

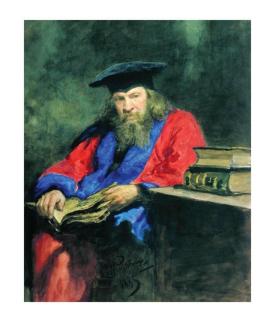
### Lecture 04

# Periodic Properties of the Elements

bảng tuần hoàn

## Mendeleev (1834–1907)

- Ordered elements by atomic mass
- Saw a repeating pattern of properties
- Periodic law: When the elements are arranged in order of increasing atomic mass, certain sets of properties recur periodically.



- Put elements with similar properties in the same column
- Used pattern to predict properties of undiscovered elements
- Where atomic mass order did not fit other properties, he reordered by other properties.
  - Te and I

## **Mendeleev's Predictions**

#### Gallium (eka-aluminum)



Atomic mass

Melting point

Formula of oxide

Density

Mendeleev's predicted properties

About 68 amu

Low

Actual properties

69.72 amu

29.8 °C

 $5.9 \text{ g/cm}^3$  $5.90 \text{ g/cm}^3$ 

 $Ga_2O_3$  $X_2O_3$ 

Formula of chloride  $XCl_3$ GaCl<sub>3</sub>

#### Germanium (eka-silicon)



Mendeleev's predicted properties

Actual properties

Atomic mass

Density

Formula of oxide

Formula of chloride

About 72 amu

 $5.5 \text{ g/cm}^3$ 

 $XO_2$ 

 $XCl_4$ 

72.64 amu

 $5.35 \, \text{g/cm}^3$ 

GeO<sub>2</sub>

 $GeCl_4$ 

## What versus Why

 Mendeleev's periodic law allows us to predict what the properties of an element will be based on its position on the table.

It doesn't explain why the pattern exists.

- Quantum mechanics is a theory that explains why the periodic trends in the properties exist.
  - Knowing why allows us to predict what.

## Coulomb's Law

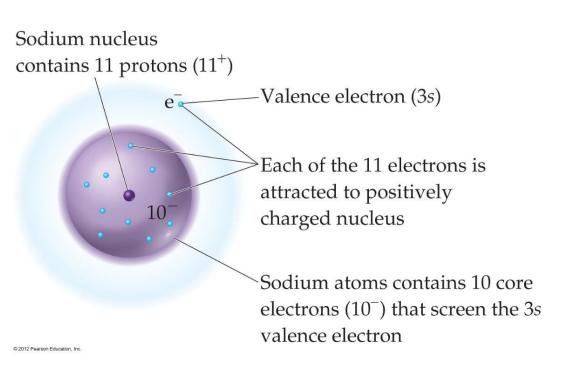
$$E = \frac{1}{4\pi\varepsilon_0} \frac{q_1 q_2}{r}$$

- Coulomb's law describes the attractions and repulsions between charged particles.
- For like charges, the potential energy (E) is positive and decreases as the particles get farther apart as r increases.
- For opposite charges, the potential energy is negative and becomes more negative as the particles get closer together.
- The strength of the interaction increases as the size of the charges increases.
  - Electrons are more strongly attracted to a nucleus with a 2+ charge than a nucleus with a 1+ charge.

## **Shielding and Effective Nuclear Charge**

- Each electron in a multielectron atom experiences both the attraction to the nucleus and the repulsion by other electrons in the atom.
- These repulsions cause the electron to have a net reduced attraction to the nucleus; it is shielded from the nucleus.
- The total amount of attraction that an electron feels for the nucleus is called the effective nuclear charge of the electron.

## **Shielding and Effective Nuclear Charge**



The effective nuclear charge,  $Z_{\text{eff}}$ , is found this way:

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

where Z is the atomic number and S is a screening constant, usually close to the number of inner electrons.

