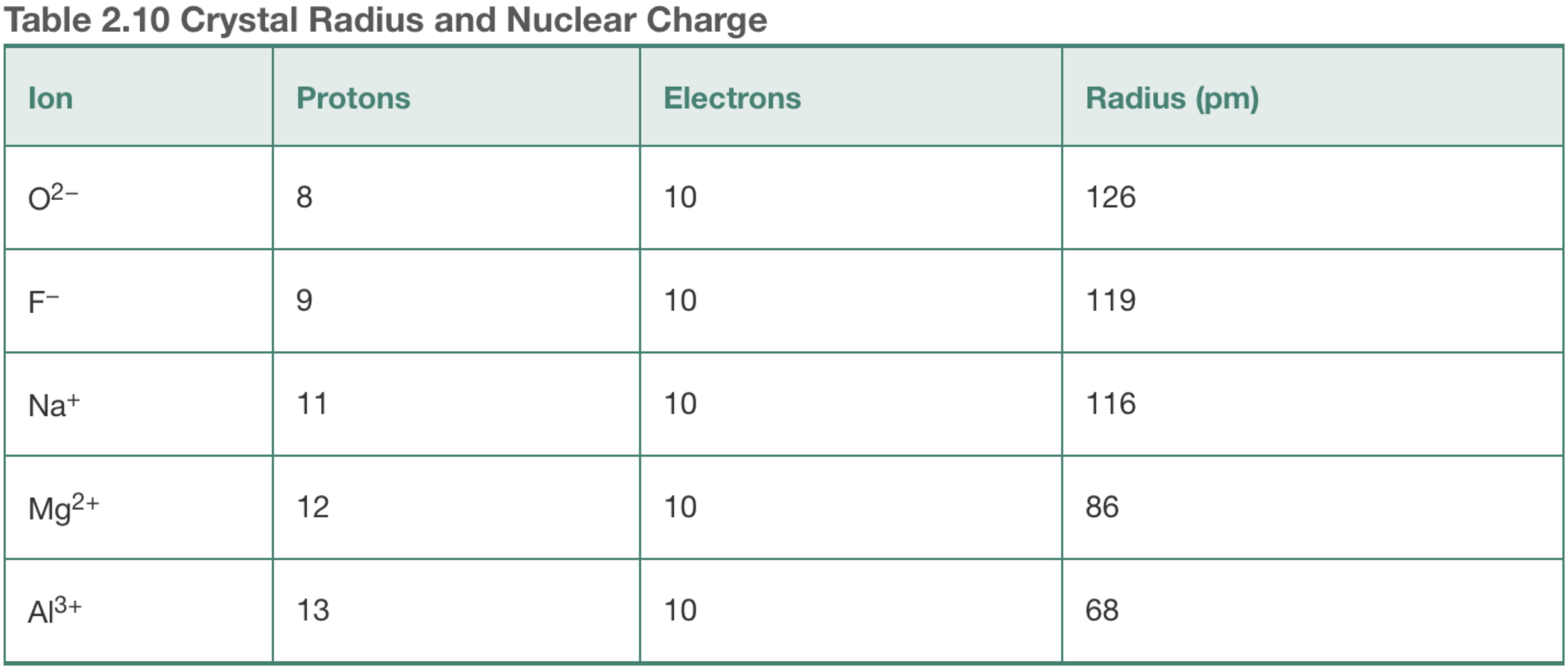


Table 2.10 Crystal Radius and Nuclear Charge

Ion	Protons	Electrons	Radius (pm)
O^{2-}	8	10	126
F^{-}	9	10	119
Na^{+}	11	10	116
Mg^{2+}	12	10	86
Al^{3+}	13	10	68

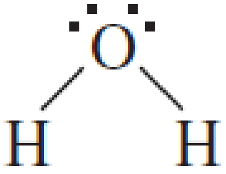
LEWIS DOT STRUCTURES

Lewis dot structures and VSEPR

- These simplified approaches to thinking about bonding and molecular shape allow us to obtain approximate pictures of what molecules look like
- It is ESSENTIAL for you to know how to execute these approaches quickly
- In Chapter 5, we will use Molecular Orbital Theory to better describe the bonding in molecules

Review of Lewis Electron Dot Diagrams

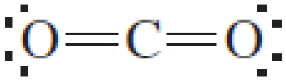
- This is a simplified way of thinking about bonding in molecules, provides a good starting point when we want to figure out the shapes of molecules
- Based on the idea that a filled valence shell is particularly stable
  - Octet rule for p-block elements, $ns^2\ np^6$
  - H: $1s^2$
  - A parallel concept for d-block: 18 electron rule (more details on this later in the course)
- Bonding electron pairs and lone electron pairs contribute to the electron count around an atom



H: 2 e^-s from O-H bond
O: 4 e^-s from 2 O-H bonds
4 e^-s from 2 lone pairs

$H-C\equiv C-H$

H: 2 e^-s from bonding pair
C: 2 e^-s from C-H bond
6 e^-s from $C\underline{=}C$ triple bond

