Unit 2
Atomic Structure and Properties
&
Chemical Bonding

Slide Color Codes

All Lectures

- Required
- Required
- OK to Skip

Section Only

- Useful
- Not Examable

Blueprint question

How can you predict engine part failure BEFORE it happens?

http://www.spectro-oil.com/laboratory-services-aviation.html
http://news.commercialaircraft.bombardier.com/wp-content/gallery/engine-run/right_engine.jpg

Learning Objectives

After mastering this unit you will be able to:

- Define the terms valence and core electrons
- Determine the number of valence electrons and core electrons based on electron configuration for atoms and ions
- Define, in words or using equations, effective nuclear charge (Z_{eff}), atomic and ionic radius, ionization energy, and electron affinity.
- Rank elements and ions according to their Z_{eff}, atomic size, ionization energy, and electron affinity.
- Rationalize the periodic trends of radii, relative ionization energies and electron affinities of atoms and ions based on nuclear charge and/or electron configurations.

Learning Objectives (continued)

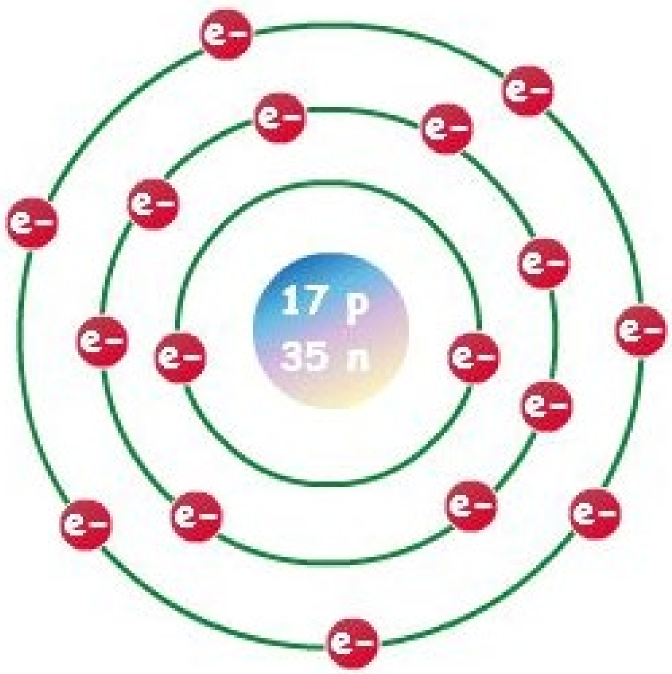
- Describe the nature of ionic and covalent bonds.
- Define electronegativity and describe how electro-negativity varies with position in the periodic table.
- Predict the nature of a chemical bond (ionic/covalent, polar/nonpolar) and justify your prediction by comparing the relative electronegativities of the atoms involved.
- Predict lattice energy trends in ionic solids & justify your predictions.

Classical vs Quantum Mechanics

- Newton's second law

$$F = ma = m\frac{d^2x}{dt^2}$$

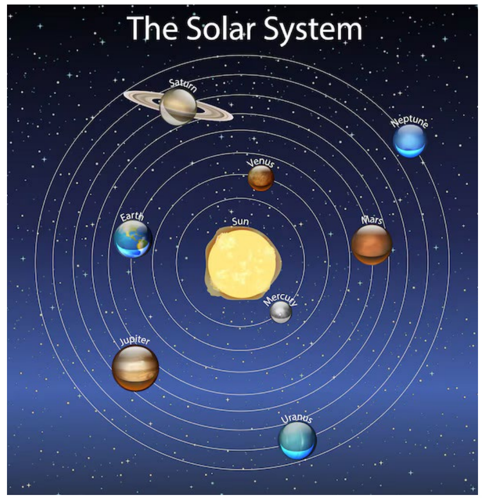
$$F = k\frac{q_1 \cdot q_2}{r^2}$$



Clicker Question

Which of the following represents the best analogy for the structure of an atom?

- a) Solar system
- b) Cotton ball
- c) Billiard Ball
- d) Onion
- e) Dumbbell



Wave properties of Electrons

Salient Features of Quantum Mechanics

- Small objects, like electrons, behave as both particles and waves which means they can interfere, diffract and spread. Orbitals give the probability for finding electrons at particular points in space.

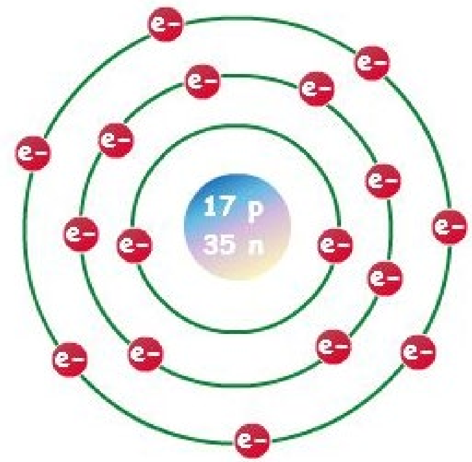
- Quantum mechanics is the theory explaining why energies and angular momenta of atoms and molecules are quantized, that is only have certain discrete values.

Classical vs Quantum Mechanics

- Newton's second law

$$F = ma = m\frac{d^2x}{dt^2}$$

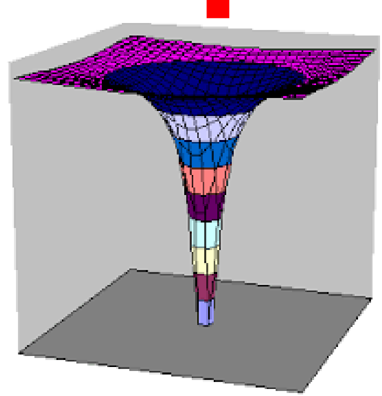
$$F = k\frac{q_1 \cdot q_2}{r^2}$$

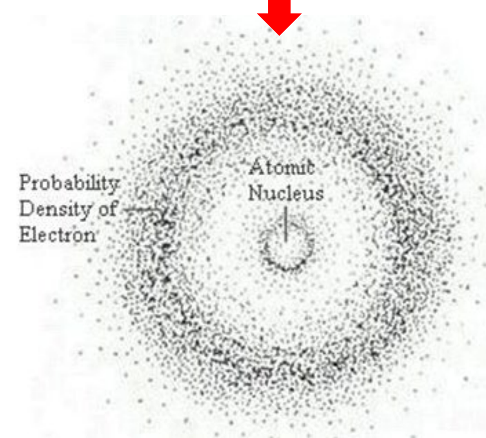


- Schrodinger Equation

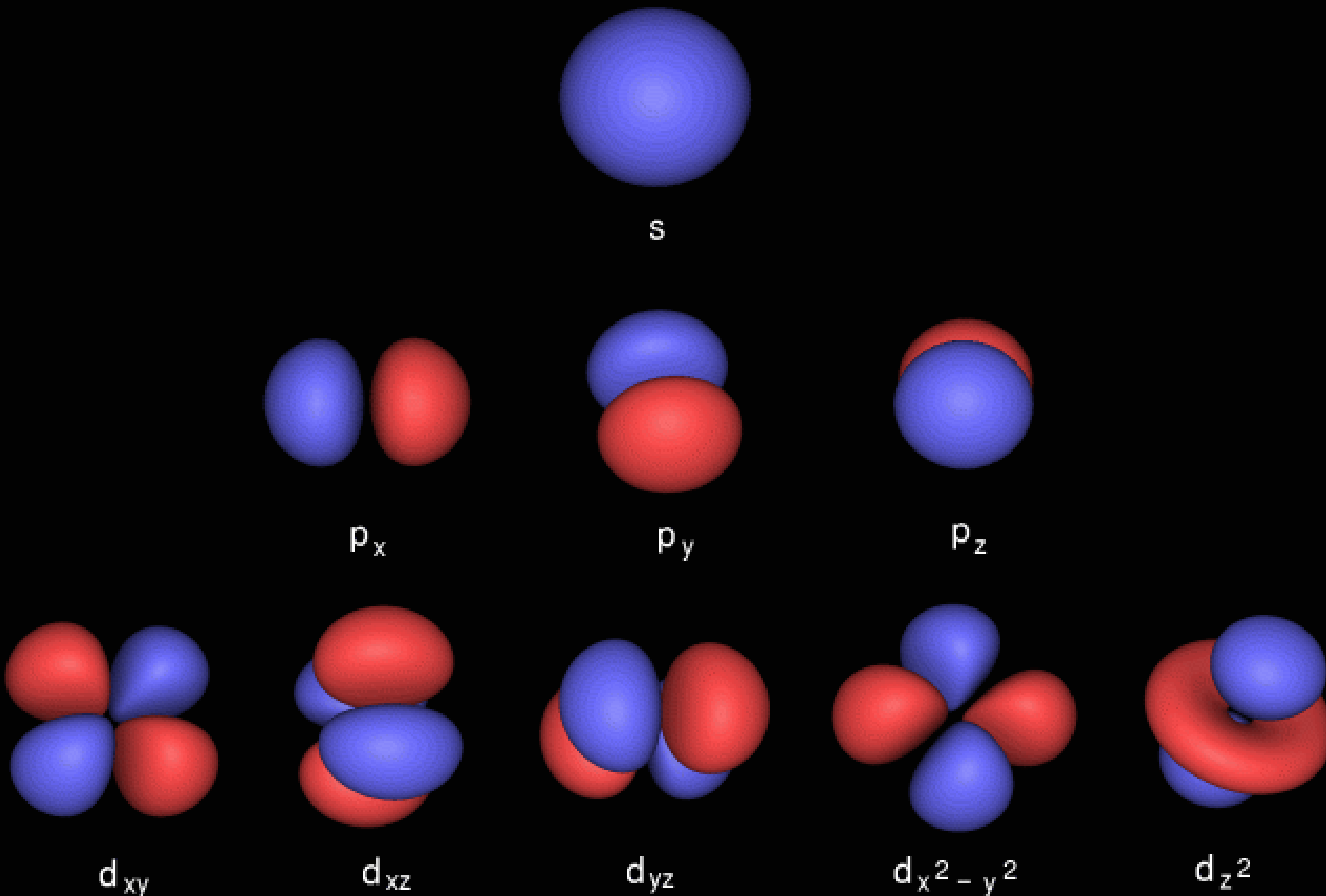
$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right]+U(x,y,z)\Psi(x,y,z)=E\Psi(x,y,z)$$

$$U = k\frac{q_1 \cdot q_2}{r}$$



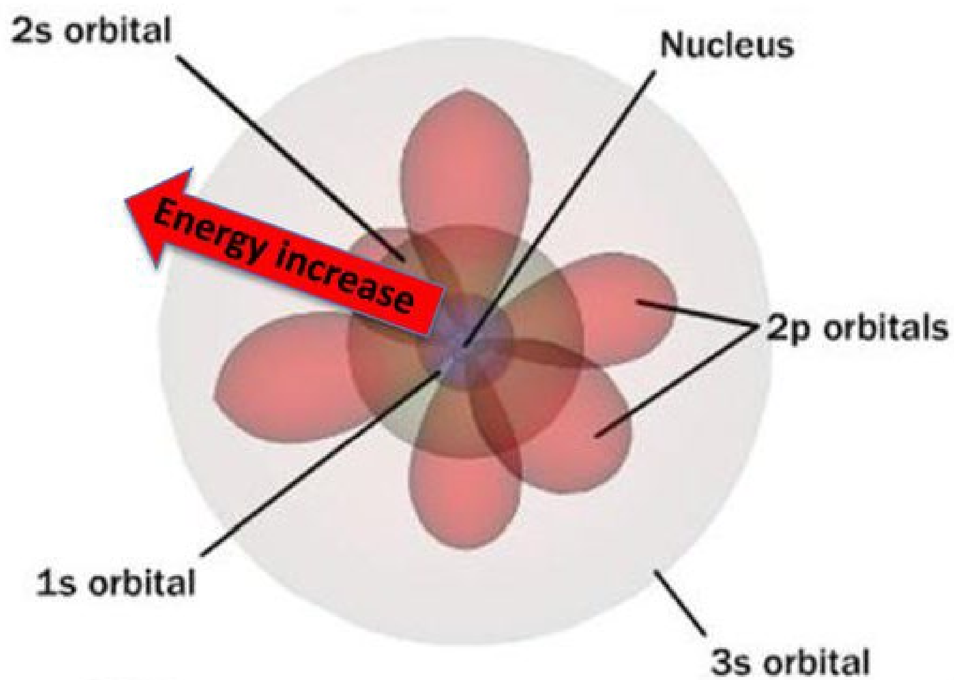


Hydrogenic Orbitals

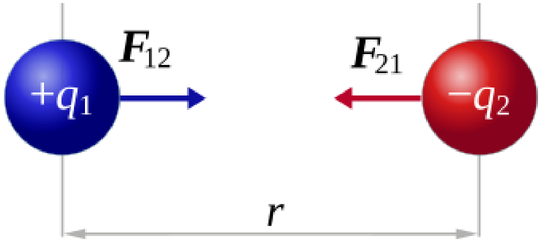


Shell Structure of Atoms

Orbitals become larger as the energy level increases



Coulomb's law



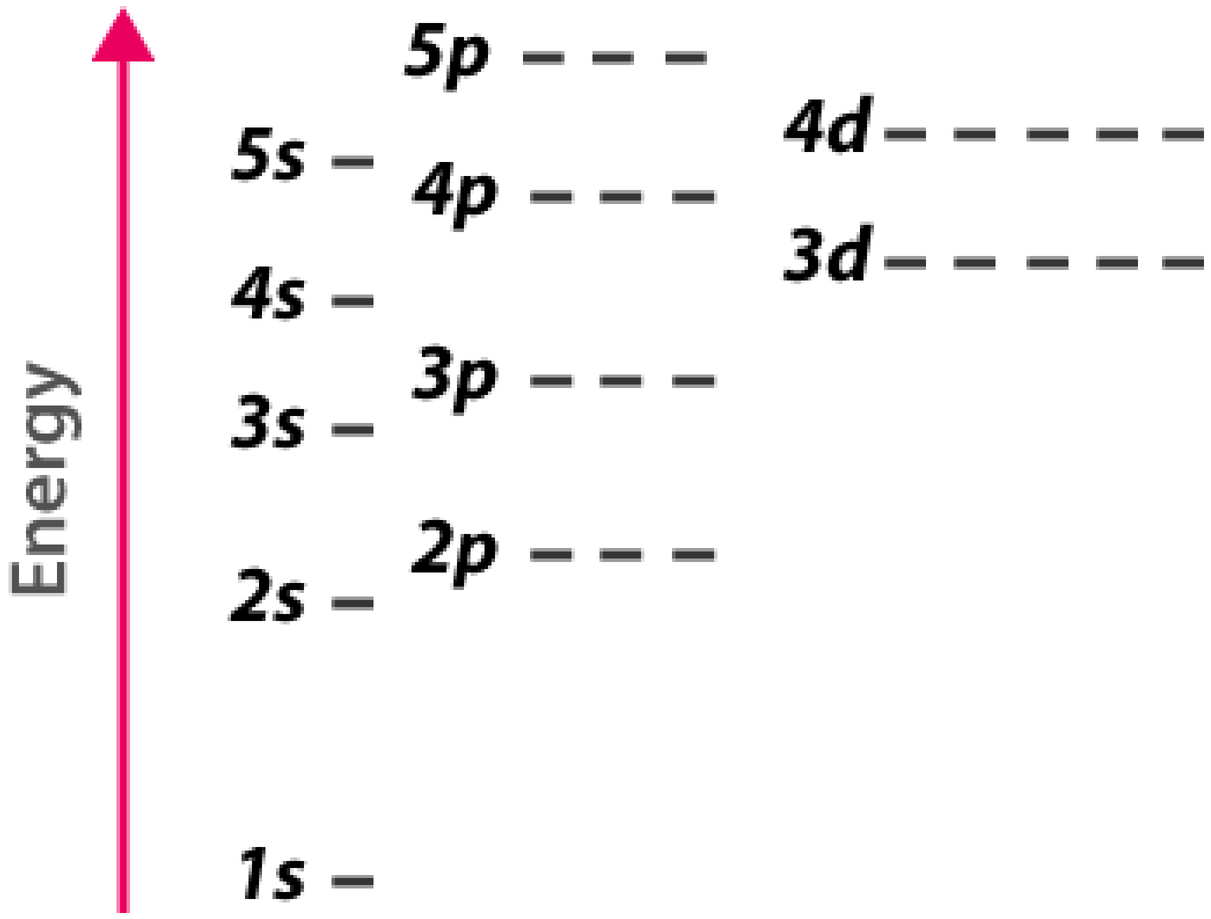
$$\left|\boldsymbol{F}_{12}\right| = \left|\boldsymbol{F}_{21}\right| = k_e \frac{|q_1 \times q_2|}{r^2}$$

- **Electrons filling order : 1s, 2s 2p, 3s**
- **Orbitals** arranged in order of **increasing energy: 1s, 2s 2p, 3s**
- **Orbitals** arranged in **increasing size: (smallest) 1s <2s <2p < 3s (largest)**

Electronic Structure

- Electrons have negative charge but are also tiny magnets. Spin is our way of describing the orientation of the poles of these magnets ("spin up ↑" or "spin down ↓").
- The Pauli Principle states a maximum of 2 electrons can be assigned to any one orbital, and the electrons must have opposite spins (↑↓).
- Orbitals are arranged in shells, labelled by n, and sub-shells. Each shell contains only certain orbitals. Starting with the lowest shell, n=1, electrons are assigned to s, p, d orbitals until they are all accounted for. Note: orbitals get bigger as n increases (a 2s orbital is bigger than a 1s orbital) thus forming the shell structure of atoms.

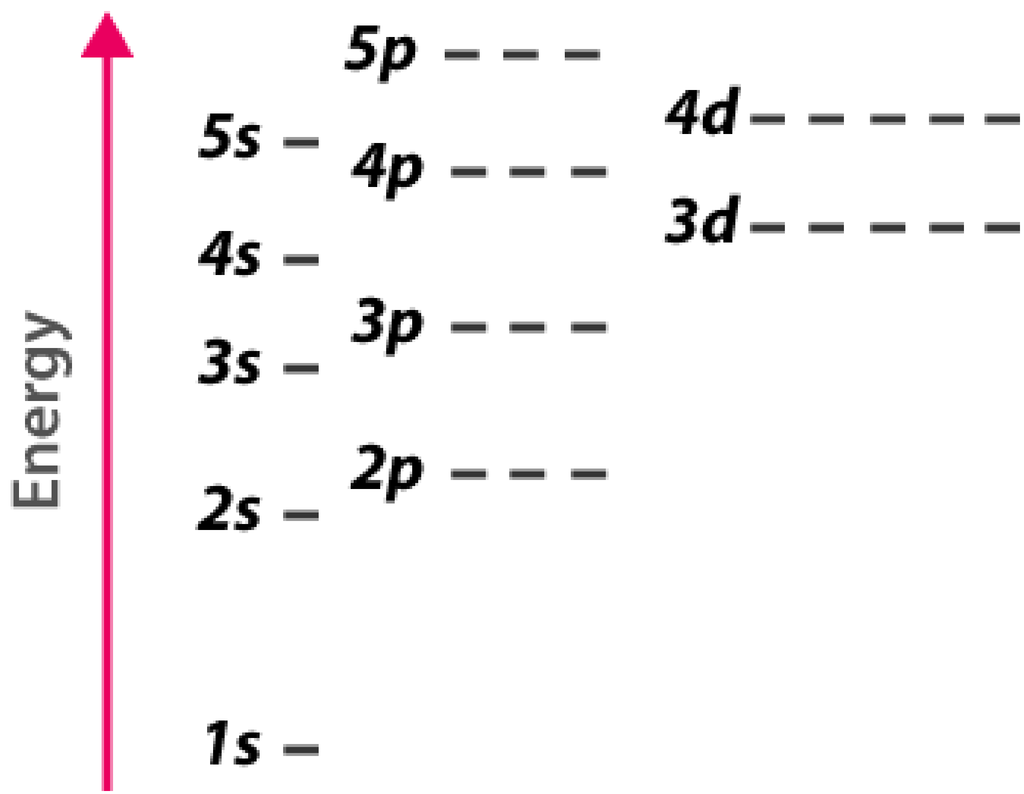
Energy of a Hydrogen Atom



Maximum Number of Electrons

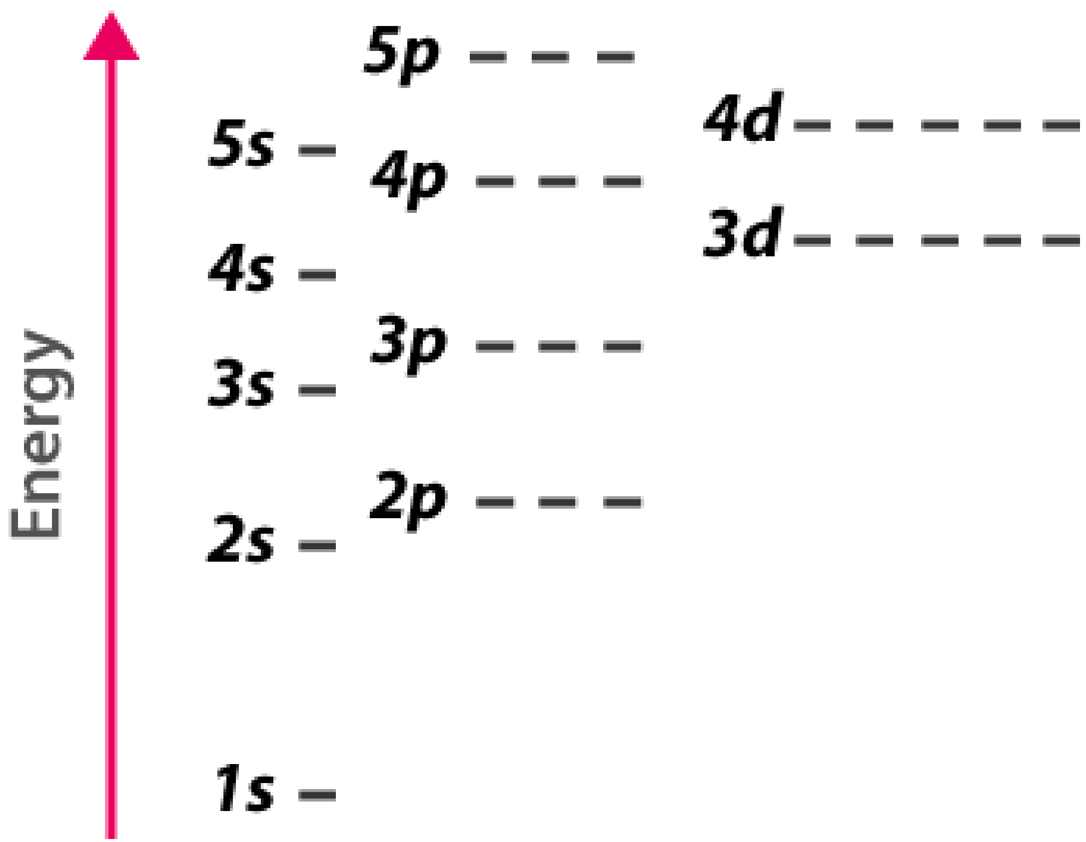
- The following table lists the first four types of subshells and the maximum number of electrons in each type of subshell:

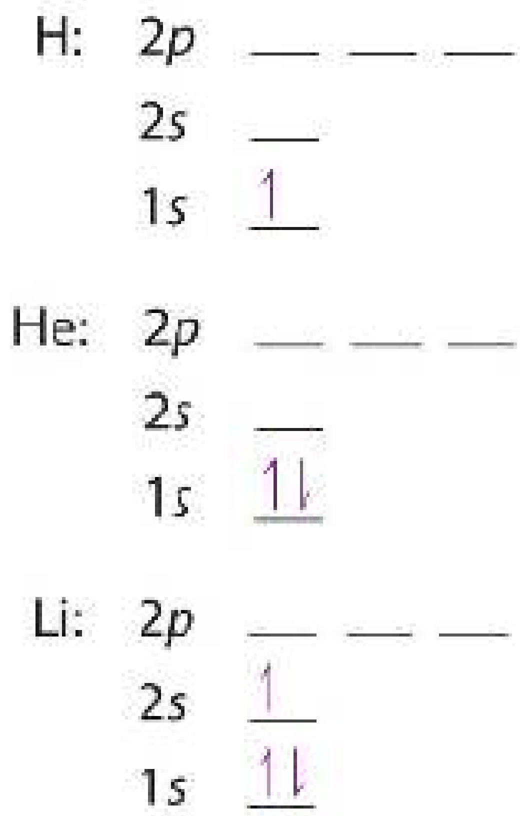
Subshell	$\#e^-$
s	2
p	6
d	10
f	14



The Aufbau (Construction) Principle

– electrons fill atomic orbitals starting <u>from the lowest available energy level</u> and then move to higher energy levels

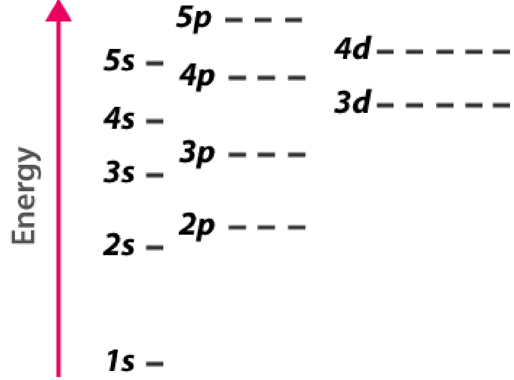


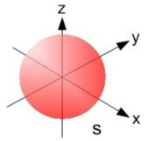


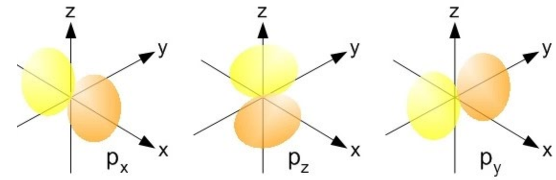
Shells and subshells

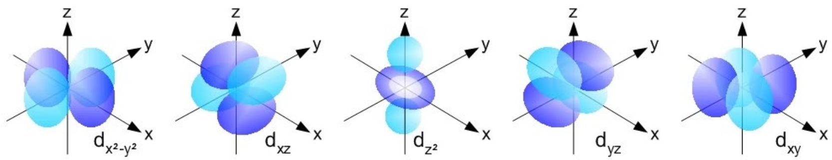
Shell (n)	Sub-shells	Max. # e^- in subshells	
1	s	2	$2(1)^2 = 2$
2	s, p	$2 + 6 = 8$	$2(2)^2 = 8$
3	s, p, d	$2 + 6 + 10 = 18$	$2(3)^2 = 18$
4	s, p, d, f	$2 + 6 + 10 + 14 = 32$	$2(4)^2 = 32$

Fill in Electrons



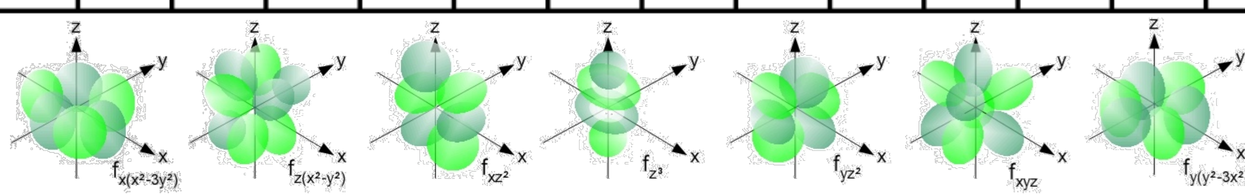






1																	2
1	2											3	4	5	6	7	8
1	2											3	4	5	6	7	8
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	2	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
1	2	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32

3	4	5	6	7	8	9	10	11	12	13	14	15	16
3	4	5	6	7	8	9	10	11	12	13	14	15	16



The Aufbau Principle

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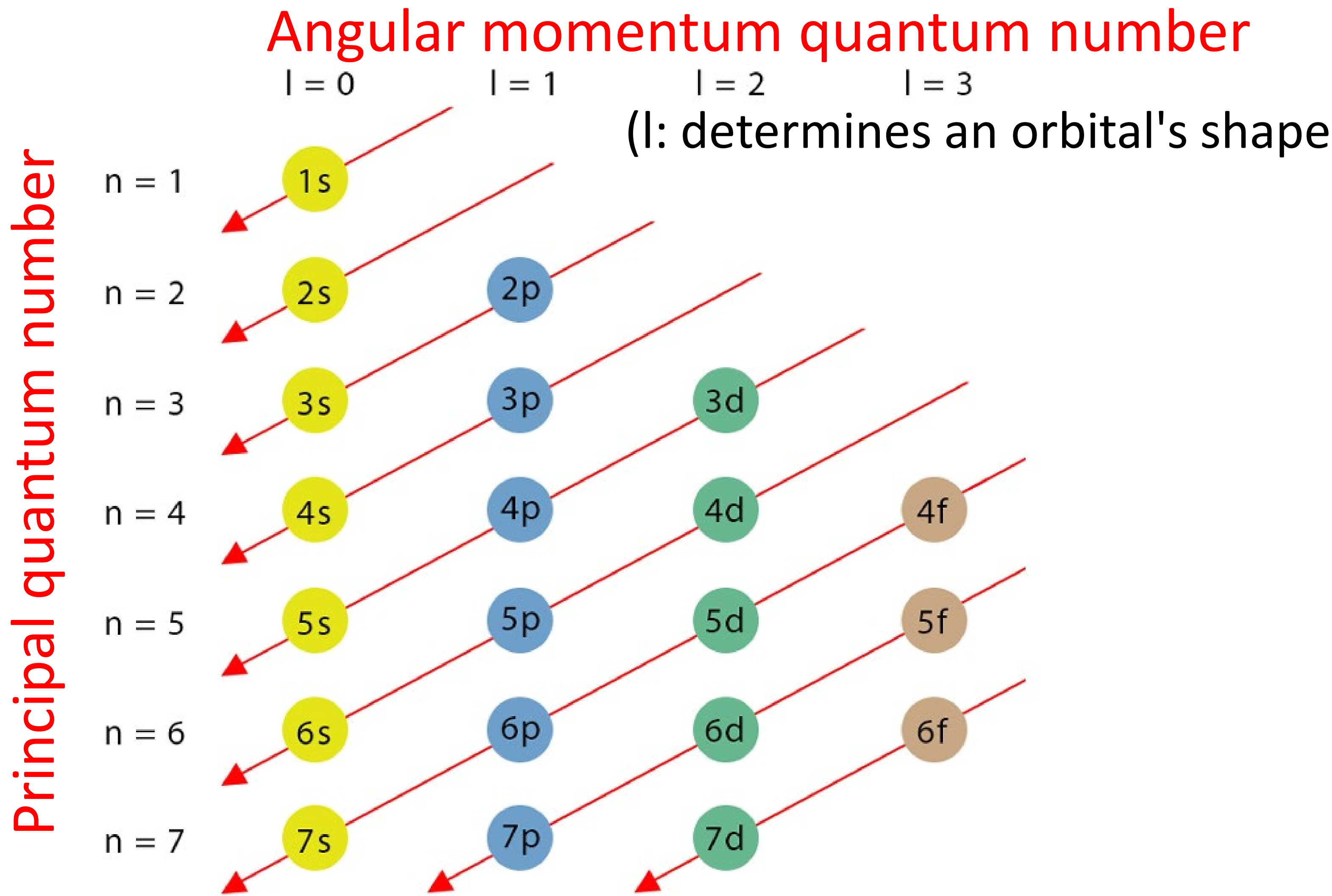
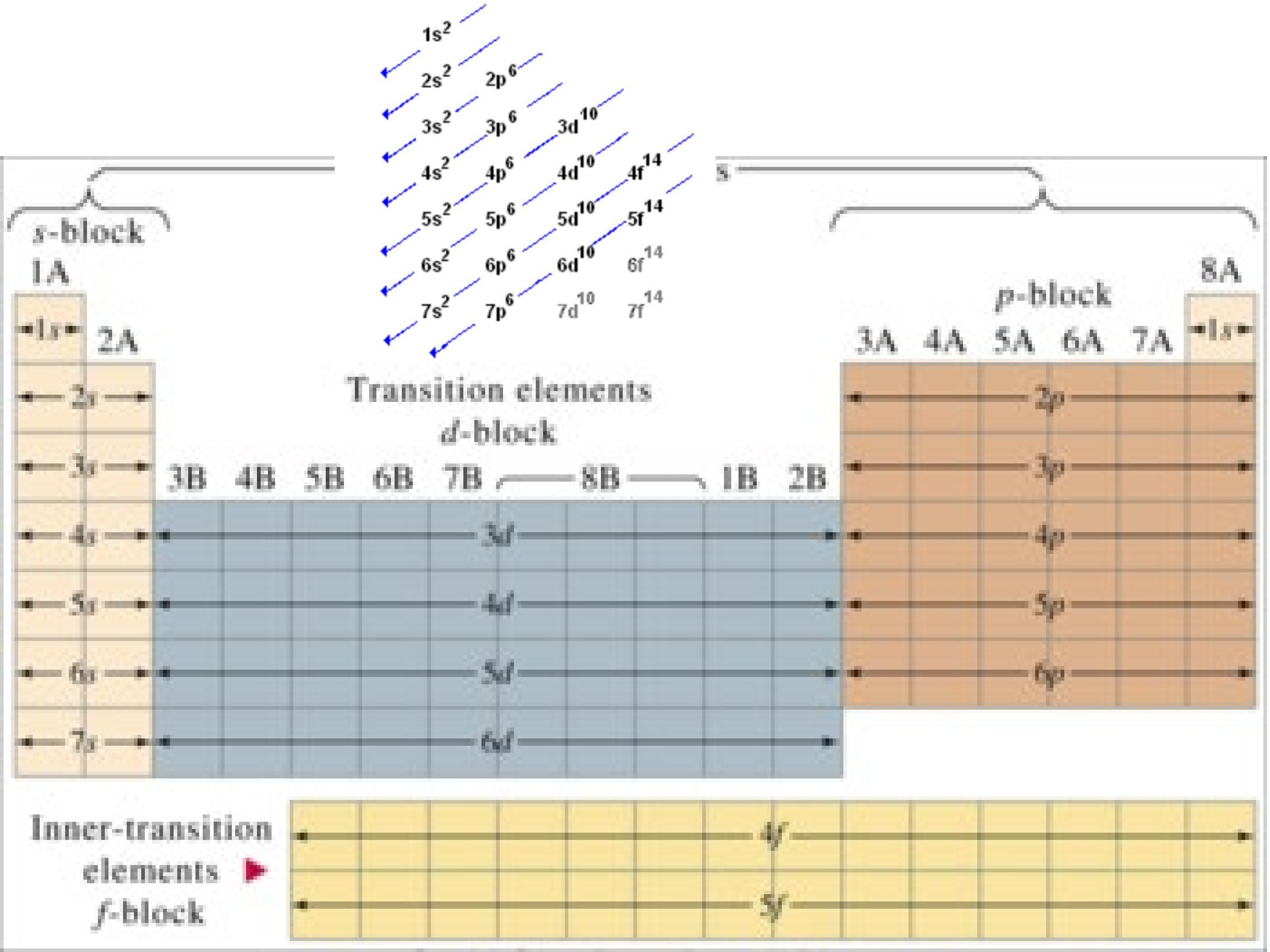


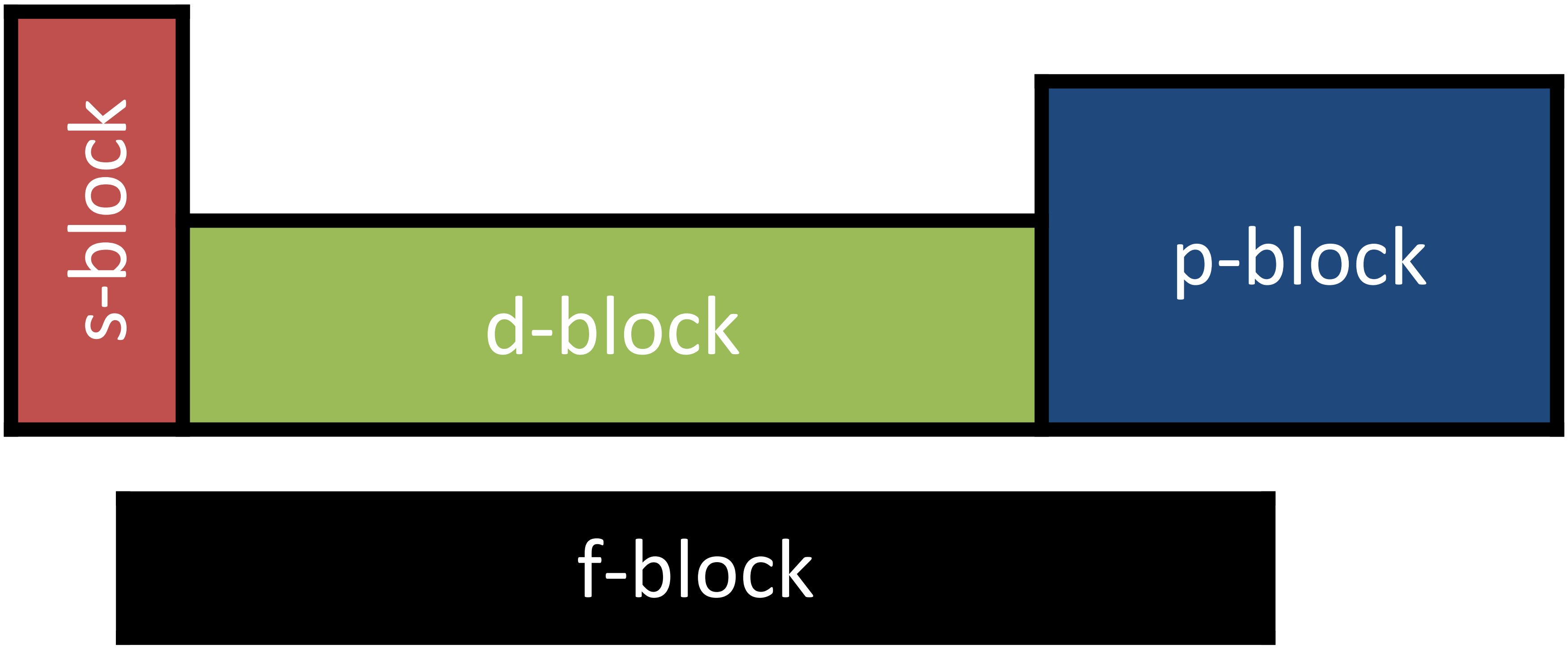


1s2
2s2 2p6
3s2 3p6 3d10
4s2 4p6 4d10 4f14
5s2 5p6 5d10 5f14
6s2 6p6 6d10 6f14
7s2 7p6 7d10 7f14
s-block
1A
2A
1s
2s
3s
4s
5s
6s
7s
Transition elements
d-block
3B 4B 5B 6B 7B 8B 1B 2B
3d
4d
5d
6d
p-block
8A
3A 4A 5A 6A 7A
2p
3p
4p
5p
6p
Inner-transition elements
f-block
4f
5f

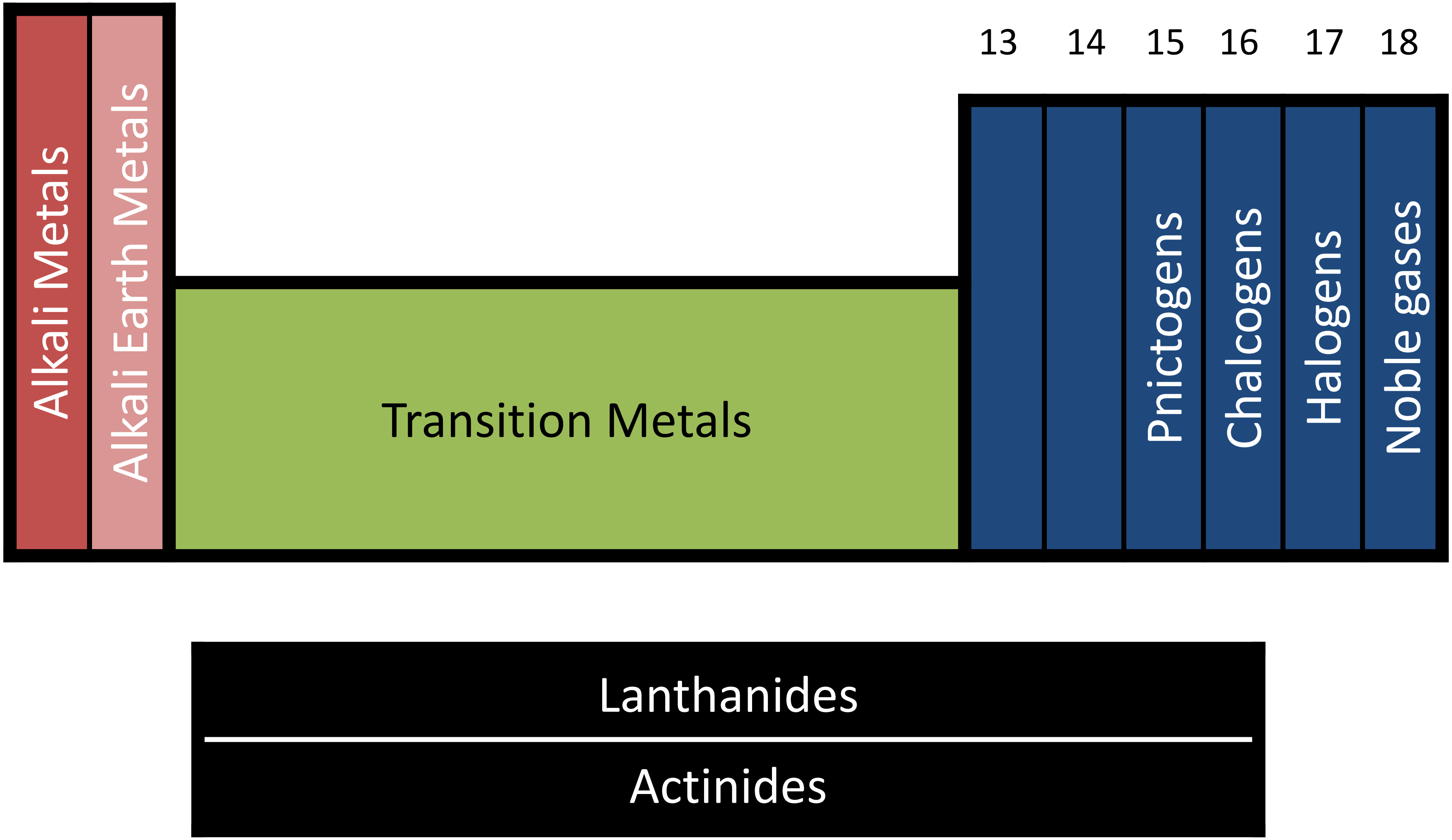
The Periodic Table

Columns in the periodic table are called groups.

Rows in the periodic table are called periods.

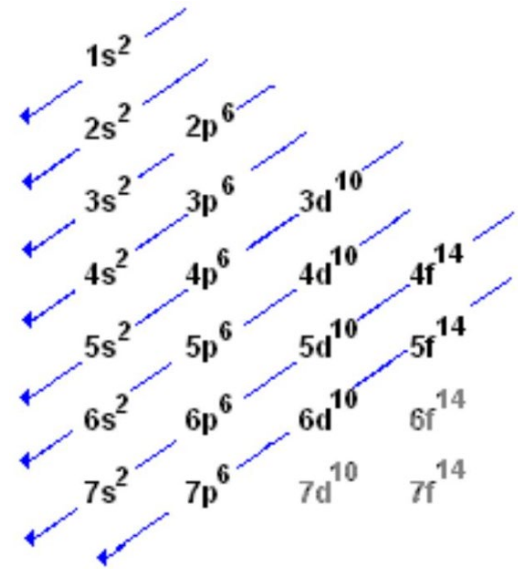


The Periodic Table



Worksheet Question #2

Write the electron configurations for the following chemical species:



a) P : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

b) S^{2-}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

c) Se: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

d) Mg^+: $1s^2\ 2s^2\ 2p^6\ 3s^1$

e) In: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^1$
or <u>condensed form</u> [Kr] $5s^2\ 4d^{10}\ 5p^1$

Condensed Form

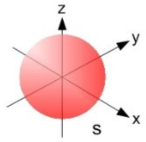
- Locate the element: on the periodic table.
- Identify the preceding noble gas: from the periodic table.
- Place the symbol of that noble gas: in square brackets.
- Add the remaining electrons: in the order of their energy levels (s, p, d, f).
- Ex:

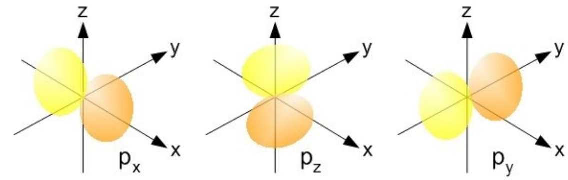
Na: $1s^2 2s^2 2p^6 3s^1$ or [Ne]$3s^1$

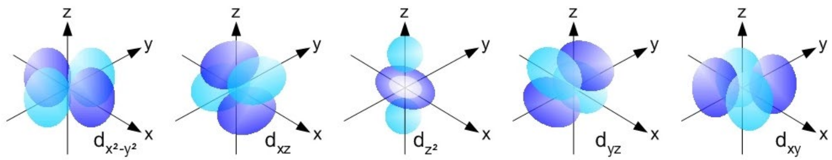
K: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$ or [Ar]$4s^1$

Br: [Ar] $4s^2\ 3d^{10}\ 4p^5$

Fill in electrons

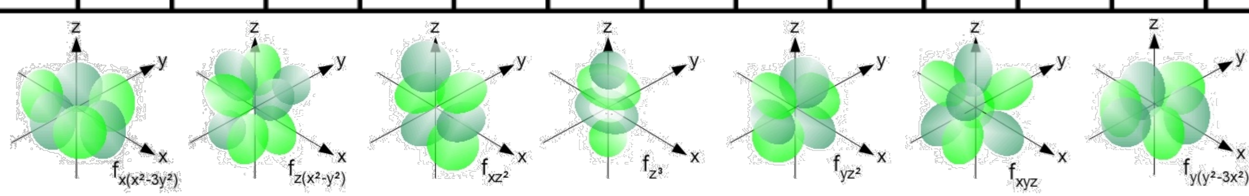






	1																	2
[He]	1	2											3	4	5	6	7	8
[Ne]	1	2											3	4	5	6	7	8
[Ar]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
[Kr]	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
[Xe]	1	2	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32
[Rn]	1	2	17	18	19	20	21	22	23	24	25	26	27	28	29	30	31	32

3	4	5	6	7	8	9	10	11	12	13	14	15	16
3	4	5	6	7	8	9	10	11	12	13	14	15	16



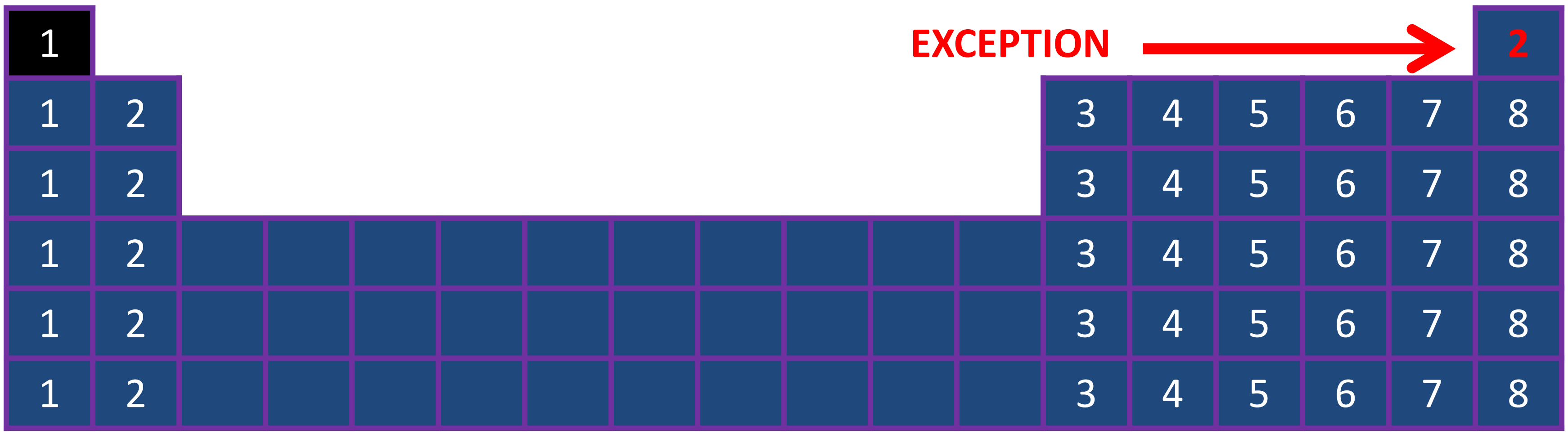
Valence Electrons

For elements in the s- and p-blocks only

The electrons occupying the *s* and *p* subshells with the largest n (for the neutral element) are called valence electrons, and the collection of occupied subshells is called the valence shell.