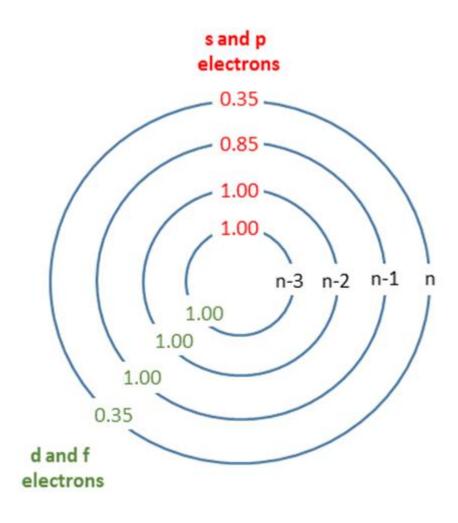
S: calculated from the Slater's rules (next slides)

### Slater's Rules

- 1) Write the electron configuration for the atom using the following design: (1s)(2s,2p)(3s,3p) (3d) (4s,4p) (4d) (4f) (5s,5p)
- 2) Any electrons to the right of the electron of interest contributes no shielding.
- 3) All other electrons in the same group as the electron of interest shield to an extent of 0.35 nuclear charge units
- 4) If the electron of interest is an s or p electron: All electrons with one less value of the principal quantum number (n-1 shell) shield to an extent of 0.85 units of nuclear charge. All electrons with two less values of the principal quantum number (n-2 shell) shield to an extent of 1.00 units.
- 5) If the electron of interest is an *d* or *f* electron: All electrons to the left shield to an extent of 1.00 units of nuclear charge.
- 6) Sum the shielding amounts from steps 2 through 5 and subtract from the nuclear charge value to obtain the effective nuclear charge.

## **Shielding and Effective Nuclear Charge**

Slater's Rules: Calculation of shielding value (S)



## **Shielding and Effective Nuclear Charge**

Slater's Rules: Calculation of shielding value (S)

#### **Element: N**

Configuration: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>3</sup>

n-value grouping: (1s)<sup>2</sup>(2s2p)<sup>5</sup>

Groupings via Slater: (1s)<sup>2</sup>(2s2p)<sup>5-1=4</sup>

Slater's shielding value:  $2 \times 0.85 + 4 \times 0.35 = 3.1$ 

 $Z_{\text{eff}}$ : 7-3.1 = 3.9

#### **Element: Zn**

Configuration: 1s<sup>2</sup>2s<sup>2</sup>2p<sup>6</sup>3s<sup>2</sup>3p<sup>6</sup>3d<sup>10</sup>4s<sup>2</sup>

n-value grouping:  $(1s)^2(2s2p)^8(3s3p)^8(3d)^{10}4s^2$ 

Groupings via Slater:  $(1s)^2(2s2p)^8(3s3p)^8(3d)^{10}4s^{2-1=1}$ 

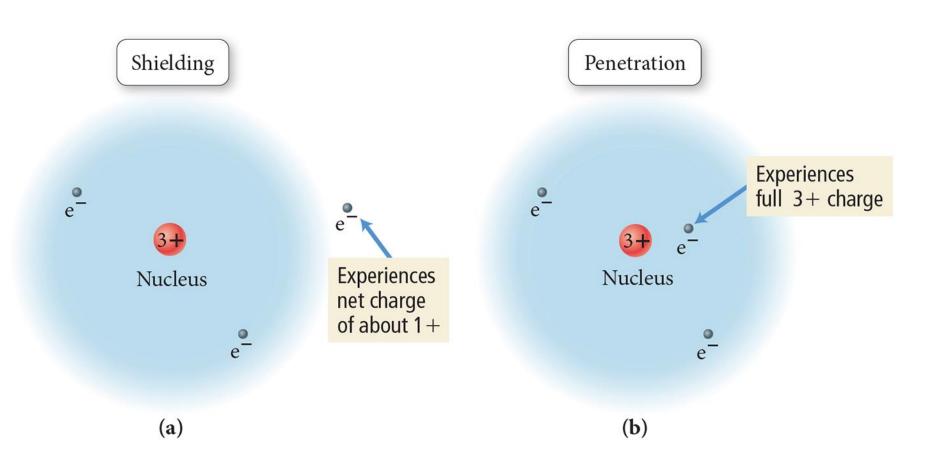
Slater's shielding value: 2x1+8x1+ 18\*0.85+1x0.35= 25.65