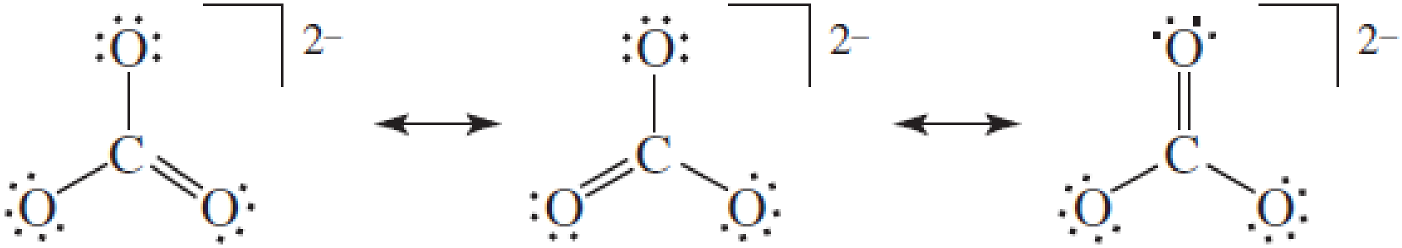


O: 4 e^-s from C=O double bond
4 e^-s from 2 lone pairs
C: 8 e^-s from 2 C=O double bond

Resonance

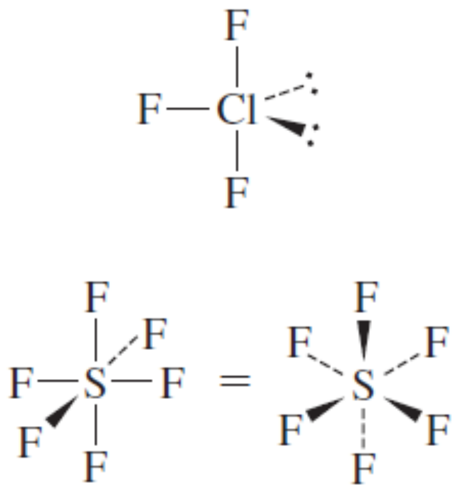
- Resonance structures exist when alternate locations for single and double bonds are possible

- The actual molecule typically has bond lengths that are between a single and a double bond



Higher electron counts

- Some p-block compounds have more electrons that the octet rule allows
- In this case, the number of electrons are increased around the central atom
- This can only be done for elements with n=3 and higher



Formal charge

Formal Charge

$$\text{FC} = \begin{matrix}\text{\# Valence e}^-\\ \text{in Free Atom}\end{matrix} - \begin{matrix}\text{Total \#}\\ \text{Nonbonding e}^-\end{matrix} - \frac{\begin{matrix}\text{Total \#}\\ \text{Bonding e}^-\end{matrix}}{2}$$

- Formal charge is a good tool for assessing Lewis structures, however it is not a measure of actual charge on the atoms

- Favorable configurations:
  - Smaller magnitude formal charges
  - Negative formal charge on more electronegative elements
  - Smaller separation of charges

VSEPR

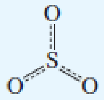
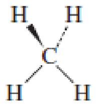
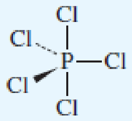
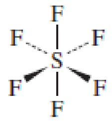
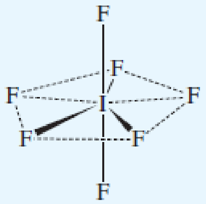
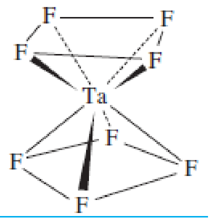
Valence Shell Electron Pair Repulsion

- A way to predict shapes of molecules based on repulsion between electron pairs
- Optimal geometries minimize repulsive energy

- Steps:
- 1) Draw Lewis dot structure
- 2) Determine number of electron pairs around central atom
- 3) Choose arrangement such that lone pair repulsion is minimized

You should know the geometries associated with different steric numbers and bond angles for idealized systems (Table 3.8)

The systems in this table have the same groups surrounding the central atom

Steric Number	Geometry	Examples	Calculated Bond Angles	
2	Linear	CO_2	180°	$O{=}C{=}O$
3	Trigonal (triangular)	SO_3	120°	
4	Tetrahedral	CH_4	109.5°	
5	Trigonal bipyramidal	PCl_5	120°, 90°	
6	Octahedral	SF_6	90°	
7	Pentagonal bipyramidal	IF_7	72°, 90°	
8	Square antiprismatic	$[TaF_8]^{3-}$	70.5°, 99.6°, 109.5°	

Lone Pair Repulsion in VSEPR

- Many molecules have a mixture of bonding electron pairs and lone electron pairs.