- Electrons which aren't valence electrons are called core electrons.
- In solids, valence orbitals on atoms overlap to form valence bands extending throughout the material.
- Valence electrons are fundamental to chemistry because they are involved in the formation of bonds. Core electrons are not involved in chemical bonding.

Valence electrons for neutral elements



Clicker Question

- Which of the following species has six valence electrons?

a) S^{2-}

b) B

c) Ge^{2-}

d) C

e) Ar^{+}

Group

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	2											3	4	5	6	7	8
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.99	12 Mg 24.305											13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.064	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.9	23 V 50.941	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.7	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.8
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.22	41 Nb 92.906	42 Mo 95.94	43 Tc "(98)"	44 Ru 101.07	45 Rh 102.9	46 Pd 106.4	47 Ag 107.87	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.6	53 I 126.9	54 Xe 131.3
55 Cs 132.9	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 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po "(209)"	85 At "(210)'	86 Rn "(222)"
87 Fr 223	88 Ra 226.03	89 Ac# 227.03	104 Rf	105 Db {261}	106 Sg	107 Bh	108 Hs	109 Mt									
		*	58 Ce 140.12	59 Pr 140.91	60 Nd 144.24	61 Pm 145	62 Sm 150.4	63 Eu 151.96	64 Gd 157.25	65 Tb 158.92	66 Dy 162.5	67 Ho 164.93	68 Er 167.26	69 Tm 168.93	70 Yb 173.04	71 Lu 174.97	
		#	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260	

Clicker Question

How many valence electrons does Li have?

a) 0

b) 1

c) 2

d) 8

e) 4

Group

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
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55 Cs 132.9	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 192.22	78 Pt 195.09	79 Au 196.97	80 Hg 200.59	81 Tl 204.37	82 Pb 207.2	83 Bi 208.98	84 Po "(209)"	85 At "(210)'	86 Rn "(222)"
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		#	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260	

Clicker Question

How many valence electrons does Li^+ have?

a) 0
b) 1
c) 2
d) 8
e) 4

Clicker Question

How many valence electrons does O^{2-} have?

a) 0

b) 1

c) 2

d) 8

e) 4

Group

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	6 16	17	18
1 H 1.008																	2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.811	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
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		#	90 Th 232.04	91 Pa 231.04	92 U 238.03	93 Np 237.05	94 Pu 244	95 Am 243	96 Cm 247	97 Bk 247	98 Cf 251	99 Es 252	100 Fm 257	101 Md 258	102 No 259	103 Lr 260	

Exercises

1. For each of the following species, determine the number of valence electrons.

(a) P (5)

(b) Cl^{-} (8)

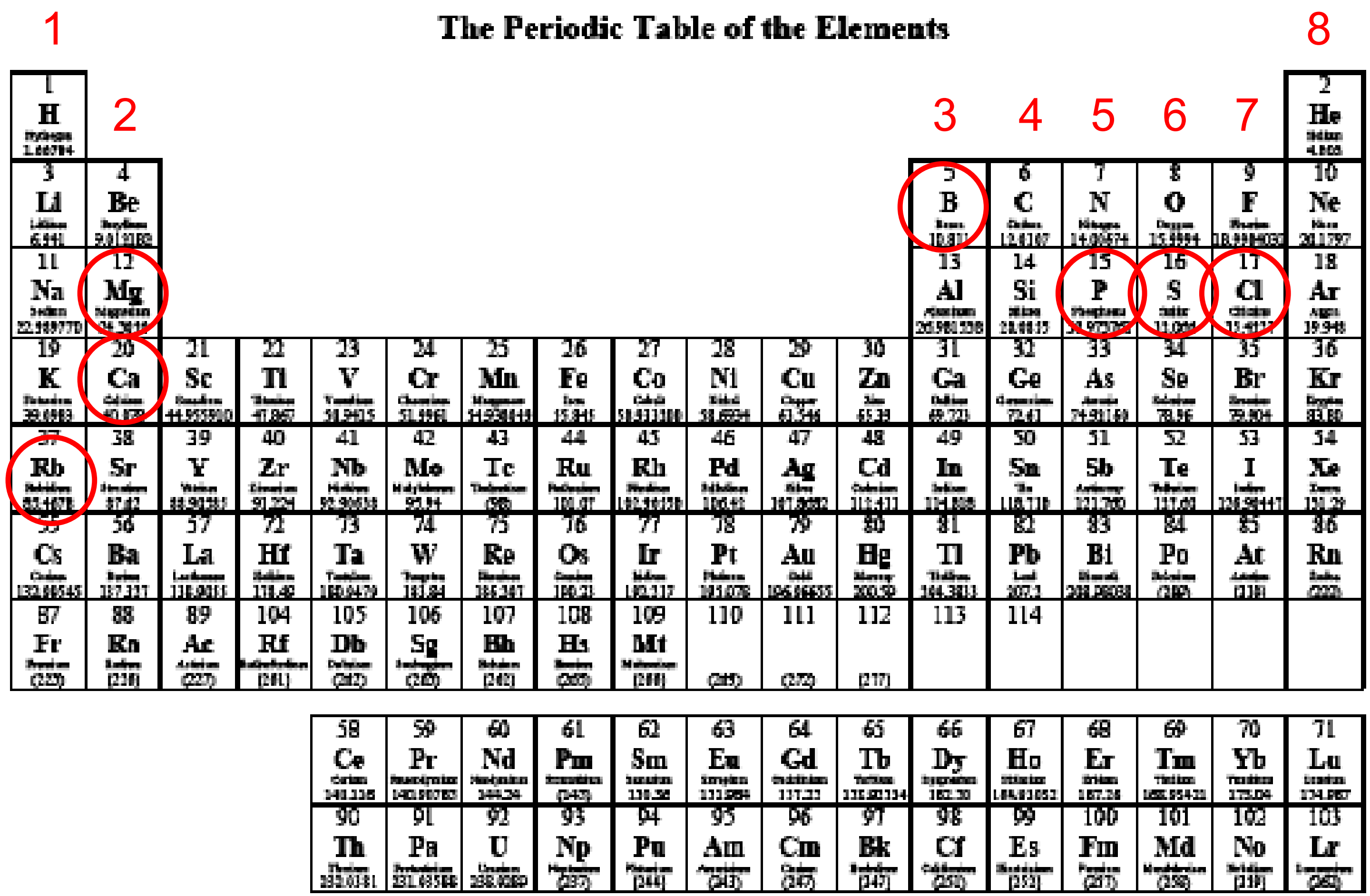
(c) Mg^{+} (1)

(d) Ca^{2+} (0)

(e) S^{2-} (8)

(f) B^{-} (4)

(g) Rb^{+} (0)



Lab Connection

EXPT. 22 – *Using WebMO to understand* Periodic/ atomic/ molecular properties

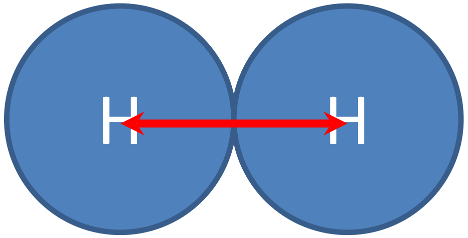
- Effective nuclear charge
- Atomic radius/ ionic radius/ metallic radius
- Ionization energy
- Electron affinity
- Electronegativity
- Orbitals – wave representations of the space with highest probability of finding the electron
- Types and sizes of orbitals – s, p, d, f and variation based on the “n” value and type of species (atom, cation, anion)

Periodic Properties

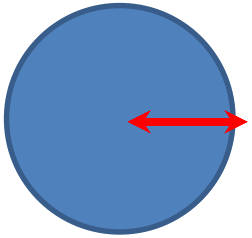
- Atomic radius
- Effective nuclear charge (Z_{eff})
- Ionization energy
- Electron affinity
- Electronegativity (EN)

Atomic Radius

- Atomic radius is calculated by measuring the internuclear distance and dividing by 2

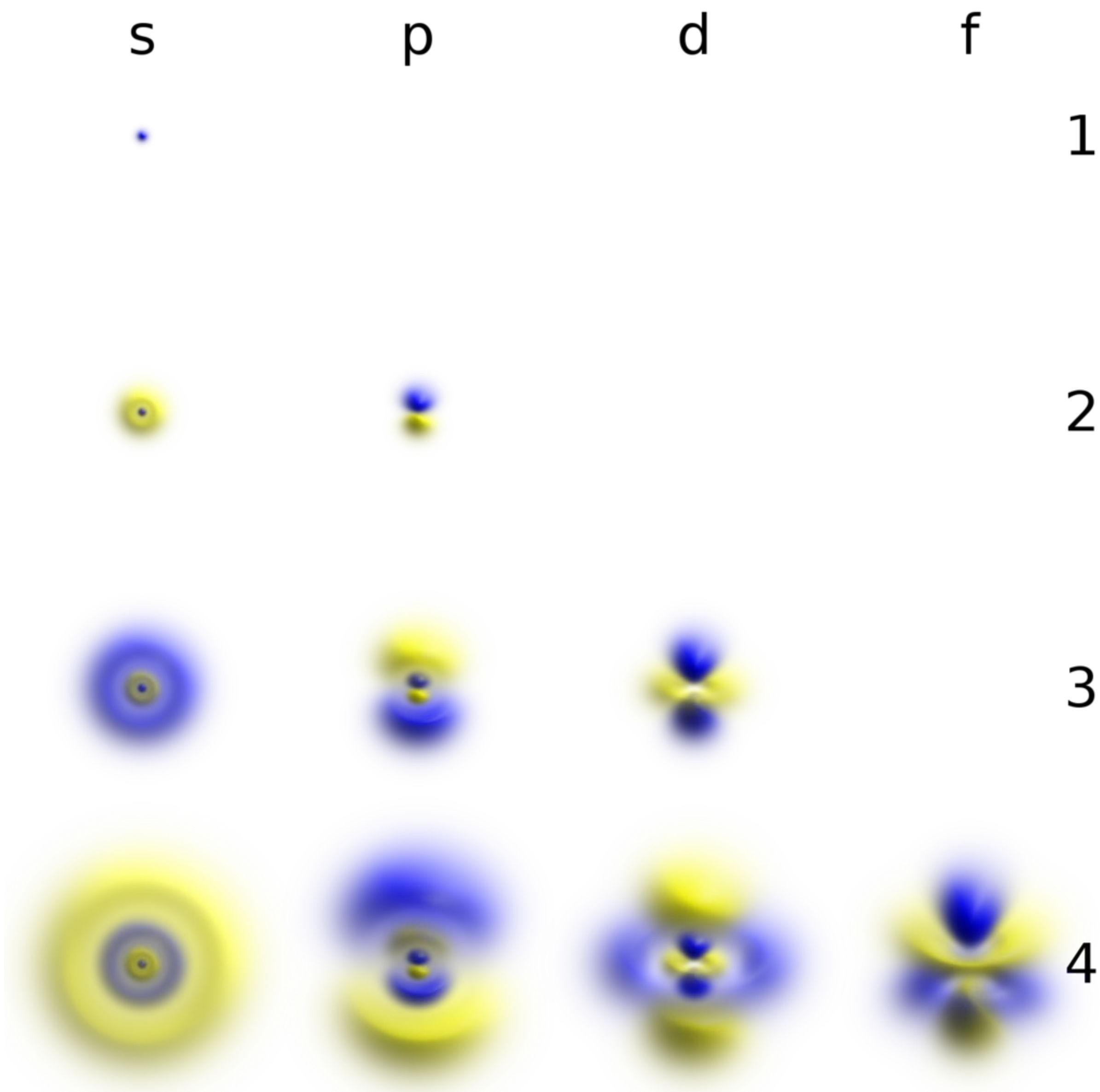
Internuclear distance: 

$$\text{Atomic Radius} = \frac{\text{Internuclear distance}}{2}$$



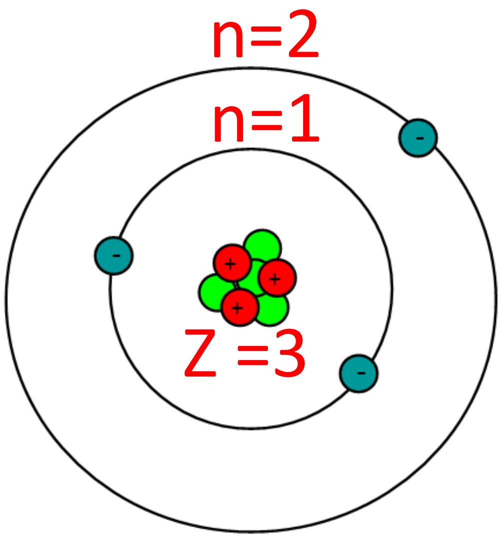
- The bond distance for H_2 is 0.74 Å, half of which is 0.37 Å.
- The calculated radius is 0.53 Å using the Bohr model.
- $1\ \text{Å} = 1 \times 10^{-10}$ m

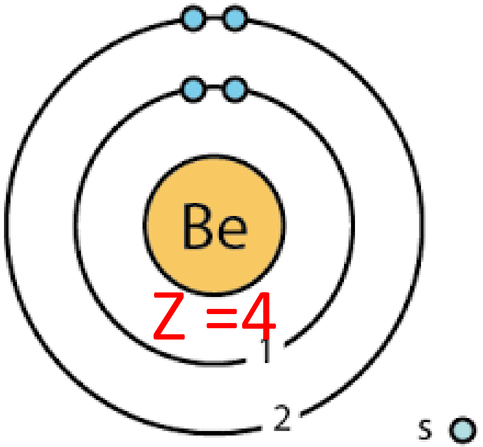
Relative Orbital Sizes



Atomic Radius (across a period)

Element	Radius (Å)
Li	1.28
Be	0.96
B	0.84
C	0.76
N	0.71
O	0.66
F	0.57
Ne	n/a no diatomic molecule



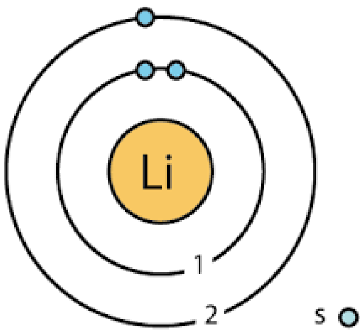


- Z is increasing but n is constant.

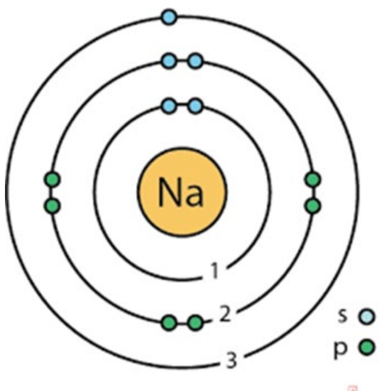
Atomic radius (down a group)

Element	Radius (Å)
Li	1.28
Na	1.66
K	2.03
Rb	2.20
Cs	2.44
Fr	n/a

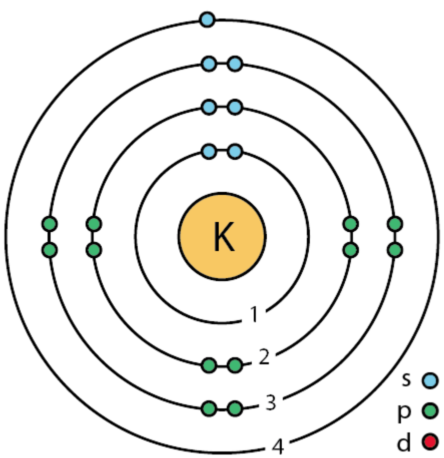
Z = 3



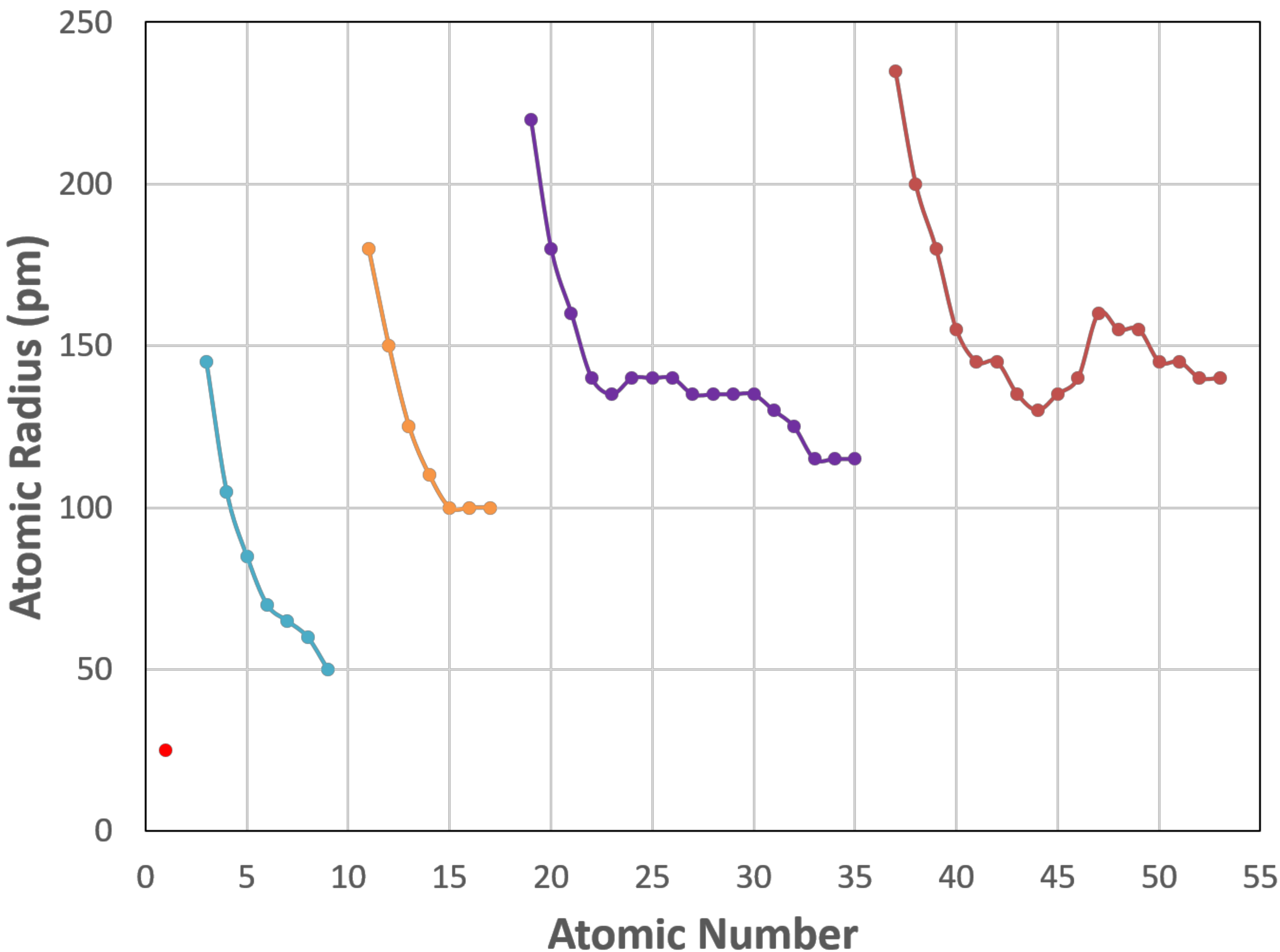
Z = 11



Z = 19

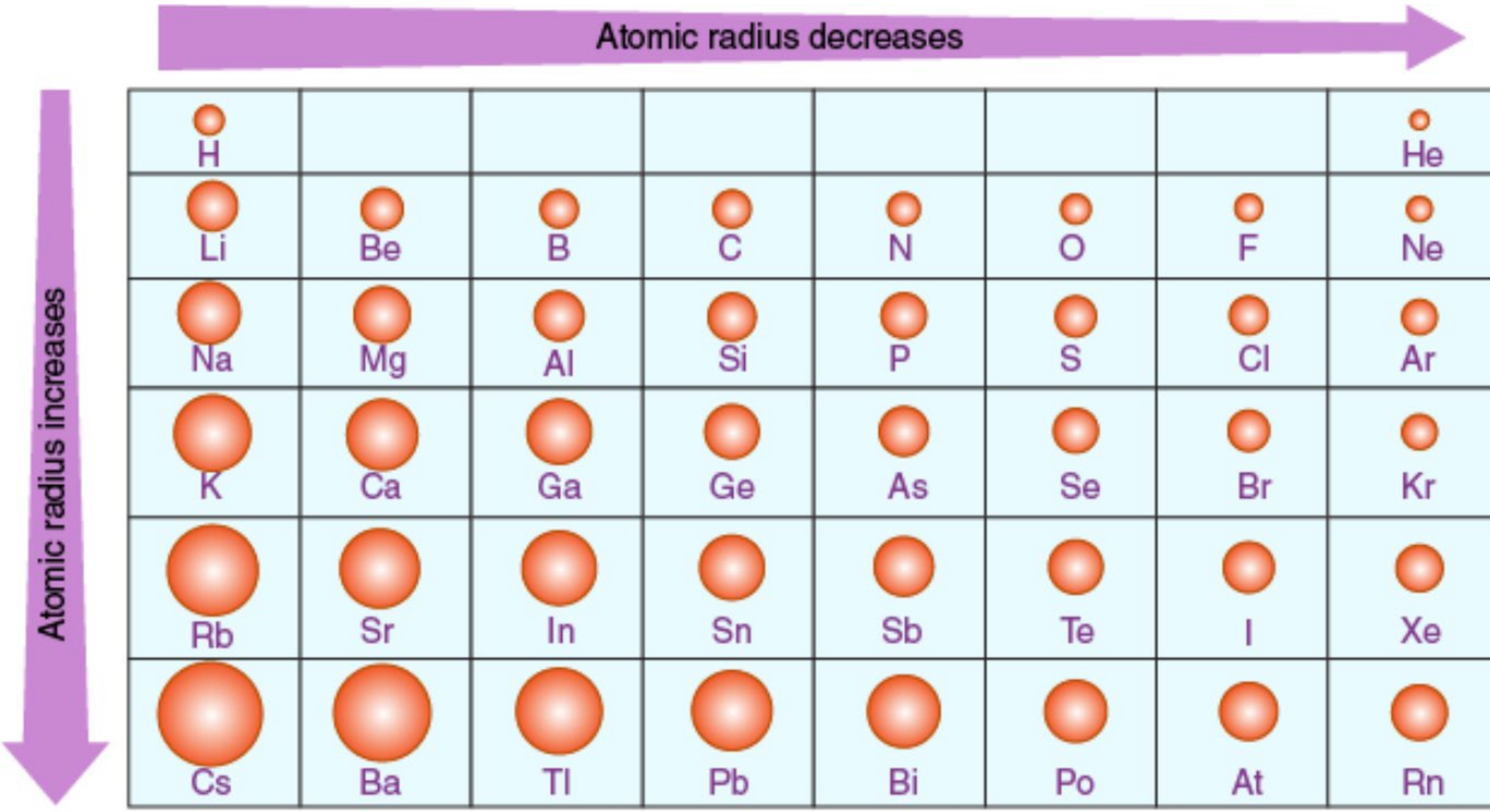


- Down a group, both Z and n are increasing.