 $Z_{\text{eff}}$ : 30- 25.65 = 4.35

## **Penetration**

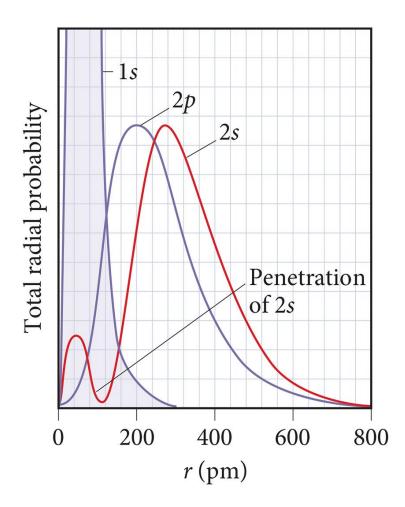
- The closer an electron is to the nucleus, the more attraction it experiences.
- The better an outer electron is at penetrating through the electron cloud of inner electrons, the more attraction it will have for the nucleus.
- The degree of penetration is related to the orbital's radial distribution function.
  - In particular, the distance the maxima of the function are from the nucleus

## **Shielding and Penetration**



## **Penetration and Shielding**

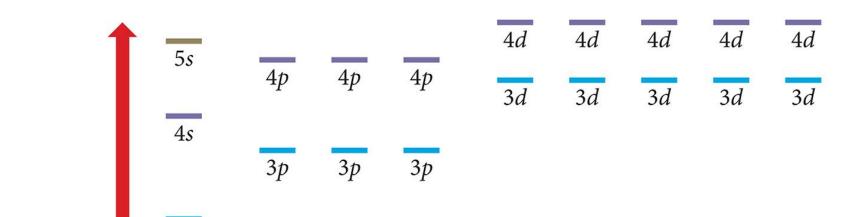
- The radial distribution function shows that the 2s orbital penetrates more deeply into the 1s orbital than does the 2p.
- The weaker penetration of the 2*p* sublevel means that electrons in the 2*p* sublevel experience more repulsive force; they are more shielded from the attractive force of the nucleus.
- The deeper penetration of the 2s electrons means electrons in the 2s sublevel experience a greater attractive force to the nucleus and are not shielded as effectively.



## **Effect of Penetration and Shielding**

- Penetration causes the energies of sublevels in the same principal level to not be degenerate.
- In the fourth and fifth principal levels, the effects of penetration become so important that the s orbital lies lower in energy than the d orbitals of the previous principal level.
- The energy separations between one set of orbitals and the next become smaller beyond the 4s.
  - The ordering can therefore vary among elements, causing variations in the electron configurations of the transition metals and their ions.

#### **General Energy Ordering of Orbitals for Multielectron Atoms**



Energy

2*s* 

3s

## **Valence Electrons**

 The electrons in all the sublevels with the highest principal energy shell are called the valence electrons.

Electrons in lower energy shells are called core electrons.

 One of the most important factors in the way an atom behaves, both chemically and physically, is the number of valence electrons.

## **Outer Electron Configurations of Elements 1–18**

1A							8A
1							2 <b>He</b>
<b>H</b> 1s <sup>1</sup>	2A	3A	4A	5A	6A	7A	$1s^2$
3 <b>Li</b> 2s <sup>1</sup>	4 Be 2s <sup>2</sup>	$ \begin{array}{c} 5 \\ \mathbf{B} \\ 2s^2 2p^1 \end{array} $	$ \begin{array}{c} 6 \\ \mathbf{C} \\ 2s^2 2p^2 \end{array} $	$ \begin{array}{c} 7 \\ \mathbf{N} \\ 2s^2 2p^3 \end{array} $	$\begin{array}{c c} 8 \\ \mathbf{O} \\ 2s^2 2p^4 \end{array}$	$ \begin{array}{c} 9 \\ \mathbf{F} \\ 2s^2 2p^5 \end{array} $	$ \begin{array}{c c} 10 \\ \mathbf{Ne} \\ 2s^2 2p^6 \end{array} $
11 <b>Na</b> 3s <sup>1</sup>	12 <b>Mg</b> 3s <sup>2</sup>	$ \begin{array}{c} 13 \\ \mathbf{Al} \\ 3s^2 3p^1 \end{array} $	14	15	16	17	18

## Electron Configuration and the Periodic Table

 The group number corresponds to the number of valence electrons.

 The length of each "block" is the maximum number of electrons the sublevel can hold.

 The period number corresponds to the principal energy level of the valence electrons.