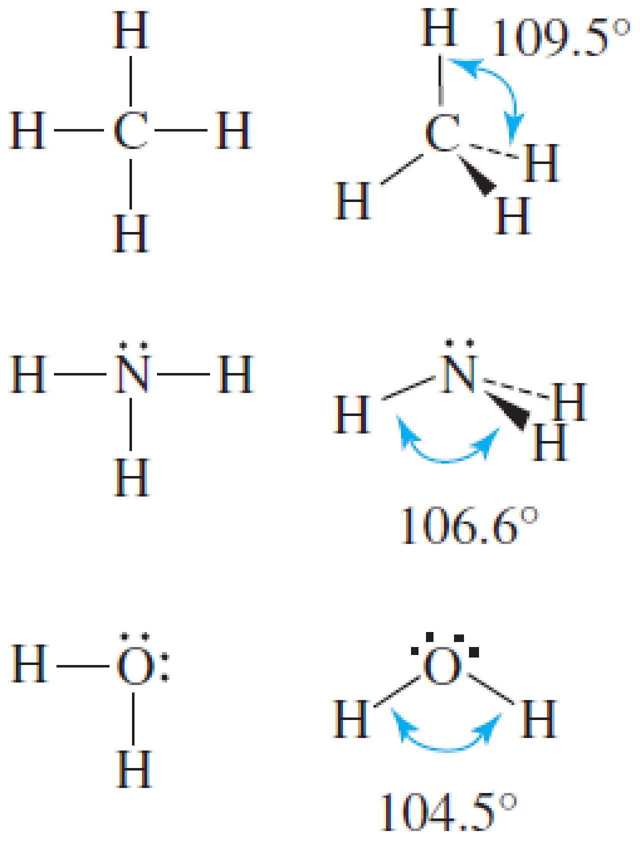
- VSEPR predicts that electron-pair repulsions involving lone pairs (lp) are stronger than those involving bonding pairs (bp)
  - lp-lp repulsions > lp-bp repulsions > bp-bp repulsions

Lone Pair Repulsion in VSEPR

Steric number 4:

- Methane vs ammonia vs water
- All generally have a tetrahedral shape if you consider the geometry of all electron pairs around the central atom, however the lone pairs in ammonia and water cause distortion of the bond angles

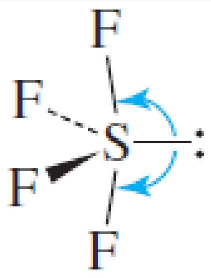
- You are not expected to know the specific angles for NH_3 and H_2O, however it is important for you to know the trend



Lone Pair Repulsion in VSEPR

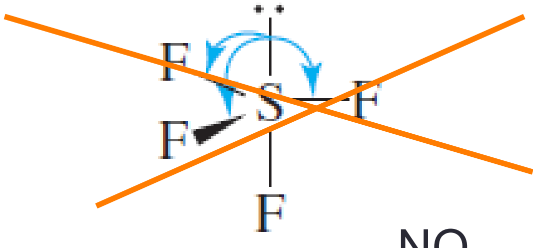
Steric number 5:

- In trigonal bipyramidal geometry, electron pairs can be either equatorial of axial
- Example: SF_4
- Four bonding pairs, one lone pair
- Best structure puts lone pair as far away from other pairs as possible, minimizes 90° interactions with bonding pairs



YES

Equatorial lone pair
(observed structure)



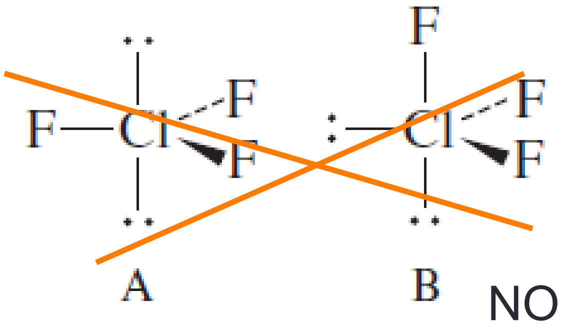
NO

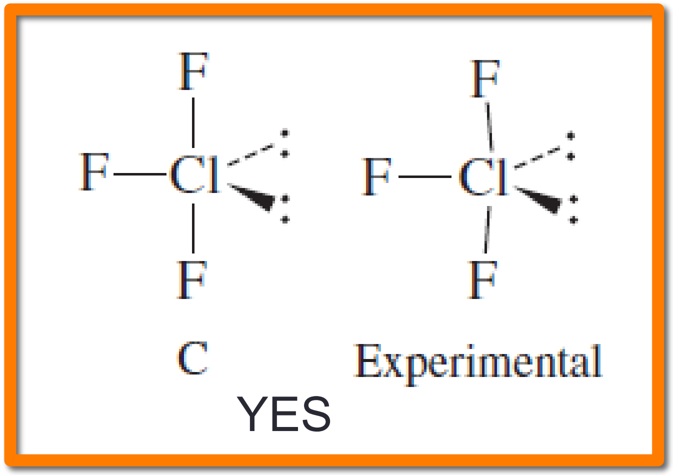
Axial lone pair

Lone Pair Repulsion in VSEPR

Steric number 5:

- Example: ClF_3
- Three bonding pairs, two lone pairs
- Best structure puts lone pair as far away from other pairs as possible, minimizes 90° interactions with bonding pairs





Multiple bonds in VSEPR

- Double and triple bonds are considered to be more repulsive than single bonds according the VSEPR

- Much like lone pairs, these occupy more space than single bonds

- Lone pairs have a greater influence than multiple bonds