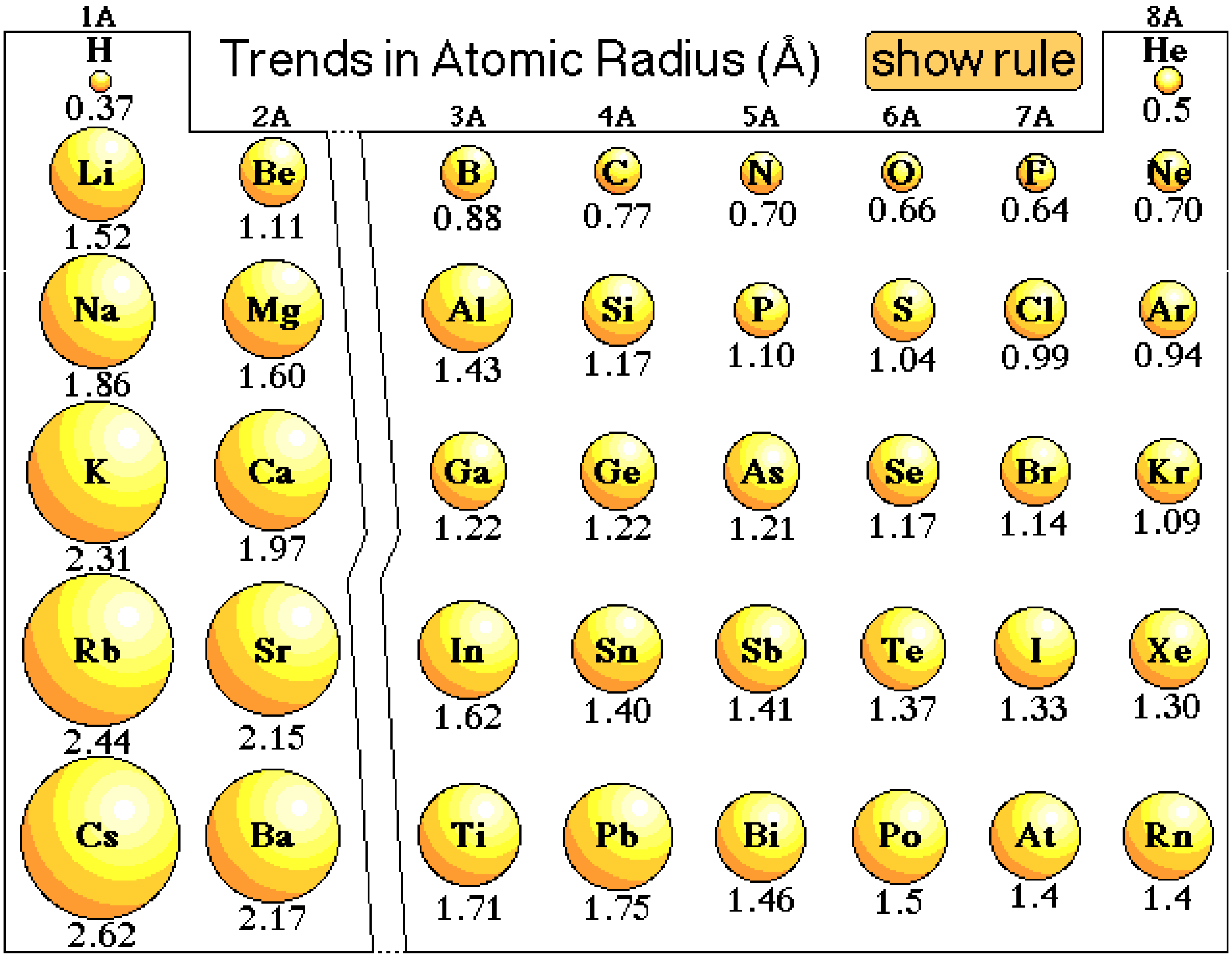
Atomic Radius (pm)
250
200
150
100
50
0
0
5
10
15
20
25
30
35
40
45
50
55
Atomic Number

Atomic Radius



Atomic Radius

You do NOT need to know the values for exams but you should know the trend



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Worksheet Question #4

Calculate the atomic radius of silicon (one of the most important elements in the microelectronics industry), given the following information:

- the H-H bond distance in H_2 is 0.74 Å
- the Si-H bond distance in SiH_4 is 1.46 Å

Ans: 1.46-(0.74/2) = 1.10 Å

Clicker Question

Select the sequence of atoms that are correctly listed in order of increasing size.

a) F < Br < Ge < K

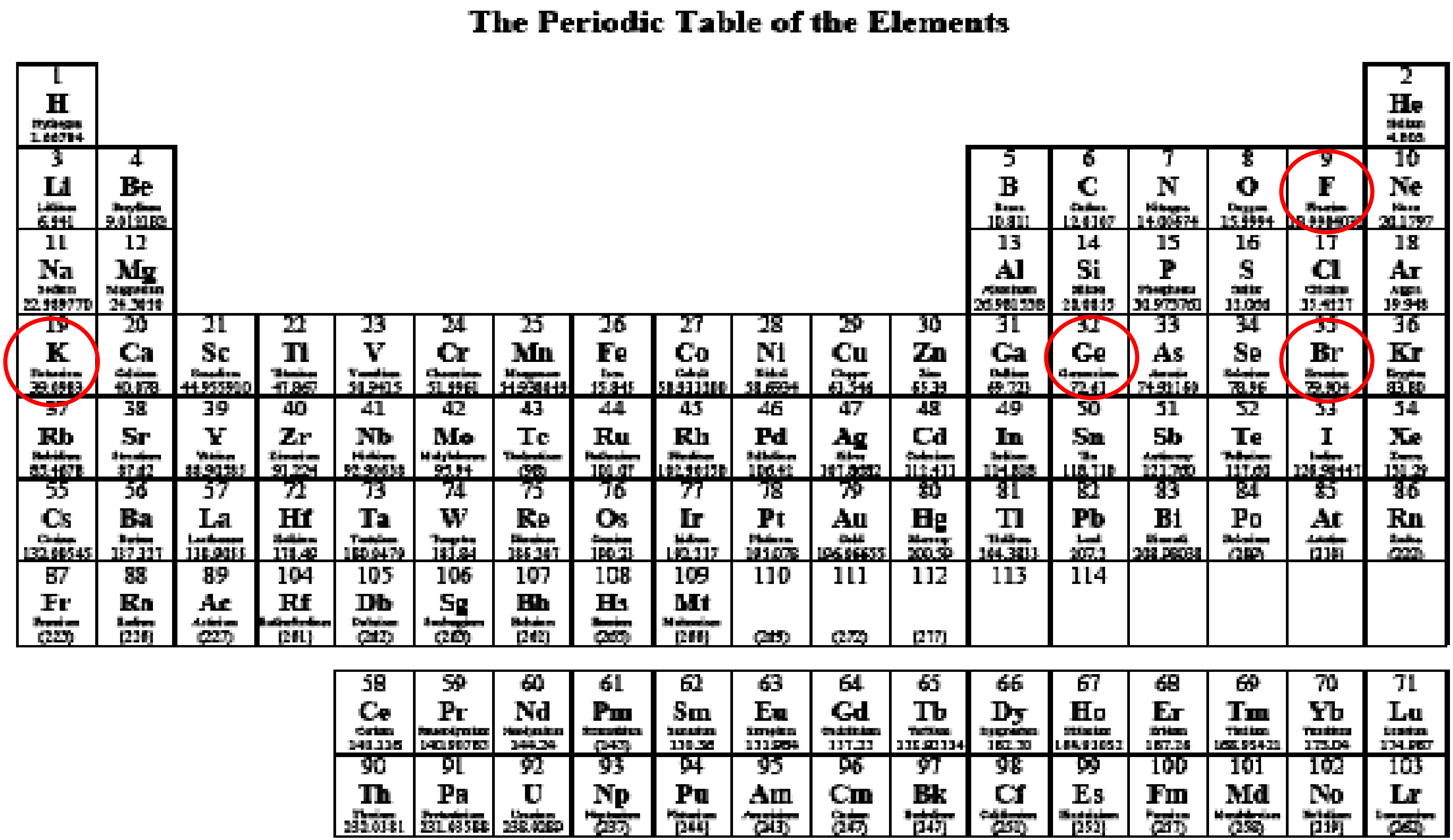
b) Na < Al < P < S

c) Ba < Ca < Mg < Be

d) Cl < Si < C < B

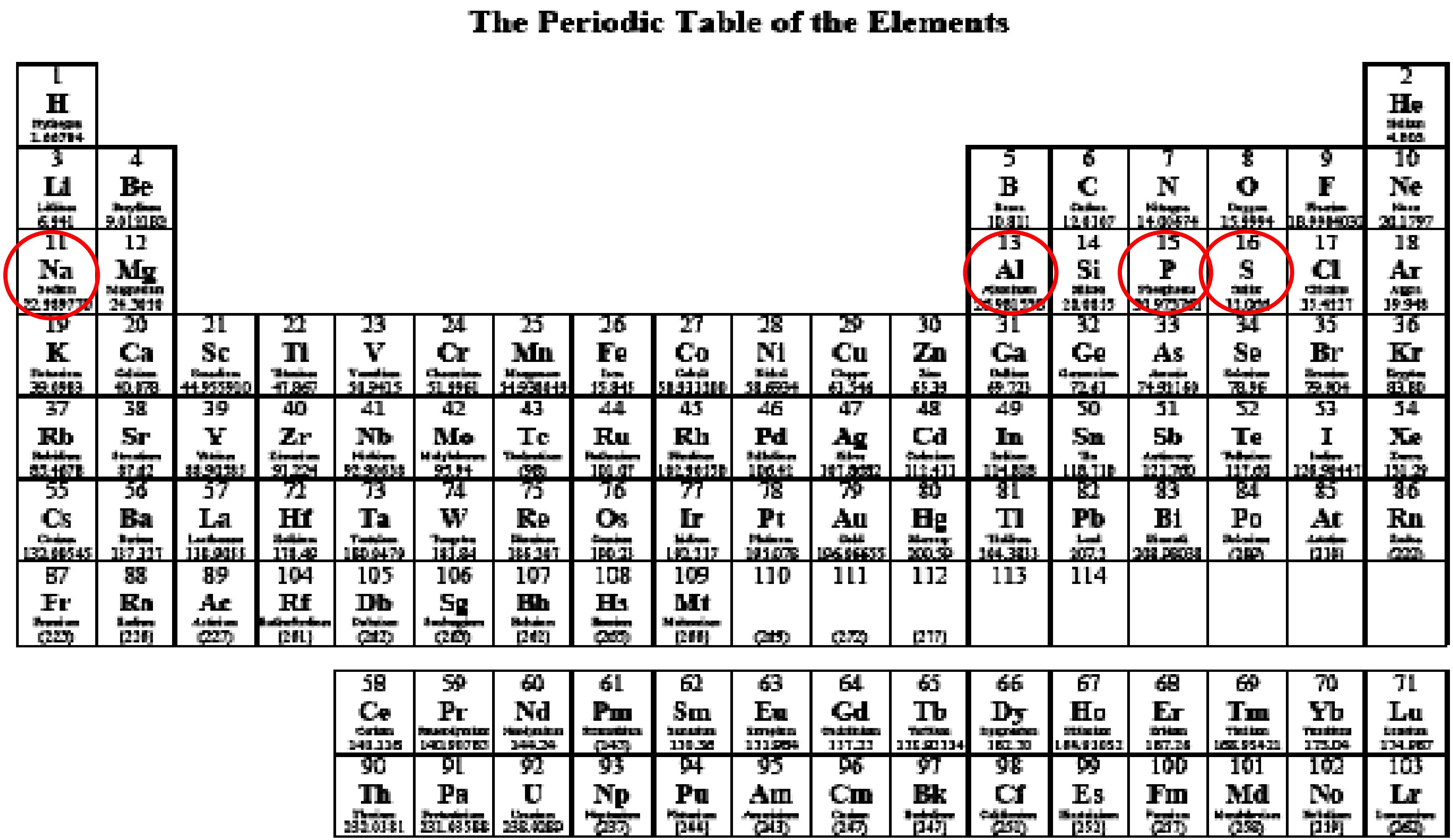
Clicker Question

a) F < Br < Ge < K



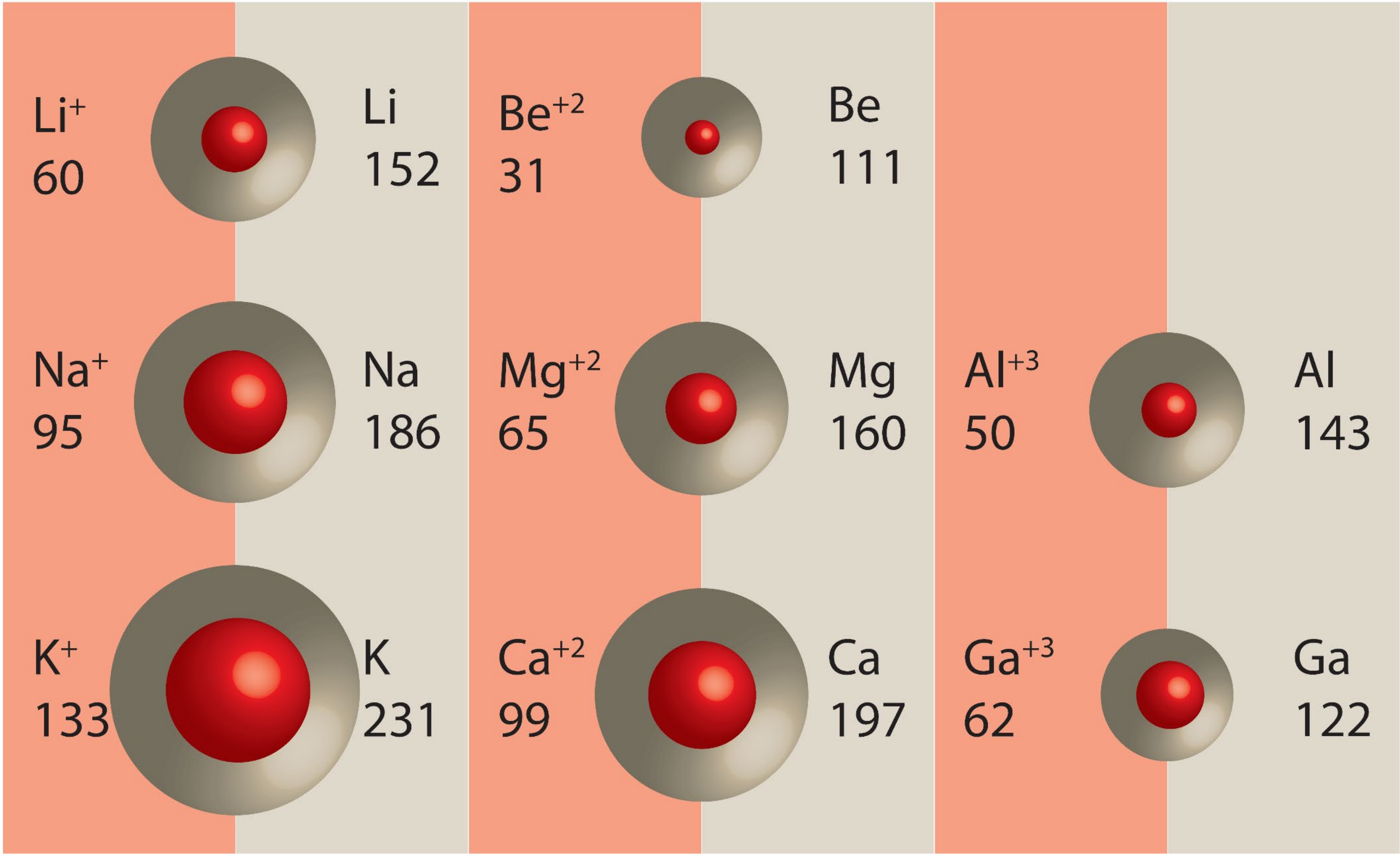
Clicker Question

b) Na < Al < P < S



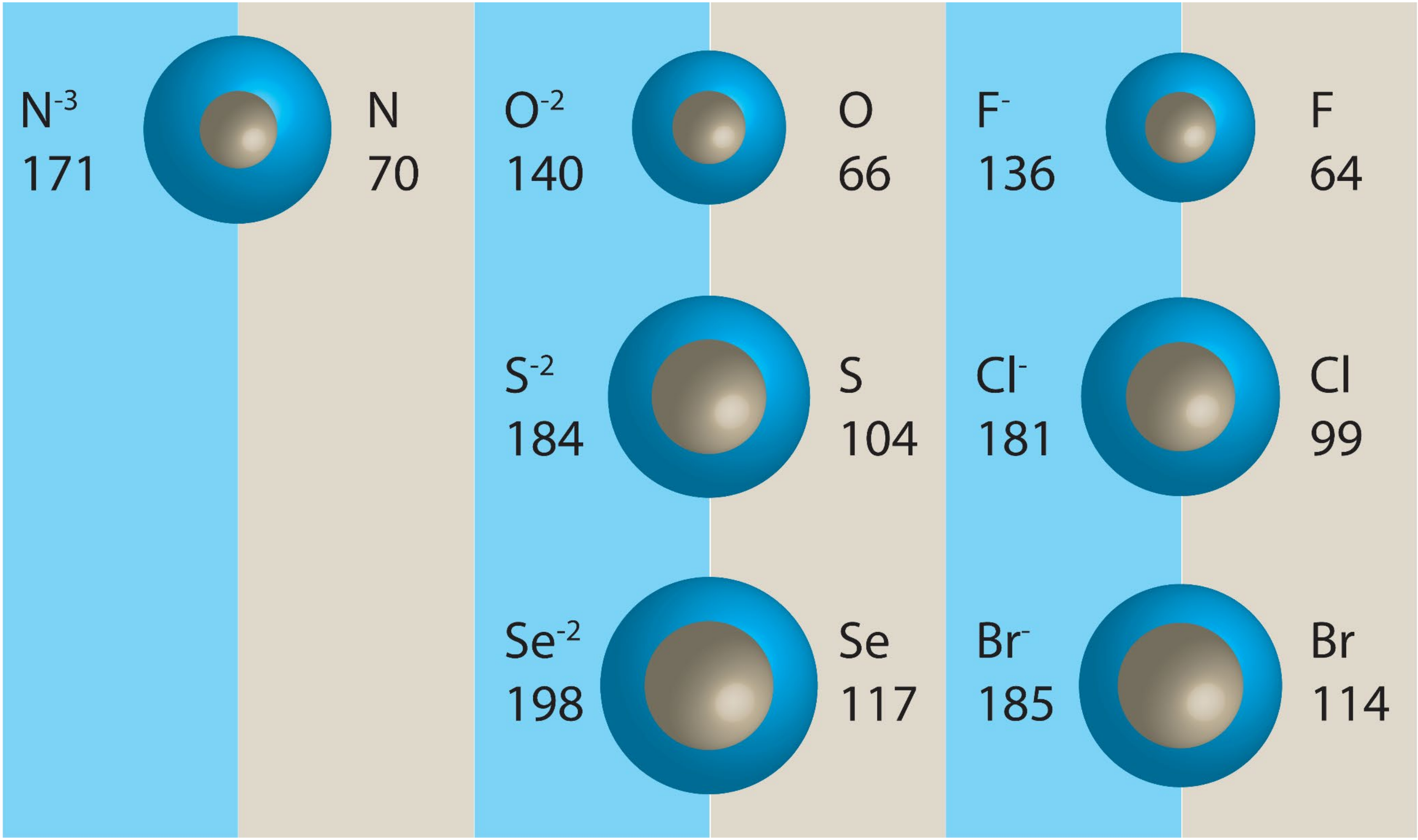
Cationic radii

For a given atom, its cation is always smaller than the neutral species.



Anionic radii

For a given atom, its anion is always larger than the neutral species.



Worksheet Question #5

Rationalize the difference in the atomic and ionic radii of the following species:

(a) Se (117 pm) and Se^{2-} (198 pm)

(b) K (231 pm) and K^{+} (133 pm)

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

Se^{2-} : [Ar] $4s^2\ 3d^{10}\ 4p^6$

- gaining two electrons increases electron-electron repulsion

Worksheet Question #5

Rationalize the difference in the atomic and ionic radii of the following species:

(a) Se (117 pm) and Se^{2-} (198 pm)

(b) K (231 pm) and K^{+} (133 pm)

K: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6 4s^1$

K^+ : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

- The radius of K is determined by the 4th shell.
- The radius of K^+ is determined by the 3rd shell.

Isoelectronic species

Atoms and ions with the same number of electrons are said to be *isoelectronic*. In a set of isoelectronic species, the most negative species has the largest radius.