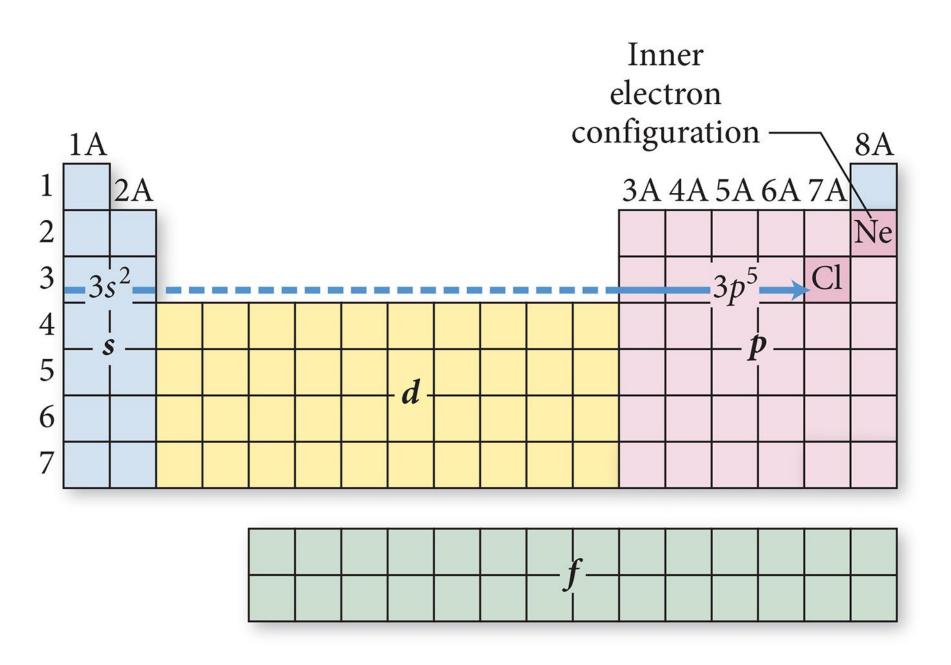
#### **Orbital Blocks of the Periodic Table**