K^+ Ar Cl^-

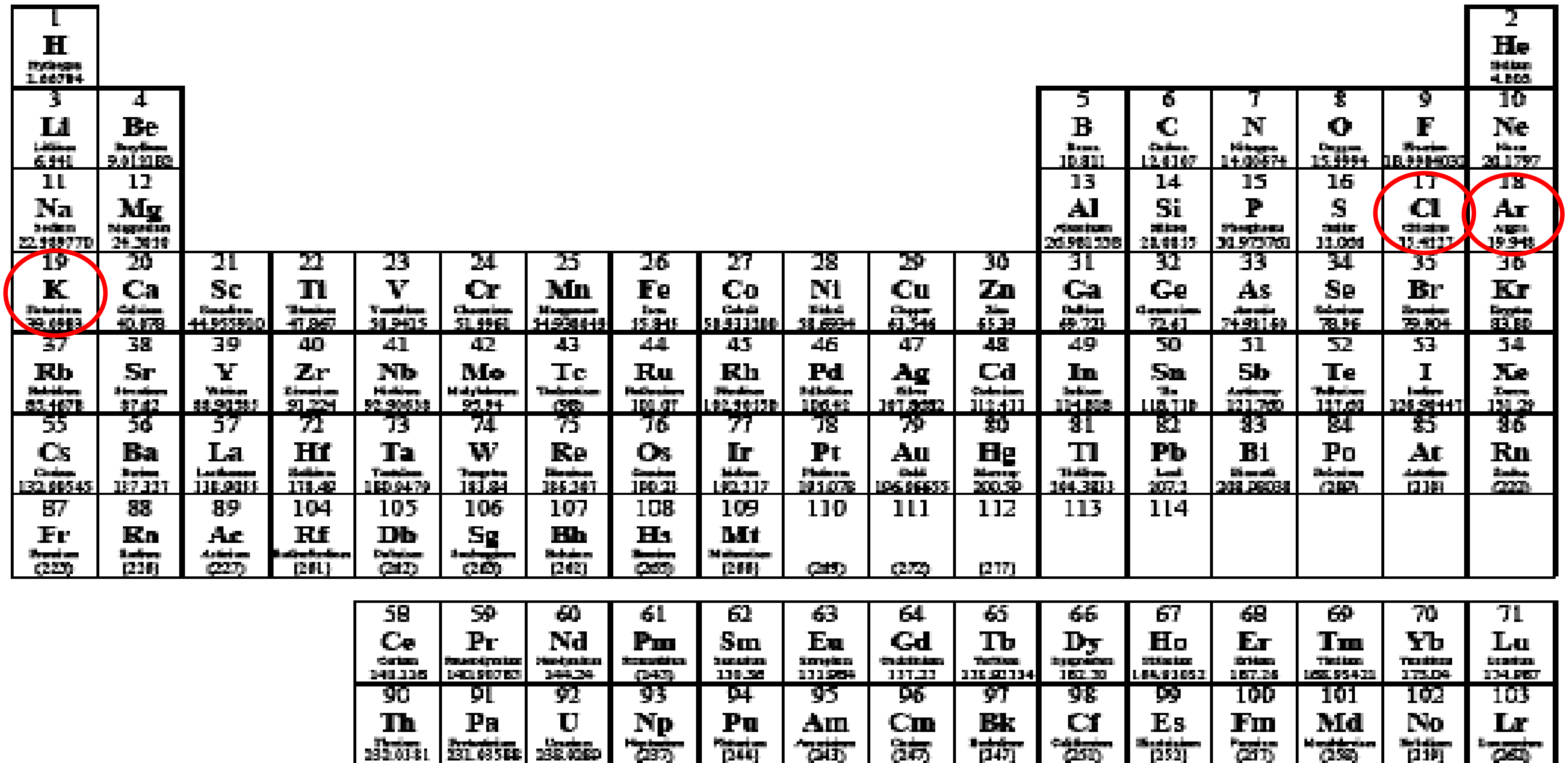
Increasing Atomic or Ionic Radius

Isoelectronic species

K^+ Ar Cl^-

Z = 19 > Z = 18 > Z = 17c

Larger Z, smaller radius



Clicker Question

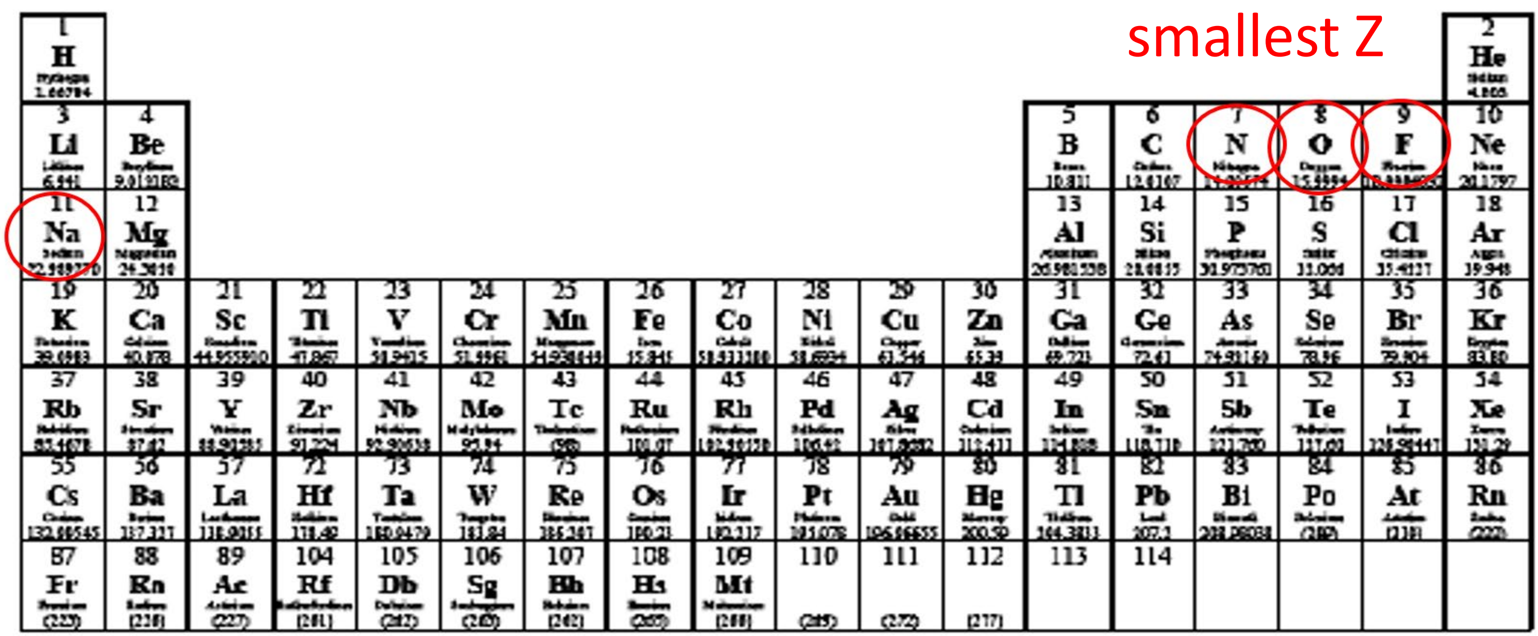
Which of the following isoelectronic species is expected to have the largest radius?

a. O^{2-}

b. N^{3-}

c. Na^{+}

d. F^{-}



DEMO TIME

$$2M(s) + 2H_2O(l) \rightarrow 2M^+(aq) + 2OH^-(aq) + H_2(g)$$

Or

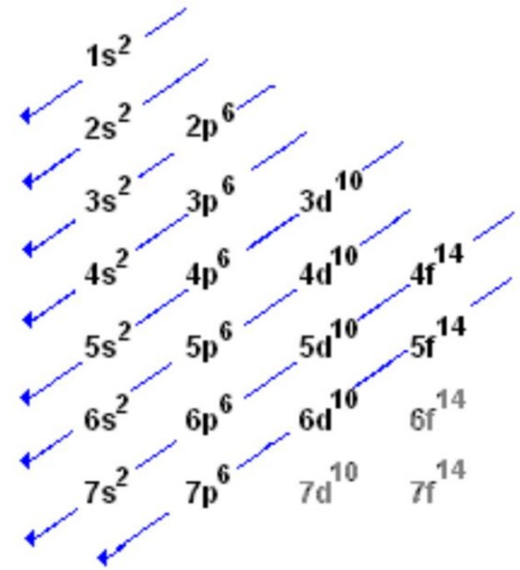
$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$$

where M = Li, Na, K.

- Metals are ionized.
- The solution become more basic since OH^- is being produced.
- Reactivity Order K > Na > Li

Worksheet Question #2

Write the electron configurations for the following chemical species:



a) P : $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

b) S^{2-}: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$

c) Se: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^4$

d) Mg^+: $1s^2\ 2s^2\ 2p^6\ 3s^1$

e) In: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^1$

or condensed form [Kr] $5s^2\ 4d^{10}\ 5p^1$

or [Kr] $4d^{10}\ 5s^2\ 5p^1$

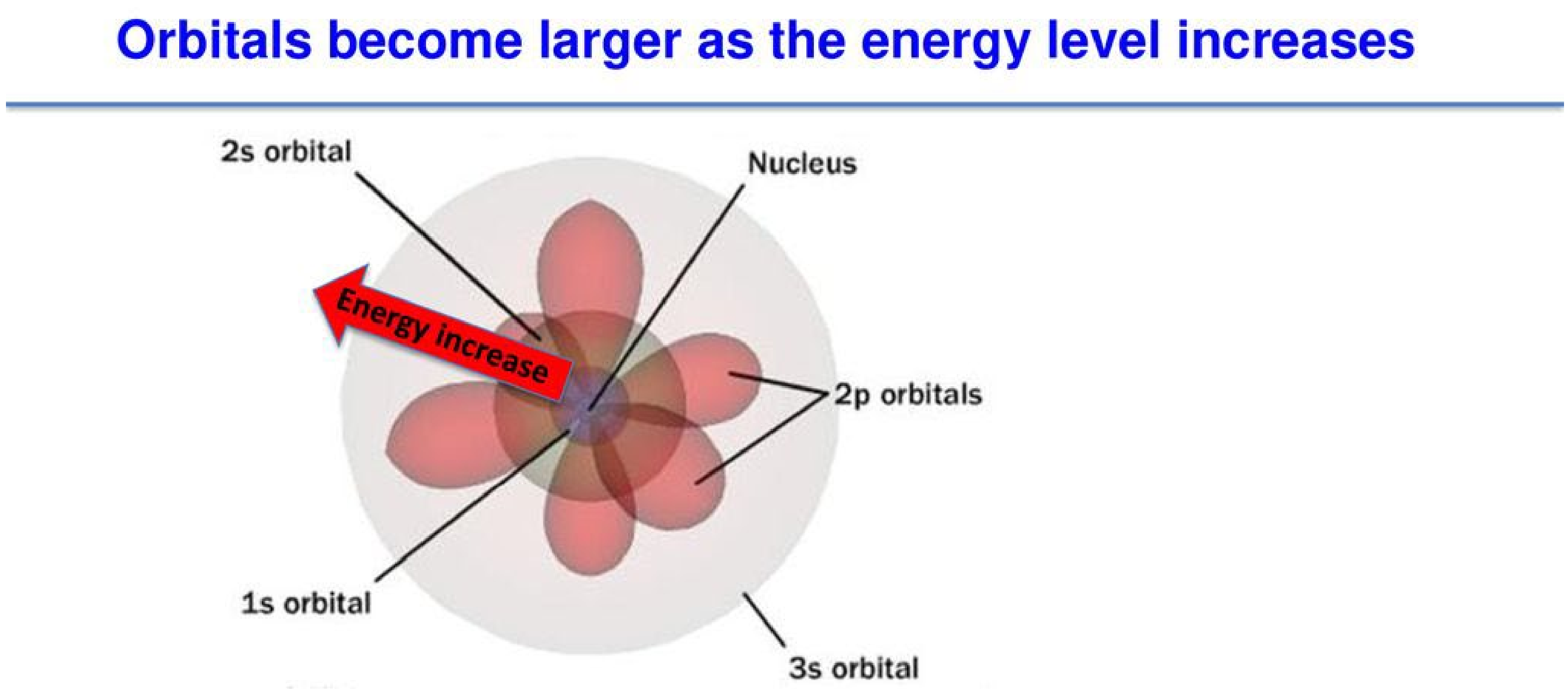
Effective nuclear charge (Z_{eff})

Coulomb's Law $$U = k\frac{q_1 \cdot q_2}{r}$$

Core electrons are close to the nucleus and effectively screen some of its positive charge from valence electrons further away. Valence electrons also partially screen each other from the nuclear charge. Thus, a valence electron "feels" an effective nuclear charge (Z_{eff}) that is less than the actual nuclear charge Z.

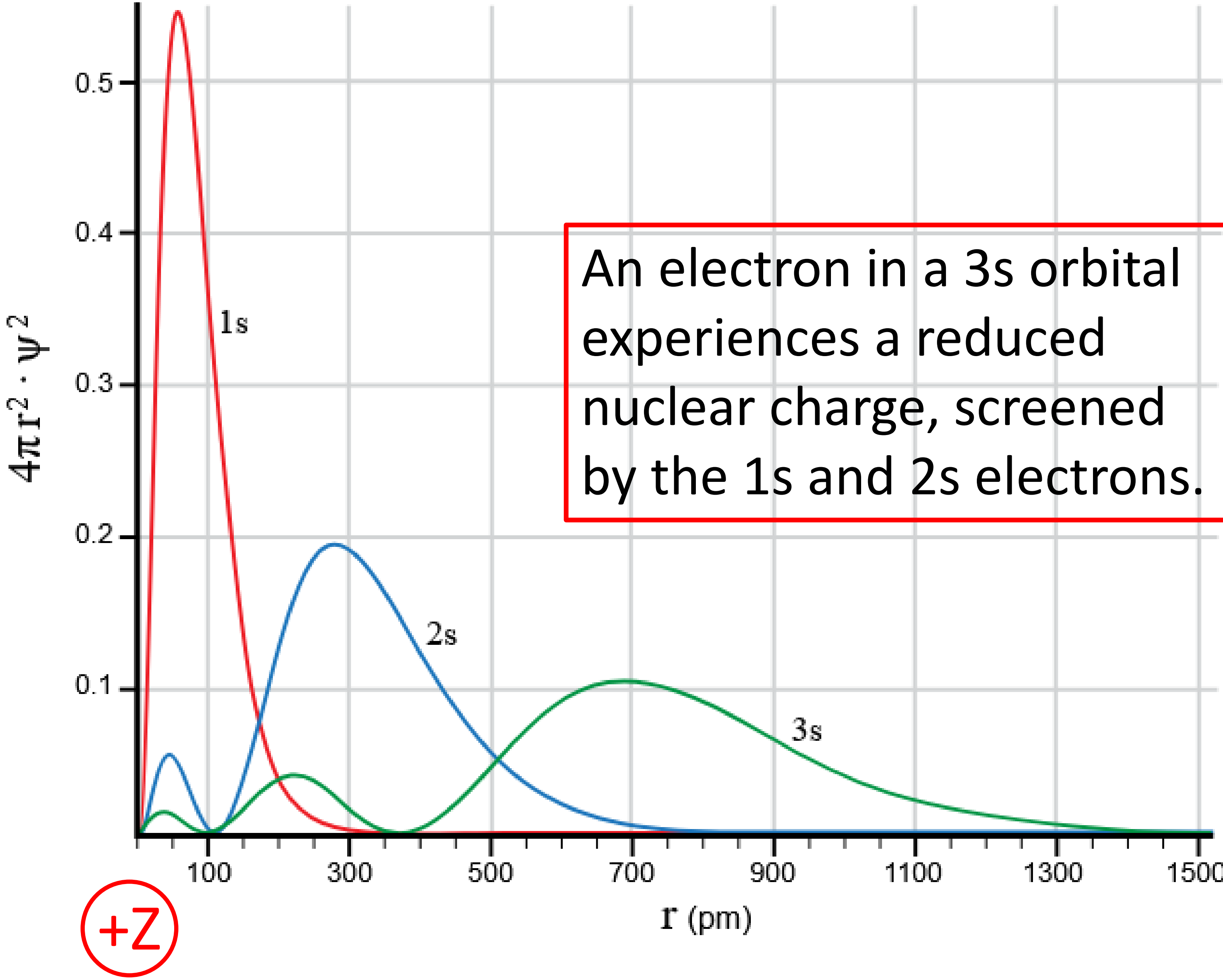
Note: Z_{eff} is a theoretically calculated property.

Shell Structure of Atoms



- **Electrons filling order : 1s, 2s 2p, 3s**
- **Orbitals** arranged in order of **increasing energy: 1s, 2s 2p, 3s**
- **Orbitals** arranged in **increasing size: (smallest) 1s <2s <2p < 3s (largest)**

Radial Distribution Functions of Orbitals



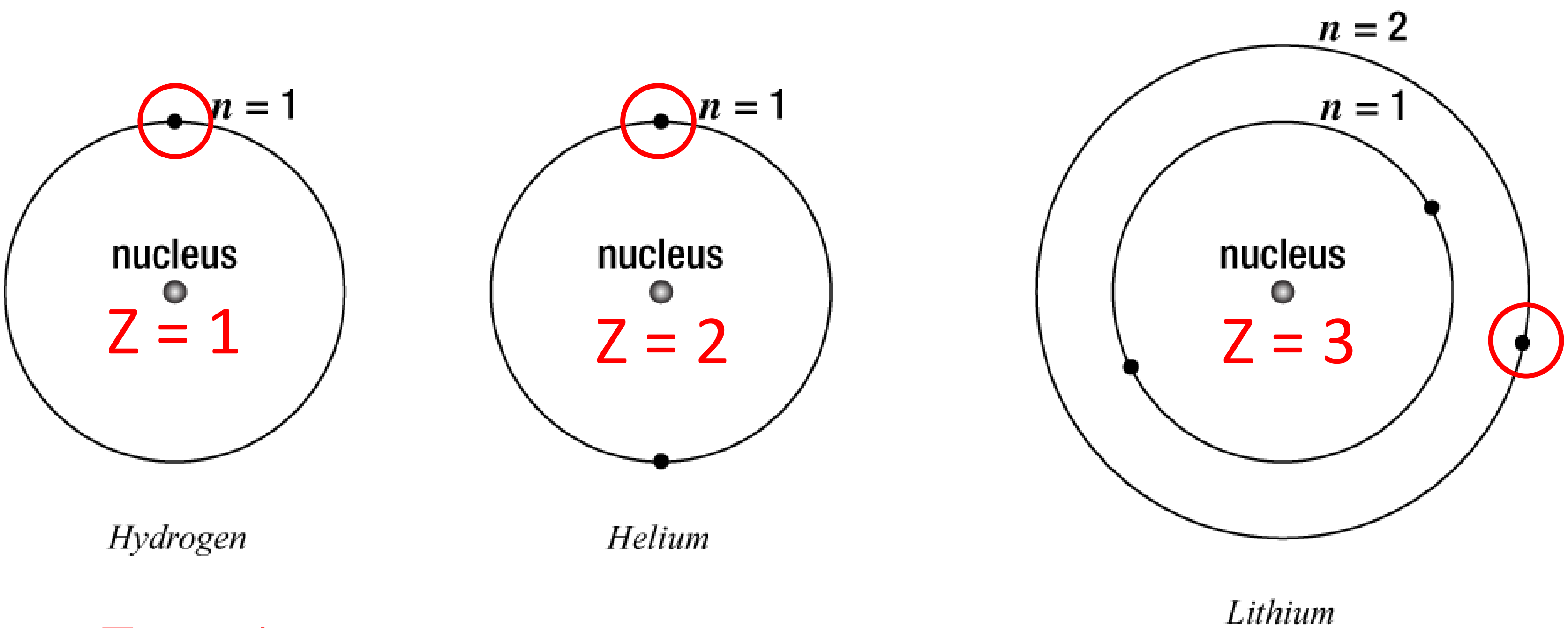
An electron in a 3s orbital experiences a reduced nuclear charge, screened by the 1s and 2s electrons.

Effective nuclear charge

- **Effective nuclear charge (Z_{eff})**

  - the net positive charge experienced by an electron

Coulomb's Law $F = k\frac{q_1 \cdot q_2}{r^2}$; Potential Energy $U = k\frac{q_1 \cdot q_2}{r}$



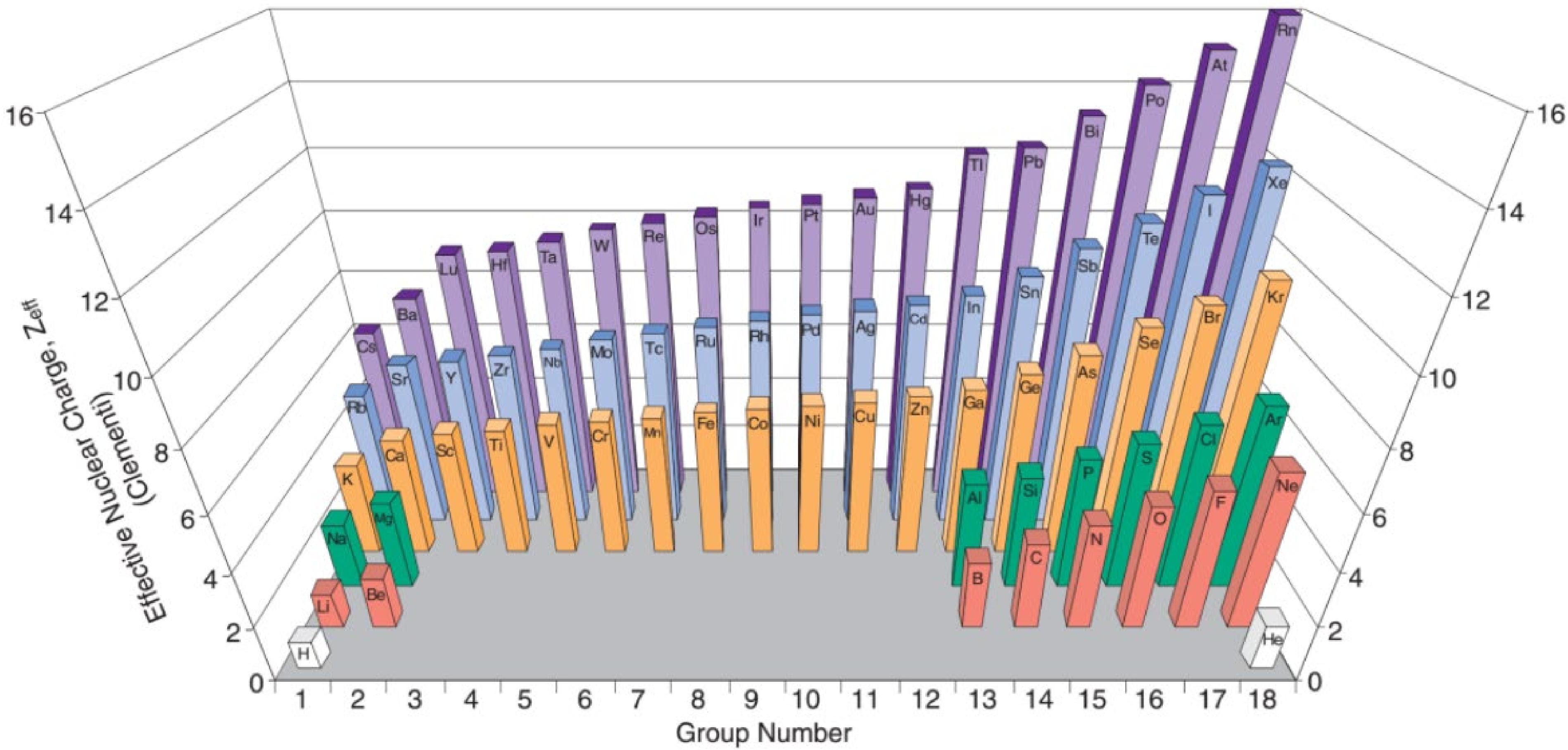
$Z_{eff} = 1$

$Z_{eff} = 1.7$

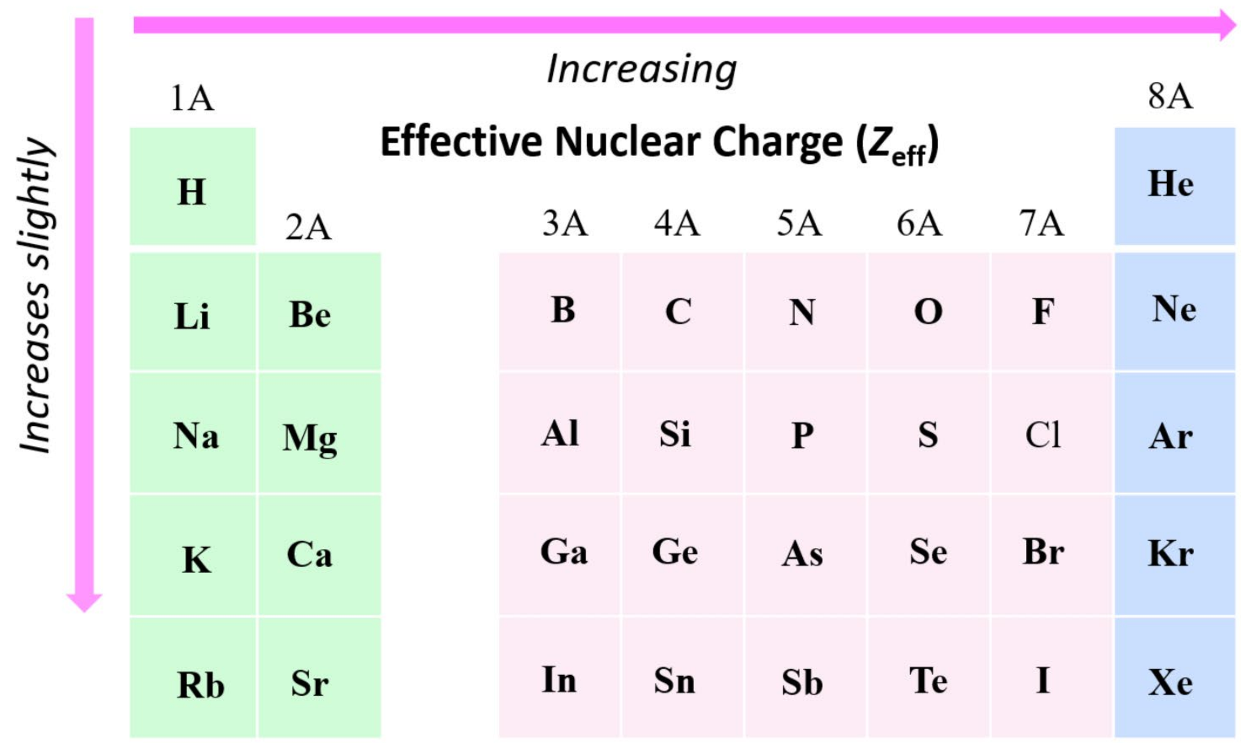
1s: $Z_{eff} = 2.69$

2s: $Z_{eff} = 1.28$

Z_{eff} experienced by the valence electrons



Effective Nuclear Charge Z_{eff}



- Across a period, the number of core electrons doesn't increase, so majority of increase in Z passes through to Z_eff.
- Going down a group, the valence shell is the same but add core electrons.

Ionization Energy (IE)

For atoms, molecules or ions: the minimum energy required to remove a single electron from an atom, molecule or ion in its gaseous state.

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

For solids: the minimum energy required to remove an electron from the **valence band** of the solid.

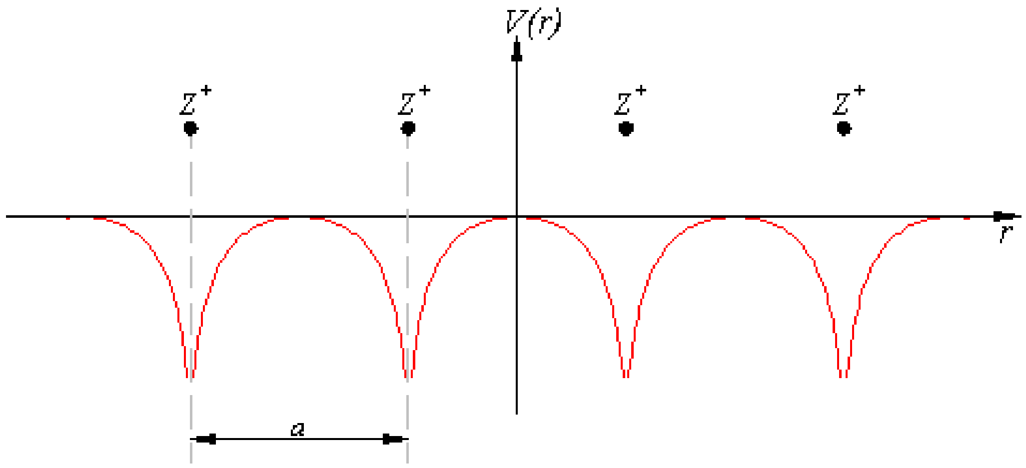
As many elements are solids, values may be available for both, and differ due to the nature of bonding in solids. The elemental values always refer to the gas phase.

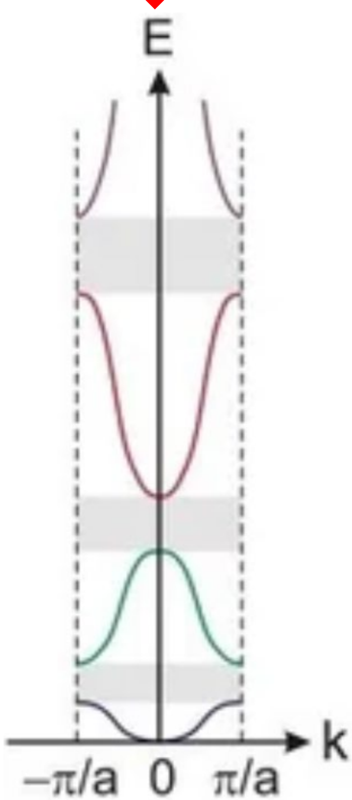
Valence band

- Schrodinger Equation

$$\frac{-\hbar^2}{2m}\left[\frac{\partial^2\Psi}{\partial x^2}+\frac{\partial^2\Psi}{\partial y^2}+\frac{\partial^2\Psi}{\partial z^2}\right]+U(x,y,z)\Psi(x,y,z)=E\Psi(x,y,z)$$

- Potential in a solid:

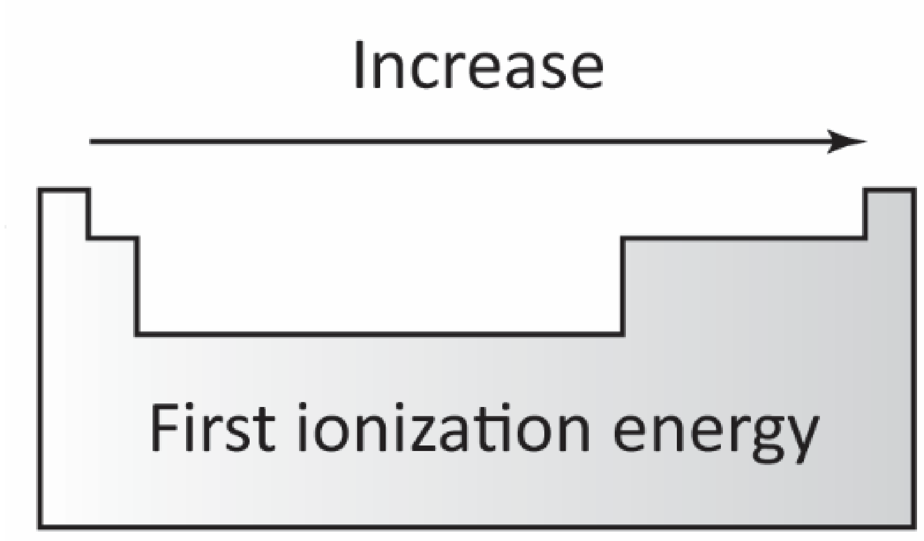




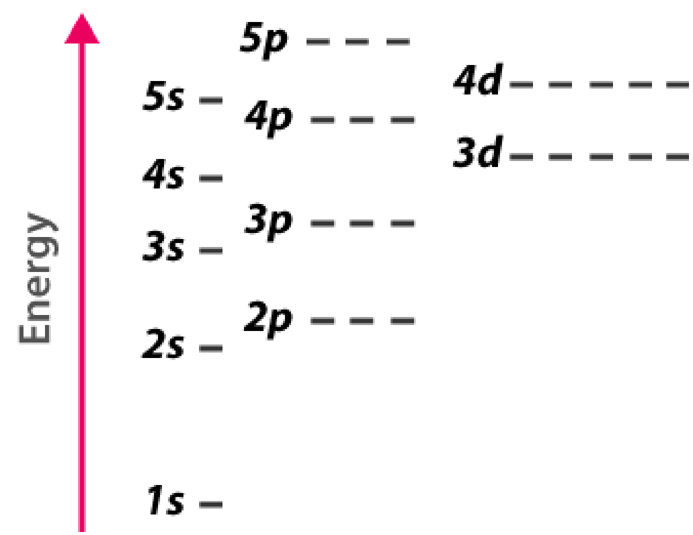
Valence band: the highest-energy band of electrons that are normally present at 0K.

Ionization Energy

Element	IE_1 (kJ/mol)
Li	520
Be	899
B	801
C	1086
N	1402
O	1314
F	1681
Ne	2081

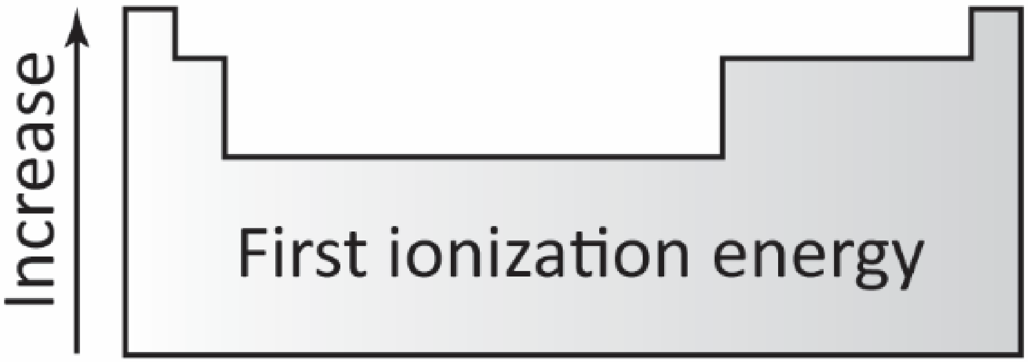


- Increasing Z but not increasing n



Ionization Energy

Element	IE_1 (kJ/mol)
Li	520
Na	496
K	419
Rb	403
Cs	376
Fr	~375



- Decreasing n, so electrons are closer nucleus.

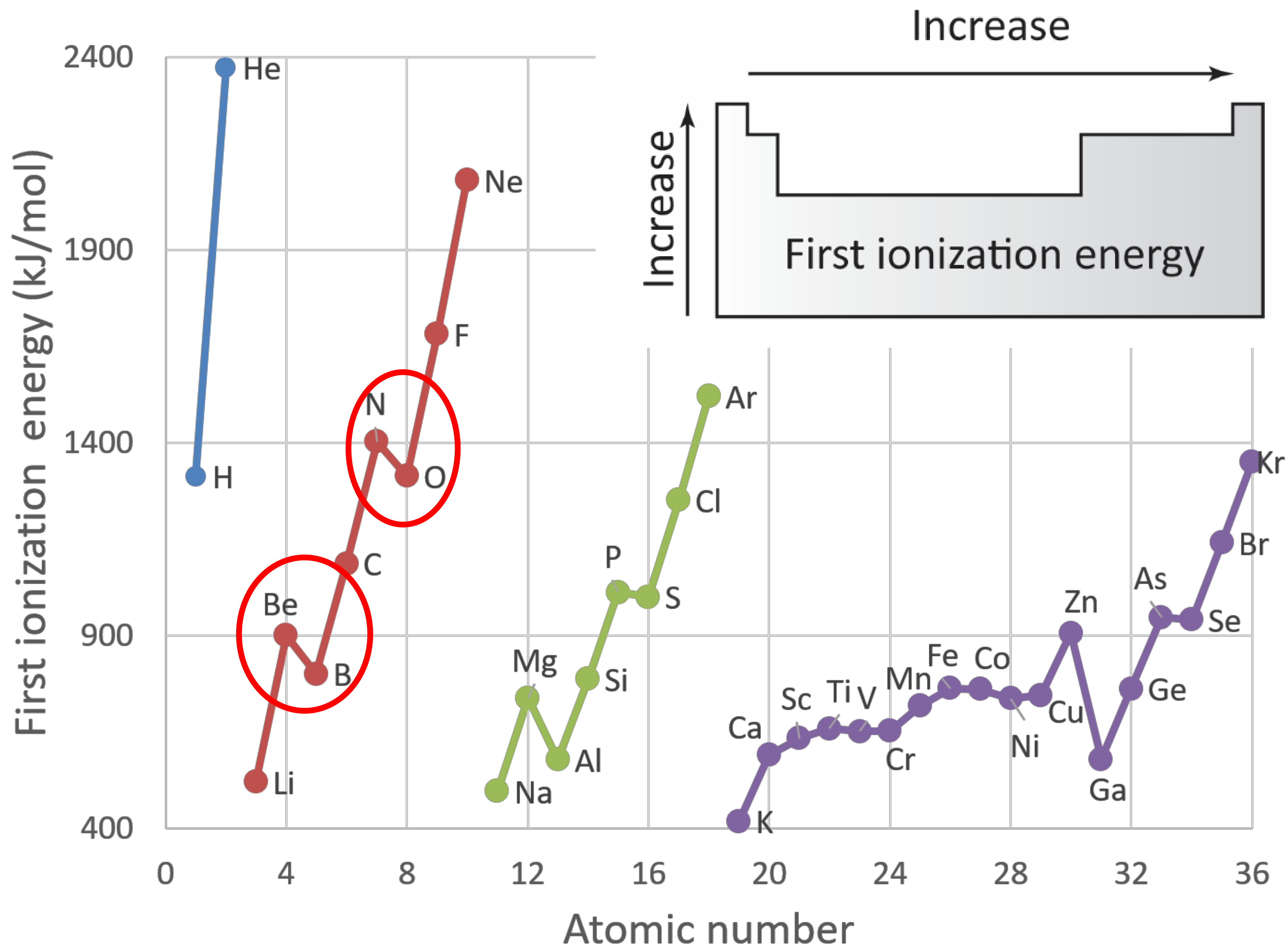
Ionization Energy

You do NOT need to know the values for exams but you should know the trend

375.7 kJ/mol — 2372.3 kJ/mol

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	**H** 1312.0																	**He** 2372.3
2	**Li** 520.2	**Be** 899.5											**B** 800.6	**C** 1086.5	**N** 1402.3	**O** 1313.9	**F** 1681.0	**Ne** 2080.7
3	**Na** 495.8	**Mg** 737.7											**Al** 577.5	**Si** 786.5	**P** 1011.8	**S** 999.6	**Cl** 1251.2	**Ar** 1520.6
4	**K** 418.8	**Ca** 589.8	**Sc** 633.1	**Ti** 658.8	**V** 650.9	**Cr** 652.9	**Mn** 717.3	**Fe** 762.5	**Co** 760.4	**Ni** 737.1	**Cu** 745.5	**Zn** 906.4	**Ga** 578.8	**Ge** 762.2	**As** 944.5	**Se** 941.0	**Br** 1139.9	**Kr** 1350.8
5	**Rb** 403.0	**Sr** 549.5	**Y** 599.9	**Zr** 640.1	**Nb** 652.1	**Mo** 684.3	**Tc** 702	**Ru** 710.2	**Rh** 719.7	**Pd** 804.4	**Ag** 731.0	**Cd** 867.8	**In** 558.3	**Sn** 708.6	**Sb** 830.6	**Te** 869.3	**I** 1008.4	**Xe** 1170.3
6	**Cs** 375.7	**Ba** 502.9	**La** 538.1	**Hf** 658.5	**Ta** 728.4	**W** 758.8	**Re** 755.8	**Os** 814.2	**Ir** 865.2	**Pt** 864.4	**Au** 890.1	**Hg** 1007.1	**Tl** 589.4	**Pb** 715.6	**Bi** 703.0	**Po** 812.1	**At**	**Rn** 1037.1
7	**Fr** 393.0	**Ra** 509.3	**Ac** 498.8	**Rf** 580	**Db**	**Sg**	**Bh**	**Hs**	**Mt**	**Ds**	**Rg**	**Uub**	**Uut**	**Uuq**	**Uup**			

Lanthanides 6	**Ce** 534.4	**Pr** 528.1	**Nd** 533.1	**Pm** 538.6	**Sm** 544.5	**Eu** 547.1	**Gd** 593.4	**Tb** 565.8	**Dy** 573.0	**Ho** 581.0	**Er** 589.3	**Tm** 596.7	**Yb** 603.4	**Lu** 523.5
Actinides 7	**Th** 608.5	**Pa** 568	**U** 597.6	**Np** 604.5	**Pu** 581.4	**Am** 576.4	**Cm** 578.1	**Bk** 598.0	**Cf** 606.1	**Es** 619	**Fm** 627	**Md** 635	**No** 642	**Lr** 472.8



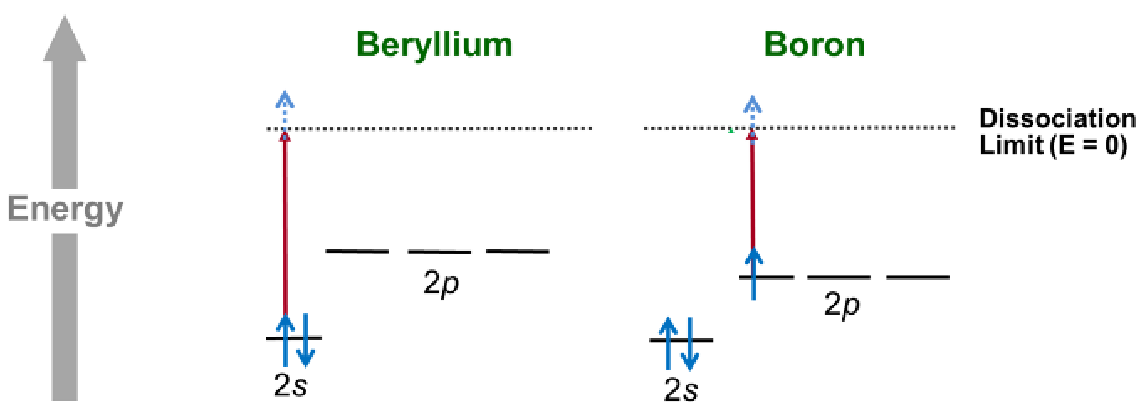
Increase
Increase
First ionization energy
First ionization energy (kJ/mol)
Atomic number
2400
1900
1400
900
400
0
4
8
12
16
20
24
28
32
36
He
H
Ne
F
N
O
C
Be
B
Li
Ar
Cl
P
S
Mg
Si
Al
Na
Kr
Br
As
Se
Zn
Ge
Fe
Co
Mn
Sc
Ti
V
Ca
Cu
Ni
Cr
Ga
K

Ionization Energy

The IE_1 drops or decreases modestly on changing from ionization of a lower energy *ns* electron to ionization of a higher energy *np*^{1} electron.

The ionization energy is lower than expected because the higher energy of the *np* orbital more than compensates for the decrease in orbital energy due to increasing Z* and the lack of Coulombic repulsion.

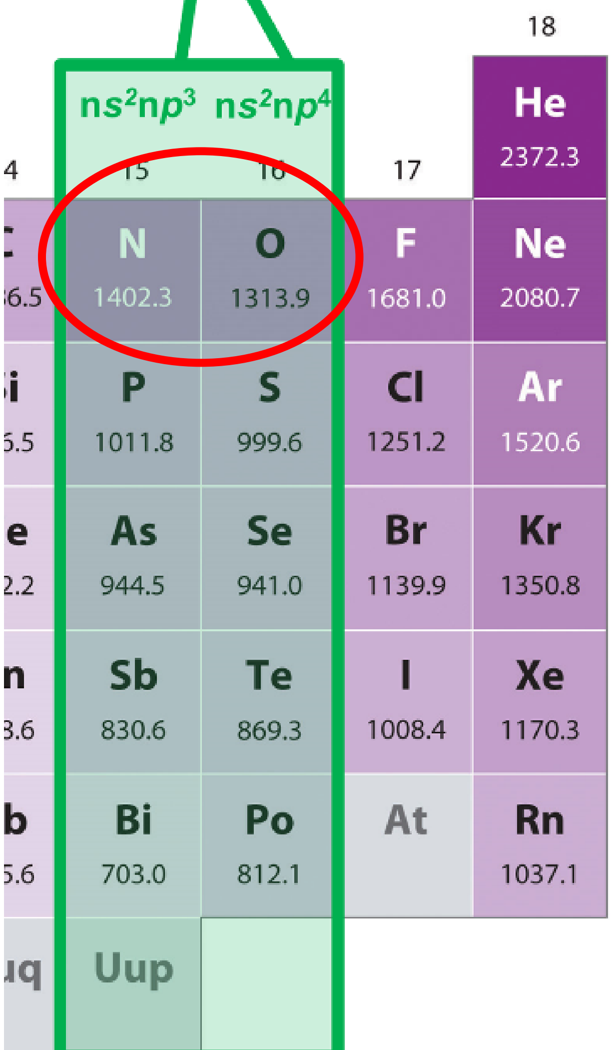
Example: Be (group 2) and B (group 13)



	1	2 (ns^2)	13 (ns^2np^1)	14
1	H 1312.0			
2	Li 520.2	Be 899.5	B 800.6	C 108
3	Na 495.8	Mg 737.7	Al 577.5	S 786
4	K 418.8	Ca 589.8	Ga 578.8	G 762
5	Rb 403.0	Sr 549.5	In 558.3	S 708
6	Cs 375.7	Ba 502.9	Tl 589.4	P 715
7	Fr 393.0	Ra 509.3	Uut	Uu

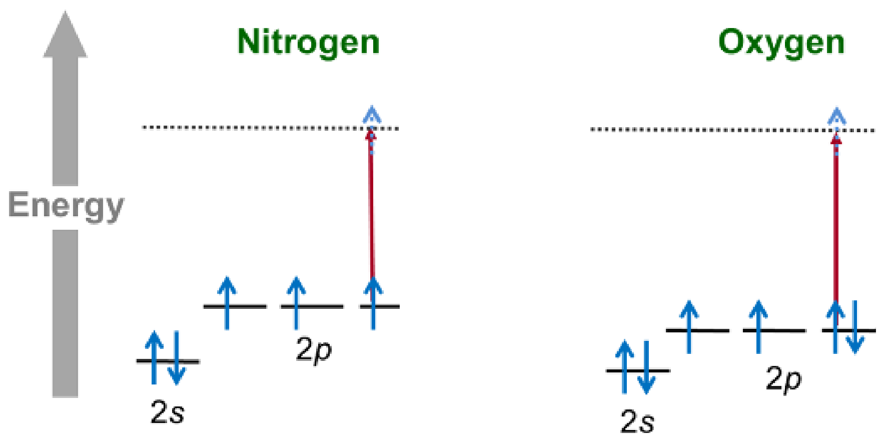
Ionization Energy

The IE_1 drops or decreases modestly on changing from ionization of a electron from a singly occupied *p* orbital in the pnictides to ionization of an electron from a double occupied *p* orbital in the chalgogenides



The ionization energy is lower than expected because of the Coulombic repulsion energy associated with the doubly occupied *p* orbital.