	Groups 1																	18
1	1A 1 H 1s <sup>1</sup>	2 2A				ock elei lock ele		p	13 3A	14 4A	15 5A	16 6A	17 7A	8A 2 <b>He</b> 1s <sup>2</sup>				
2	3 <b>Li</b> 2s <sup>1</sup>	4 Be 2s <sup>2</sup>										ĺ	$\mathbf{\overset{5}{B}}_{2s^22p^1}$	$ \begin{array}{c} 6 \\ C \\ 2s^2 2p^2 \end{array} $	$ \begin{array}{c} 7 \\ \mathbf{N} \\ 2s^2 2p^3 \end{array} $	$\mathbf{O}$ $2s^22p^4$	9 <b>F</b> 2s <sup>2</sup> 2p <sup>5</sup>	10 Ne 2s <sup>2</sup> 2p <sup>6</sup>
3	11 <b>Na</b> 3s <sup>1</sup>	12 <b>Mg</b> 3s <sup>2</sup>	3 3B	4 4B	5 5B	6 6B	7 7B	8	9 — 8B —	10	11 1B	12 2B	13 <b>Al</b> 3s <sup>2</sup> 3p <sup>1</sup>	14 <b>Si</b> 3s <sup>2</sup> 3p <sup>2</sup>	$ \begin{array}{c} 15 \\ \mathbf{P} \\ 3s^2 3p^3 \end{array} $	16 <b>S</b> 3s <sup>2</sup> 3p <sup>4</sup>	$CI$ $3s^23p^5$	$ \begin{array}{c} 18 \\ \mathbf{Ar} \\ 3s^2 3p^6 \end{array} $
Periods 4	19 <b>K</b> 4s <sup>1</sup>	20 <b>Ca</b> 4s <sup>2</sup>	$ \begin{array}{c} 21 \\ \mathbf{Sc} \\ 4s^2 3d^1 \end{array} $	22 <b>Ti</b> $4s^23d^2$	$v$ $4s^23d^3$	24 Cr 4s <sup>1</sup> 3d <sup>5</sup>	$ \begin{array}{c} 25 \\ \mathbf{Mn} \\ 4s^2 3d^5 \end{array} $	26 <b>Fe</b> $4s^23d^6$	$\frac{27}{\text{Co}}$ $4s^23d^7$	28 <b>Ni</b> 4s <sup>2</sup> 3d <sup>8</sup>	29 <b>Cu</b> 4s <sup>1</sup> 3d <sup>10</sup>	$ \begin{array}{c} 30 \\ \mathbf{Zn} \\ 4s^2 3d^{10} \end{array} $	$ \begin{array}{c} 31 \\ \mathbf{Ga} \\ 4s^2 4p^1 \end{array} $	32 <b>Ge</b> 4s <sup>2</sup> 4p <sup>2</sup>	$ \begin{array}{c} 33 \\ \mathbf{As} \\ 4s^2 4p^3 \end{array} $	34 <b>Se</b> 4s <sup>2</sup> 4p <sup>4</sup>	$ \begin{array}{c} 35 \\ \mathbf{Br} \\ 4s^2 4p^5 \end{array} $	36 <b>Kr</b> 4s <sup>2</sup> 4p <sup>6</sup>
5	37 <b>Rb</b> 5s <sup>1</sup>	38 <b>Sr</b> 5s <sup>2</sup>	39 <b>Y</b> 5s <sup>2</sup> 4d <sup>1</sup>	$ \begin{array}{c} 40 \\ \mathbf{Zr} \\ 5s^2 4d^2 \end{array} $	41 <b>Nb</b> 5s <sup>1</sup> 4d <sup>4</sup>	42 <b>Mo</b> 5s <sup>1</sup> 4d <sup>5</sup>	43 <b>Tc</b> 5s <sup>2</sup> 4d <sup>5</sup>	44 <b>Ru</b> 5s <sup>1</sup> 4d <sup>7</sup>	45 <b>Rh</b> 5s <sup>1</sup> 4d <sup>8</sup>	46 <b>Pd</b> 4d <sup>10</sup>	47 <b>Ag</b> 5s <sup>1</sup> 4d <sup>10</sup>	$\frac{48}{\mathbf{Cd}}$ $5s^24d^{10}$	49 <b>In</b> 5s <sup>2</sup> 5p <sup>1</sup>	$ \begin{array}{c} 50 \\ \mathbf{Sn} \\ 5s^2 5p^2 \end{array} $	$51$ <b>Sb</b> $5s^25p^3$	52 <b>Te</b> 5s <sup>2</sup> 5p <sup>4</sup>	53 I 5s <sup>2</sup> 5p <sup>5</sup>	54 <b>Xe</b> 5s <sup>2</sup> 5p <sup>6</sup>
6	55 <b>Cs</b> 6s <sup>1</sup>	56 <b>Ba</b> 6s <sup>2</sup>	57 <b>La</b> 6s <sup>2</sup> 5d <sup>1</sup>	72 <b>Hf</b> 6s <sup>2</sup> 5d <sup>2</sup>	73 <b>Ta</b> 6s <sup>2</sup> 5d <sup>3</sup>	74 W 6s <sup>2</sup> 5d <sup>4</sup>	75 <b>Re</b> 6s <sup>2</sup> 5d <sup>5</sup>	76 <b>Os</b> 6s <sup>2</sup> 5d <sup>6</sup>	77 <b>Ir</b> 6s <sup>2</sup> 5d <sup>7</sup>	78 <b>Pt</b> 6s <sup>1</sup> 5d <sup>9</sup>	79 <b>Au</b> 6s <sup>1</sup> 5d <sup>10</sup>	80 <b>Hg</b> 6s <sup>2</sup> 5d <sup>10</sup>	81 <b>Tl</b> 6s <sup>2</sup> 6p <sup>1</sup>	82 <b>Pb</b> 6s <sup>2</sup> 6p <sup>2</sup>	83 <b>Bi</b> 6s <sup>2</sup> 6p <sup>3</sup>	84 <b>Po</b> 6s <sup>2</sup> 6p <sup>4</sup>	85 <b>At</b> 6s <sup>2</sup> 6p <sup>5</sup>	86 <b>Rn</b> 6s <sup>2</sup> 6p <sup>6</sup>
7	87 <b>Fr</b> 7s <sup>1</sup>	88 <b>Ra</b> 7 <i>s</i> <sup>2</sup>	89 <b>Ac</b> 7s <sup>2</sup> 6d <sup>1</sup>	104 <b>Rf</b> 7s <sup>2</sup> 6d <sup>2</sup>	105 <b>Db</b> 7s <sup>2</sup> 6d <sup>3</sup>	106 <b>Sg</b> 7s <sup>2</sup> 6d <sup>4</sup>	107 <b>Bh</b>	108 <b>Hs</b>	109 <b>Mt</b>	110 <b>Ds</b>	111 Rg	112 <b>Cn</b>	113	114 <b>Fl</b>	115 **	116 <b>Lv</b>	117 **	118