Example: Nitrogen (5A) and Oxygen (6A)



Clicker Question

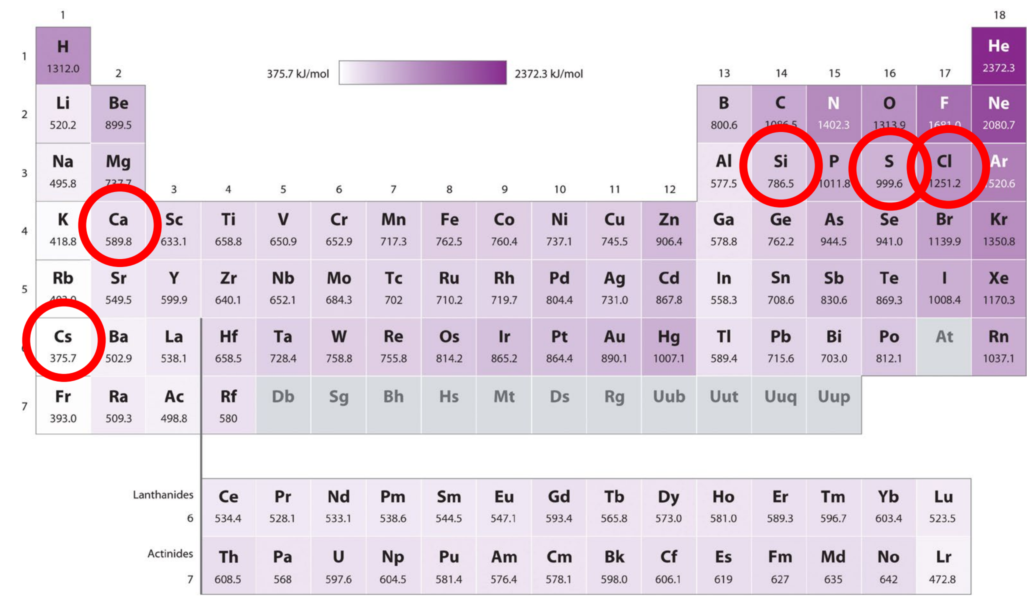
Arrange the following species in order of increasing ionization energy: Cl, Si, Ca, S, Cs.

a. Cs < S < Si < Ca < Cl

b. Cs < Si < Ca < S < Cl

c. Cl < Ca < Si < S < Cs

d. Cs < Ca < Si < S < Cl



DEMO TIME

$$2M(s) + 2H_2O(l) \rightarrow 2M^+(aq) + 2OH^-(aq) + H_2(g)$$

Or

$$2M(s) + 2H_2O(l) \rightarrow 2MOH(aq) + H_2(g)$$

where M = Li, Na, K.

- Metals are ionized.
- The solution become more basic since OH^- is being produced.
- Reactivity Order K > Na > Li

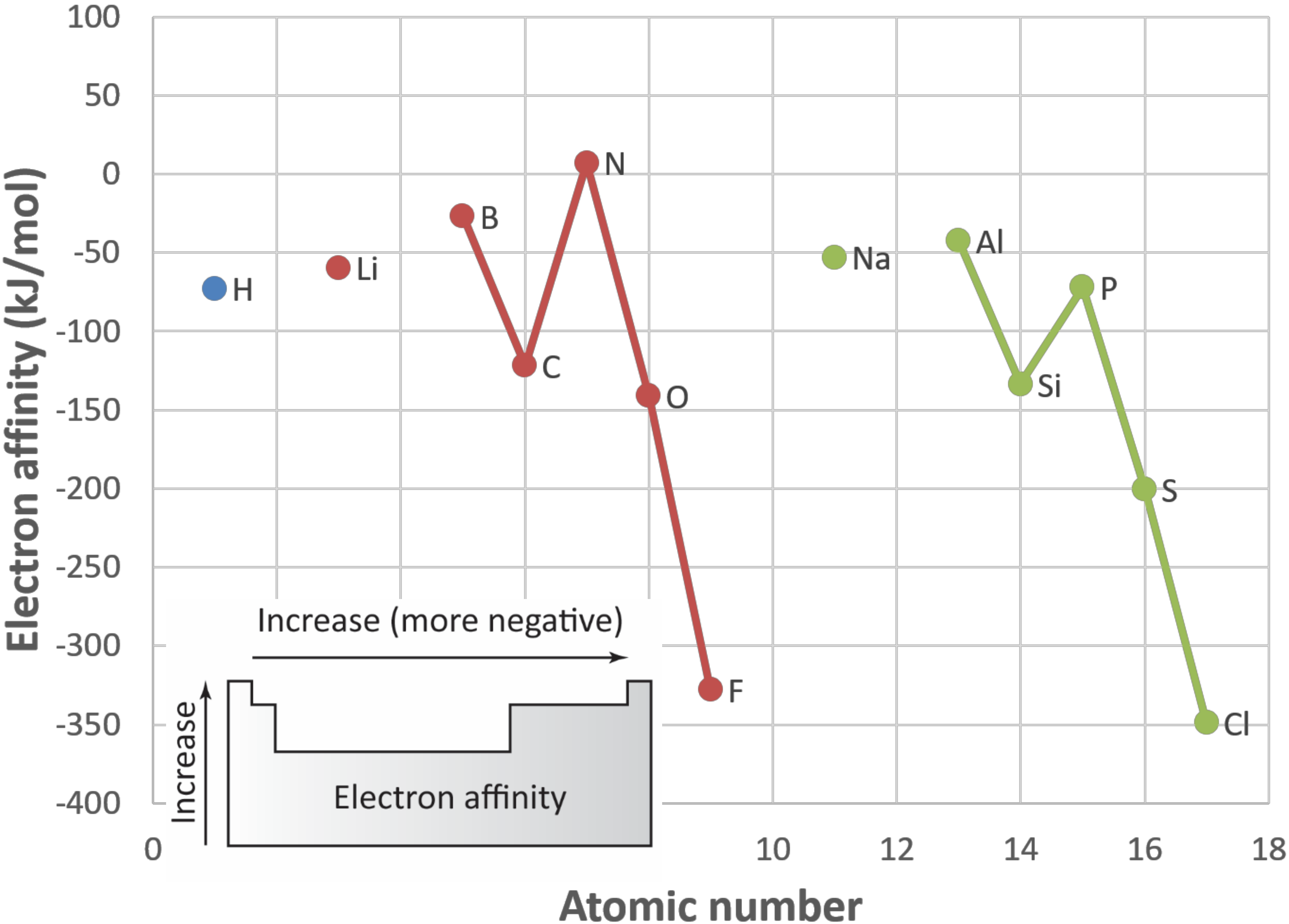
Electron Affinity (EA)

For atoms or molecules: the energy change resulting from the addition of a single electron to an atom or molecule in its gaseous state.

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

For solids: the minimum energy change resulting from adding an electron to the lowest lying electronic states (of the conduction band) of the solid.

As many elements are solids, values may be available for both, and differ due to the nature of bonding in solids. The elemental values always refer to the gas phase.



He, Be, Ne and Ar do NOT form stable anions.

Electron affinities

You do NOT need to know the values for exams but you should know the trend

≥0 kJ/mol — −348.6 kJ/mol

Period	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

Journal of Physical and Chemical Reference Data 28, no. 6 (1999).

Clicker Question

Which equation describes the <u>first ionization</u> energy of Al?

a) $Al_{(g)} + e^- \rightarrow Al^-_{(g)} + \text{energy}$

b) $Al_{(g)} + \text{energy} \rightarrow Al^+_{(g)} + e^-$

c) $Al^+_{(g)} + \text{energy} \rightarrow Al^{2+}_{(g)} + e^-$

d) $Al^-_{(g)} + \text{energy} \rightarrow Al_{(g)} + e^-$

e) $Al_{(s)} + \text{energy} \rightarrow Al^+_{(aq)} + e^-$

Clicker Question

Which equation describes the first ionization energy of Al?

a) $Al_{(g)} + e^{-} \rightarrow Al^{-}_{(g)}$ + energy (not ionization)

b) $Al_{(g)}$ + energy $\rightarrow Al^{+}_{(g)} + e^{-}$

c) $Al^{+}_{(g)}$ + energy $\rightarrow Al^{2+}_{(g)} + e^{-}$ (2nd ionization)

d) $Al^{-}_{(g)}$ + energy $\rightarrow Al_{(g)} + e^{-}$ (not ionization)

e) $Al_{(s)}$ + energy $\rightarrow Al^{+}_{(aq)} + e^{-}$ (aqueous)

Clicker Question

Which equation describes the electron <u>affinity</u> of Al?

a) $Al_{(g)} + e^- \rightarrow Al^-_{(g)}$ + energy

b) $Al_{(g)}$ + energy $\rightarrow Al^+_{(g)} + e^-$

c) $Al^+_{(g)}$ + energy $\rightarrow Al^{2+}_{(g)} + e^-$

d) $Al^-_{(g)}$ + energy $\rightarrow Al_{(g)} + e^-$

e) $Al_{(s)}$ + energy $\rightarrow Al^+_{(aq)} + e^-$

Clicker Question

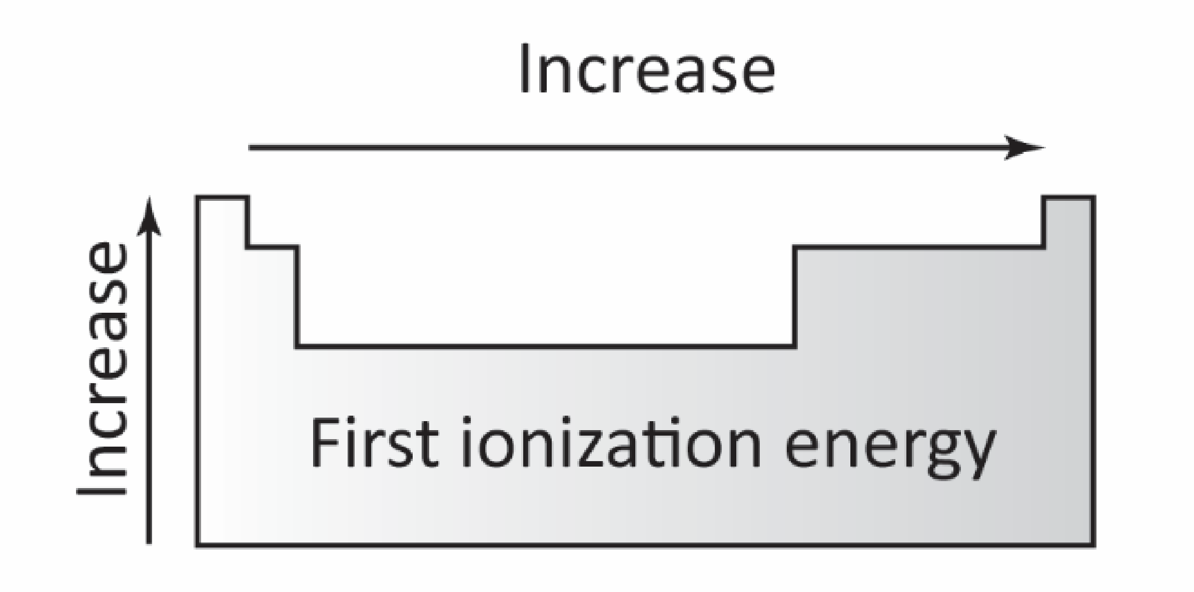
Rank the following elements in terms of increasing ionization energy:

a) Li < Na < K

b) K < Na < Li

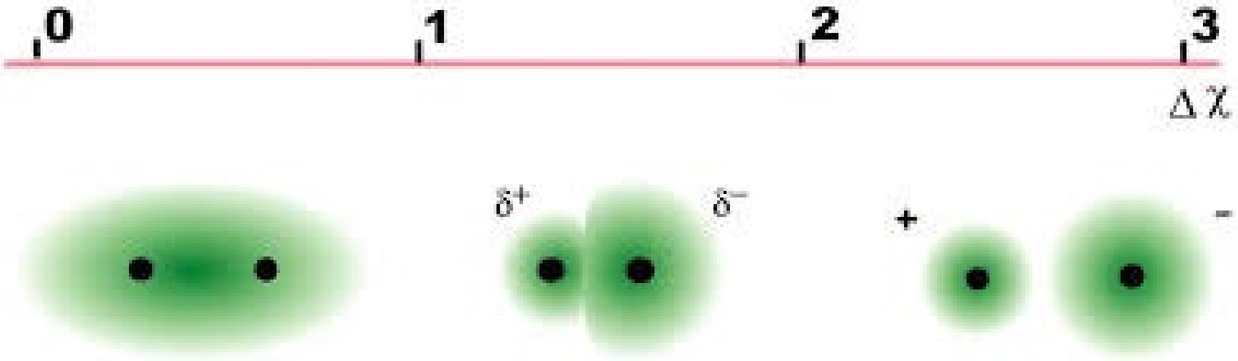
c) Na < K < Li

d) Na < Li < K



Electronegativity (EN or χ)

– The ability of an atom to <u>attract shared electrons</u> to itself <u>in a chemical bond</u>.
– <u>greater χ</u> = <u>greater affinity</u> for e^-
– not an *atomic* property because it refers to atoms in a bond
– is a <u>calculated value</u>, not measured
– correlates with IE and EA
– The greater the <u>electronegativity difference</u>, **Δ**χ , the more <u>polarized</u> a chemical bond.



Electronegativity χ Definitions

Several different prescriptions exist for χ (in kJ/mol):

- Mulliken used IE and EA values

$$\chi_{Mulliken} = 1.93 \times 10^{-3} \, (IE + |EA|) + 0.19$$

- Pauling used bond dissociation energies, E_d, to calculate EN differences between atoms A and B

$$\chi(A) - \chi(B) = 0.102 \sqrt{E_d(AB) - \tfrac{1}{2}(Ed(AA) + Ed(BB))}$$

Dissociation energy: the amount of energy required to break a chemical bond in a molecule

$E_d(AB)$: dissociation energy of A-B bond

$E_d(AA)$: dissociation energy of A-A bond

$E_d(BB)$: dissociation energy of B-B bond

Pauling Electronegativity

- Mulliken's method has no information about bonding in the Mulliken method.
- Pauling's electronegativity of an atom is a relative value of that atom's ability to attract election density toward itself when it bonds to another atom.
- **Fluorine (F)** is assigned the **highest electronegativity value of 3.98.**
- Every electronegativity value on the Pauling scale is relative to fluorine's electronegativity of 3.98.

You do NOT need to know electronegativity values for exams but you MUST know the overall trend (mnemonic: FOClN BrISCH)

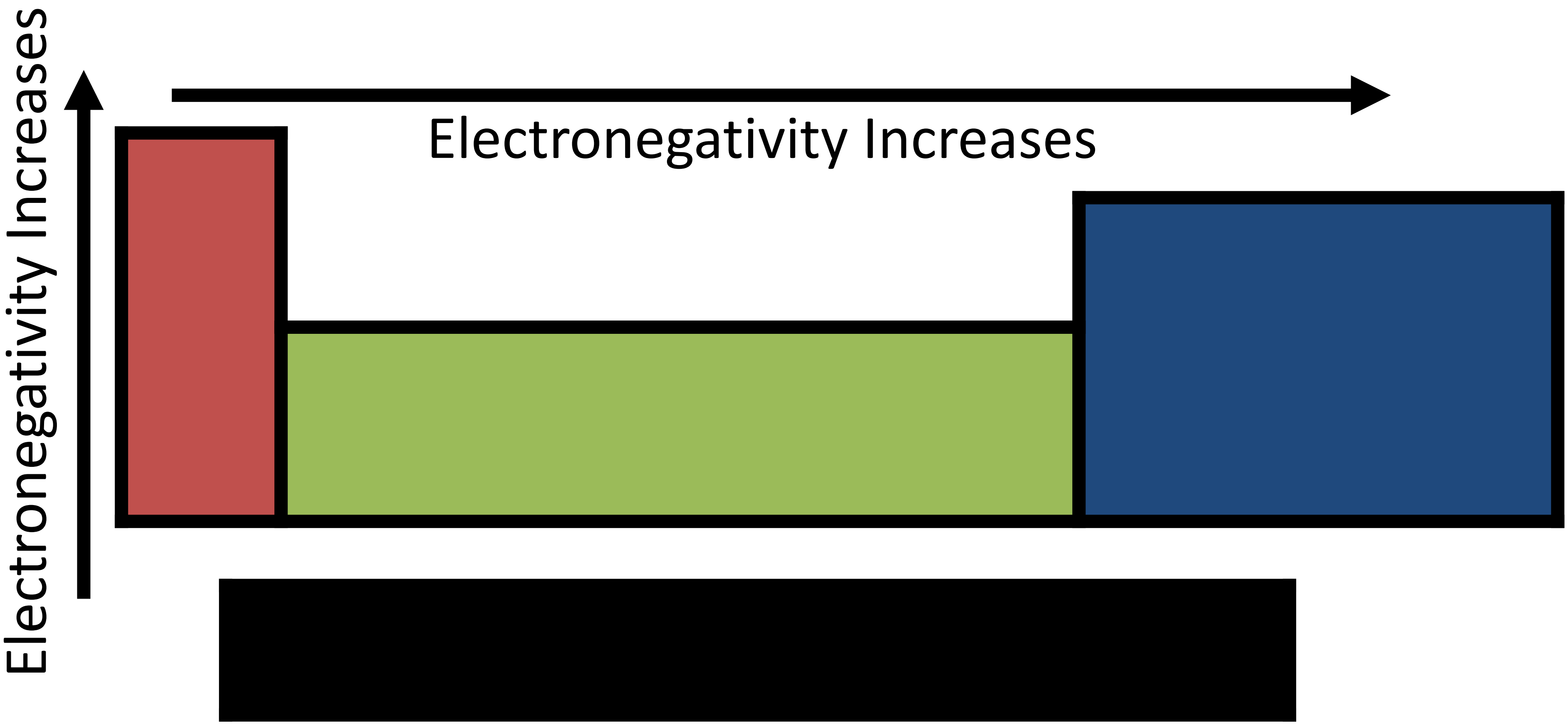
Pauling Electronegativities

H 2.20																	He
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.18	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89	La 1.1	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
Fr 0.7	Ra 0.9	Ac 1.1															

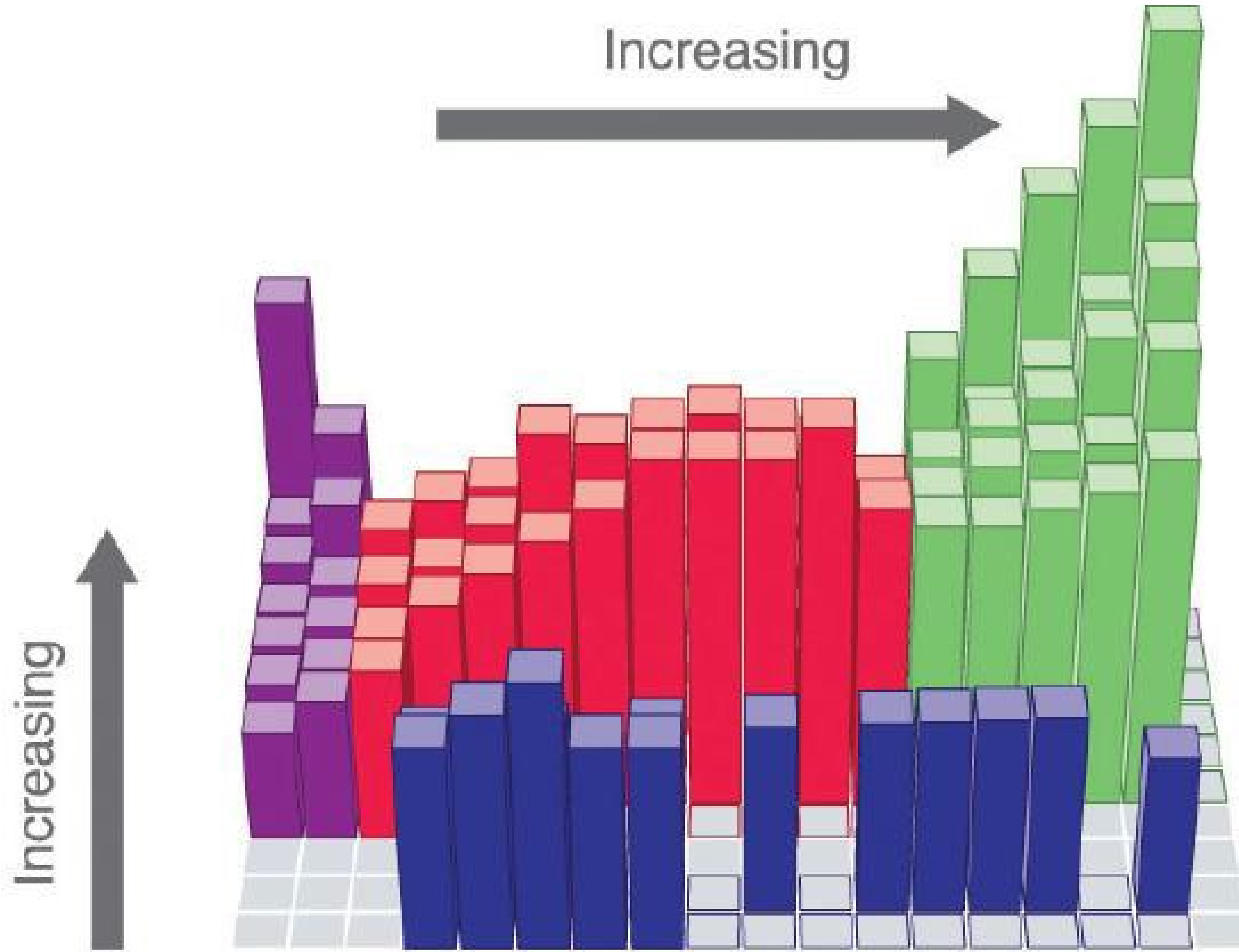
Ce 1.12	Pr 1.13	Nd 1.14	Pm 1.13	Sm 1.17	Eu 1.2	Gd 1.2	Tb 1.1	Dy 1.22	Ho 1.23	Er 1.24	Tm 1.25	Yb 1.1	Lu 1.27
Th 1.3	Pa 1.5	U 1.38	Np 1.36	Pu 1.28	Am 1.13	Cm 1.28	Bk 1.3	Cf 1.3	Es 1.3	Fm 1.3	Md 1.3	No 1.3	Lr 1.3

Electronegativity and the Periodic Table

Electronegativity generally increases from left to right of the periodic table and from bottom to top.