Lanthanides

Actinides

3	58	59	60	61	62	63	64	65	66	67	68	69	70	71
	<b>Ce</b>	<b>Pr</b>	<b>Nd</b>	<b>Pm</b>	<b>Sm</b>	<b>Eu</b>	<b>Gd</b>	<b>Tb</b>	<b>Dy</b>	<b>Ho</b>	Er	<b>Tm</b>	<b>Yb</b>	<b>Lu</b>
	6s <sup>2</sup> 4f <sup>1</sup> 5d <sup>1</sup>	6s <sup>2</sup> 4f <sup>3</sup>	6s <sup>2</sup> 4f <sup>4</sup>	6s <sup>2</sup> 4f <sup>5</sup>	6s <sup>2</sup> 4f <sup>6</sup>	6s <sup>2</sup> 4f <sup>7</sup>	6s <sup>2</sup> 4f <sup>7</sup> 5d <sup>1</sup>	6s <sup>2</sup> 4f <sup>9</sup>	6s <sup>2</sup> 4f <sup>10</sup>	6s <sup>2</sup> 4f <sup>11</sup>	6s <sup>2</sup> 4f <sup>12</sup>	6s <sup>2</sup> 4f <sup>13</sup>	6s <sup>2</sup> 4f <sup>14</sup>	6s <sup>2</sup> 4f <sup>14</sup> 5d <sup>1</sup>
3	90	91	92	93	94	95	96	97	98	99	100	101	102	103
	<b>Th</b>	<b>Pa</b>	<b>U</b>	<b>Np</b>	<b>Pu</b>	<b>Am</b>	<b>Cm</b>	<b>Bk</b>	<b>Cf</b>	<b>Es</b>	<b>Fm</b>	<b>Md</b>	<b>No</b>	<b>Lr</b>
	7s <sup>2</sup> 6d <sup>2</sup>	7s <sup>2</sup> 5f <sup>2</sup> 6d <sup>1</sup>	7s <sup>2</sup> 5f <sup>3</sup> 6d <sup>1</sup>	7s <sup>2</sup> 5f <sup>4</sup> 6d <sup>1</sup>	7s <sup>2</sup> 5f <sup>6</sup>	7 <i>s</i> <sup>2</sup> 5 <i>f</i> <sup>7</sup>	7s <sup>2</sup> 5f <sup>7</sup> 6d <sup>1</sup>	7s <sup>2</sup> 5f <sup>9</sup>	7 <i>s</i> <sup>2</sup> 5 <i>f</i> <sup>10</sup>	7 <i>s</i> <sup>2</sup> 5 <i>f</i> <sup>11</sup>	7s <sup>2</sup> 5f <sup>12</sup>	7s <sup>2</sup> 5f <sup>13</sup>	7s <sup>2</sup> 5f <sup>14</sup>	7s <sup>2</sup> 5f <sup>14</sup> 6d <sup>1</sup>



## Irregular Electron Configurations

- We know that, because of sublevel splitting, the 4s sublevel is lower in energy than the 3d; therefore, the 4s fills before the 3d.
- But the difference in energy is not large.
- Some of the transition metals have irregular electron configurations in which the ns only partially fills before the (n−1)d or doesn't fill at all.
- Therefore, their electron configuration must be found experimentally.

## **Irregular Electron Configurations**

- Expected
- $Cr = [Ar]4s^23d^4$
- Cu =  $[Ar]4s^23d^9$
- Mo =  $[Kr]5s^24d^4$
- Ru =  $[Kr]5s^24d^6$
- Pd =  $[Kr]5s^24d^8$

- Found experimentally
- $Cr = [Ar]4s^13d^5$
- $Cu = [Ar]4s^13d^{10}$
- Mo =  $[Kr]5s^14d^5$
- Ru =  $[Kr]5s^14d^7$
- Pd =  $[Kr]5s^04d^{10}$

**Properties and Electron Configuration** 

- The properties of the elements follow a periodic pattern.
  - Elements in the same column have similar properties.
  - The elements in a period show a pattern that repeats.
- The quantum-mechanical model explains this because the number of valence electrons and the types of orbitals they occupy are also periodic.