Pauling Electronegativity



Clicker Question

Select the sequence of atoms that are correctly listed in order of increasing electronegativity.

a) F < N < Si < Mg

b) Si < N < F < Mg

c) Mg < Si < F < N

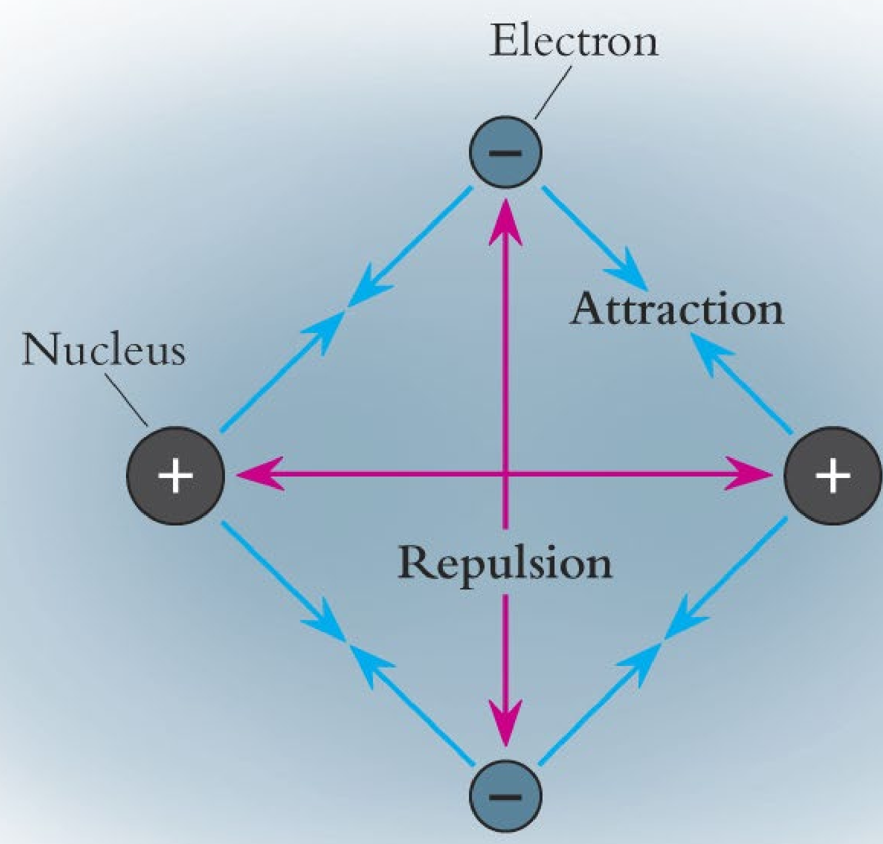
d) N < Si < Mg < F

e) Mg < Si < N < F

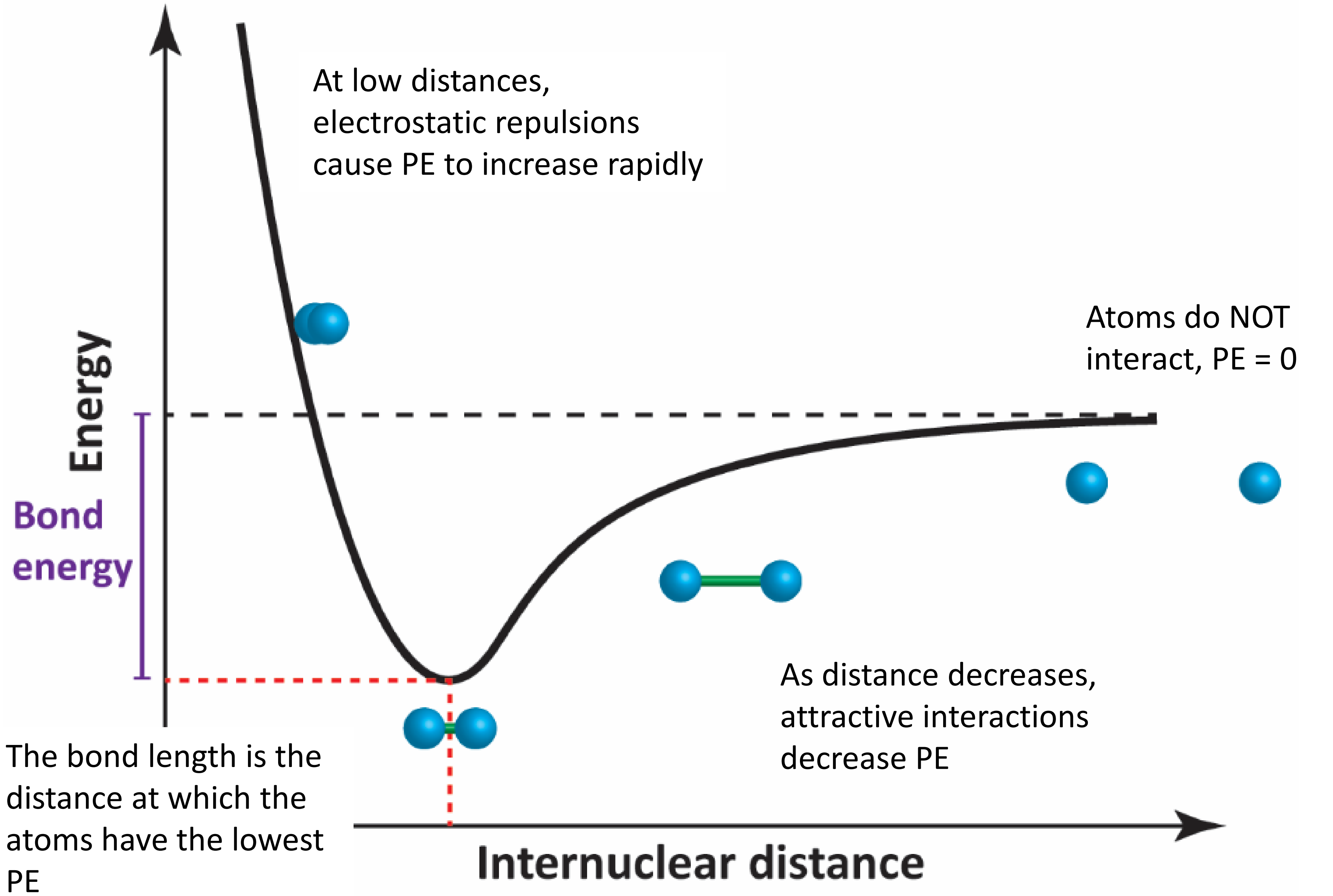
Pauling Electronegativities

H 2.20																	He
Li 0.98	Be 1.57											B 2.04	C 2.55	N 3.04	O 3.44	F 3.98	Ne
Na 0.93	Mg 1.31											Al 1.61	Si 1.90	P 2.19	S 2.58	Cl 3.16	Ar
K 0.82	Ca 1.00	Sc 1.36	Ti 1.54	V 1.63	Cr 1.66	Mn 1.55	Fe 1.83	Co 1.88	Ni 1.91	Cu 1.90	Zn 1.65	Ga 1.81	Ge 2.01	As 2.18	Se 2.55	Br 2.96	Kr 3.00
Rb 0.82	Sr 0.95	Y 1.22	Zr 1.33	Nb 1.6	Mo 2.18	Tc 1.9	Ru 2.2	Rh 2.28	Pd 2.20	Ag 1.93	Cd 1.69	In 1.78	Sn 1.96	Sb 2.05	Te 2.1	I 2.66	Xe 2.60
Cs 0.79	Ba 0.89	La 1.1	Hf 1.3	Ta 1.5	W 2.36	Re 1.9	Os 2.2	Ir 2.20	Pt 2.28	Au 2.54	Hg 2.00	Tl 1.62	Pb 1.87	Bi 2.02	Po 2.0	At 2.2	Rn 2.2
Fr 0.7	Ra 0.9	Ac 1.1															

Bonding Context



Why do bonds form?



Bond energies and bond orders

- When a bond is formed, energy is released (exothermic process).
- The **bond energy** is the energy required to break a covalent bond, and the **bond order** is the number of electron pairs shared by two atoms in a covalent bond.
- The **lattice energy** is the energy required to dissociate an ionic solid into its separate ions, and increases with the charges on the ions or as the distance between charges decreases.

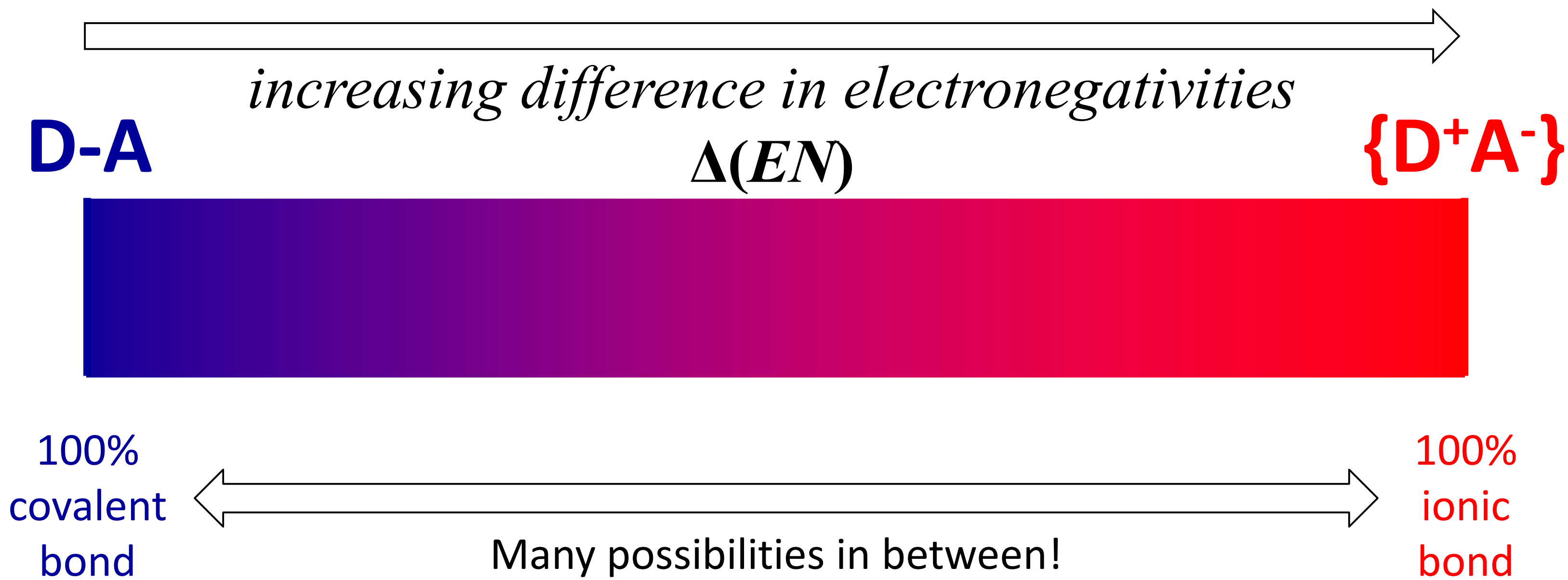
Bond energies and bond orders

Bond	Bond energy (kJ/mol)	Bond order
C-F	485	1
C-H	415	1
O-F	190	1
O-H	460	1
C – C	346	1
C = C	602	2
C ≡ C	835	3

What type of bond will form?

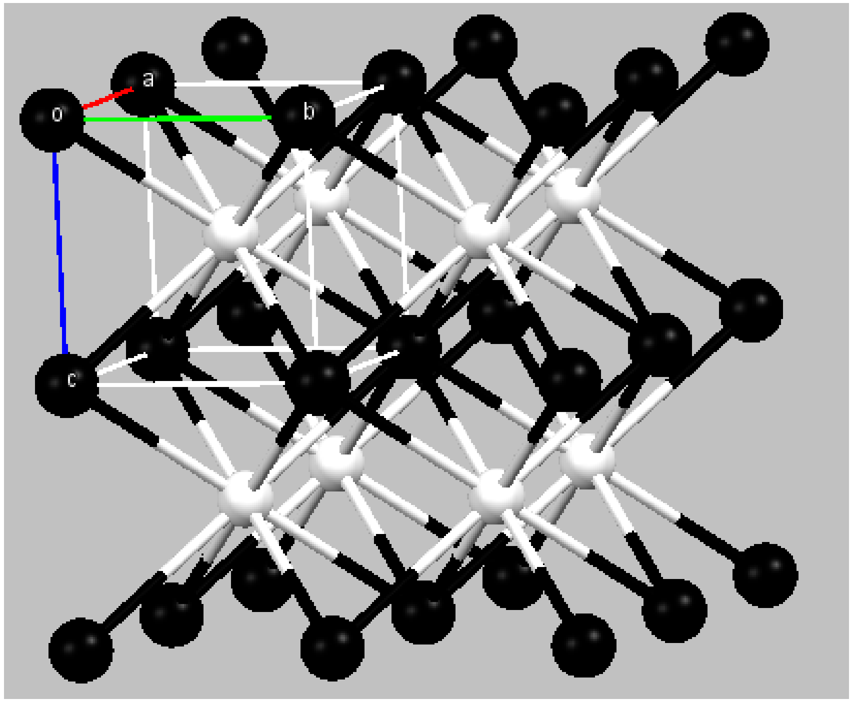
Can range from <u>covalent</u> (where a pair of electrons are <u>shared</u> between two atoms with no net charge) to <u>ionic</u> (where an electron is transferred from a donor to acceptor)

D ⇔ A



Ionic Bonding

Cesium cations (white) are electrostatically attracted to chloride anions (black). In a crystalline state, the ions form an "infinite", 3D array or lattice.



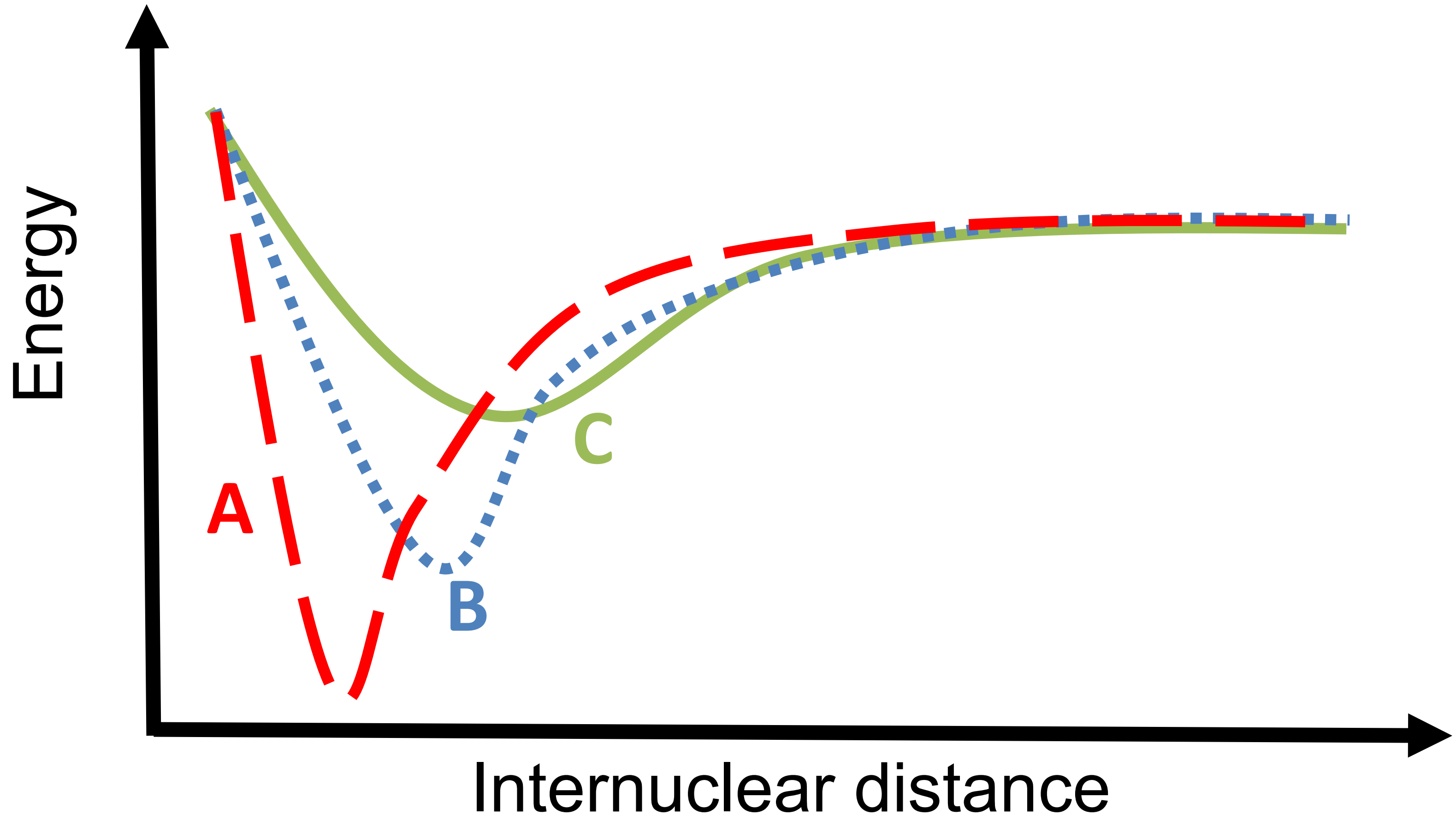
Rule of Thumb:

$\Delta(EN) \gtrsim 1.7$

for ionic bonding

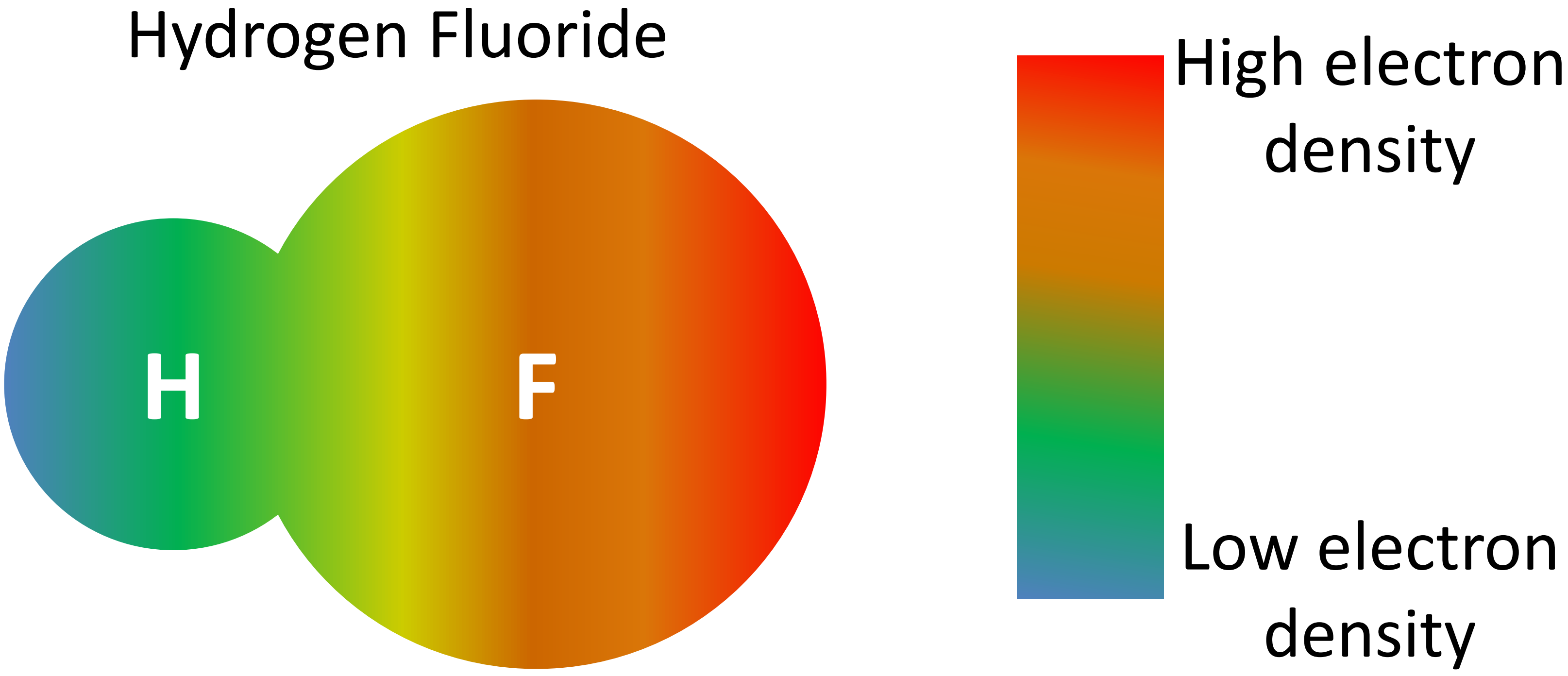
Bond Strength

- Stronger bond
  - lower potential energy
  - smaller internuclear distance



Polar covalent bonds

- In some covalent bonds electrons are not equally shared (electron density is higher in one atom than in another) due to differences in electronegativity.



Worksheet Question #9 – GOOD QUESTION

Arrange the following species in order of increasing electron density on each oxygen atom. O_2, CaO, OF_2, CO_2. *(Hint: think about what type of bonds are present)*.

$$OF_2 < O_2 < CO_2 < CaO$$

- OF_2 (polar covalent): F is more **electronegative** than O.
- O_2 (nonpolar covalent): equal electronegativity.
- CO_2 (polar covalent) : O is more **electronegative** than C.
- CaO (ionic bond): Ca is **electropositive.**

Blueprint question

http://www.spectro-oil.com/laboratory-services-aviation.html
http://news.commercialaircraft.bombardier.com/wp-content/gallery/engine-run/right_engine.jpg

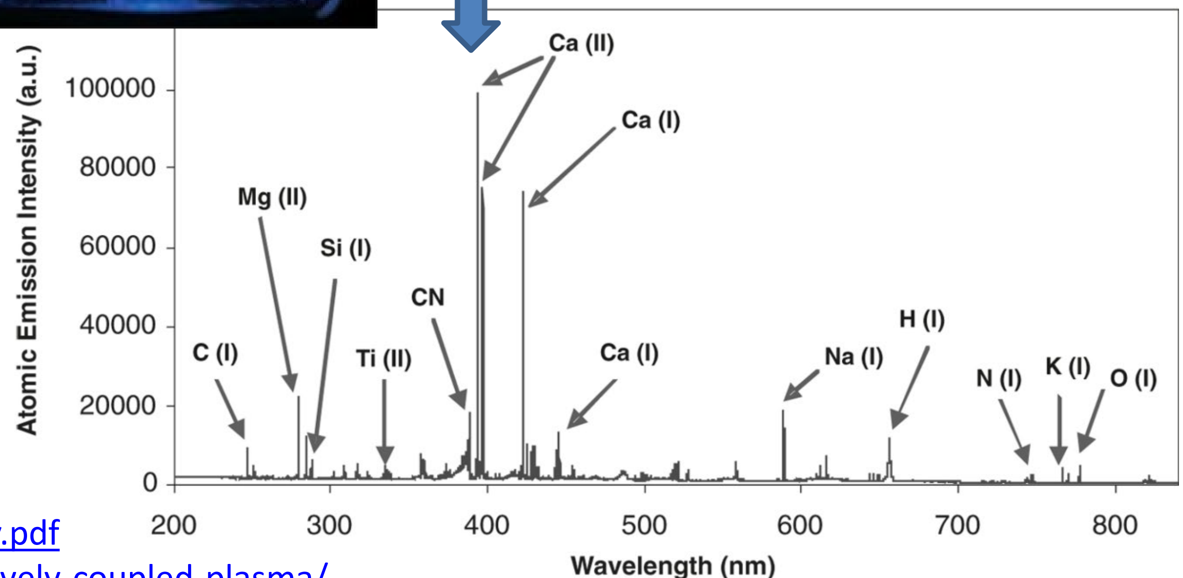
FEATURED CASE STUDY

The benefits of routine SOAP checks

<u>S</u>pectrometric <u>O</u>il <u>A</u>nalysis <u>P</u>rogram

Engine oil filtered to capture metal wear particles

Analysis of particles by **atomic emission** to determine metal composition and origin (which part?)



http://www.spectro-oil.com/borsc_case_study.pdf

http://blog.labplanet.com/2011/12/19/inductively-coupled-plasma/

Hosseinimakarem & Tavassoli, J Biomed Optics. 2011, 16(5), 057002. doi:10.1117/1.3574757