8A
2 <b>He</b> 1s <sup>2</sup>
10 <b>Ne</b> 2s <sup>2</sup> 2p <sup>6</sup>
$ \begin{array}{c} 18 \\ \mathbf{Ar} \\ 3s^2 3p^6 \end{array} $
36 <b>Kr</b> 4s <sup>2</sup> 4p <sup>6</sup>
54 <b>Xe</b> 5s <sup>2</sup> 5p <sup>6</sup>
86 <b>Rn</b> 6s <sup>2</sup> 6p <sup>6</sup>

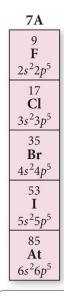
	1
Noble	
Noble	
gases	
0	

2A	
4 <b>Be</b> 2s <sup>2</sup>	
12 <b>Mg</b> 3s <sup>2</sup>	
20 <b>Ca</b> 4s <sup>2</sup>	
38 <b>Sr</b> 5s <sup>2</sup>	
56 <b>Ba</b> 6s <sup>2</sup>	
88 <b>Ra</b> 7s <sup>2</sup>	

```
Alkaline earth
metals
```

1A
3 <b>Li</b> 2s <sup>1</sup>
11 <b>Na</b> 3s <sup>1</sup>
19 <b>K</b> 4s <sup>1</sup>
37 <b>Rb</b> 5s <sup>1</sup>
55 <b>Cs</b> 6s <sup>1</sup>
87 <b>Fr</b> 7 <i>s</i> <sup>1</sup>

-	
	Alkali
	AIKaii
	metals
	metais



Halogens

## The Noble Gas Electron Configuration

- The noble gases have eight valence electrons.
  - Except for He, which has only two electrons
- They are especially nonreactive.
  - He and Ne are practically inert.
- The reason the noble gases are so nonreactive is that the electron configuration of the noble gases is especially stable.

8A
2 <b>He</b> 1s <sup>2</sup>
$ \begin{array}{c} 10 \\ \text{Ne} \\ 2s^2 2p^6 \end{array} $
$ \begin{array}{c} 18 \\ \mathbf{Ar} \\ 3s^2 3p^6 \end{array} $
$ \begin{array}{c} 36 \\ \mathbf{Kr} \\ 4s^2 4p^6 \end{array} $
$ \begin{array}{c} 54 \\ \mathbf{Xe} \\ 5s^2 5p^6 \end{array} $
86 <b>Rn</b> 6s <sup>2</sup> 6p <sup>6</sup>

Noble gases

## The Alkali Metals

 The alkali metals have one more electron than the previous noble gas.

- In their reactions, the alkali metals tend to lose one electron, resulting in the same electron configuration as a noble gas.
  - Forming a cation with a 1+ charge

1A 3 Li  $2s^1$ 11 Na  $3s^1$ 19 K  $4s^1$ 37 Rb  $5s^1$ 55 Cs  $6s^1$ 87 Fr  $7s^1$ 

Alkali metals

## The Halogens

- Have one fewer electron than the next noble gas
- In their reactions with metals, the halogens tend to gain an electron and attain the electron configuration of the next noble gas, forming an anion with charge 1-.
- In their reactions with nonmetals, they tend to share electrons with the other nonmetal so that each attains the electron configuration of a noble gas.

7A
$ \begin{array}{c} 9 \\ \mathbf{F} \\ 2s^2 2p^5 \end{array} $
$17$ Cl $3s^23p^5$
35 Br  4s24p5
$ \begin{array}{c} 53 \\ \mathbf{I} \\ 5s^2 5p^5 \end{array} $
85 <b>At</b> 6s <sup>2</sup> 6p <sup>5</sup>

Halogens

## **Electron Configuration and Ion Charge**

- We have seen that many metals and nonmetals form one ion and that the charge on that ion is predictable based on its position on the periodic table.
  - Group 1A = 1+, group 2A = 2+, group 7A = 1-, group 6A = 2-, etc.

 These atoms form ions that will result in an electron configuration that is the same as the nearest noble gas.

#### **Elements That Form Ions with Predictable Charges**

	1A	2A											3A	4A	5A	6A	7A	8A
1	Li <sup>+</sup>														N <sup>3-</sup>	O <sup>2-</sup>	F <sup>-</sup>	
2	Na <sup>+</sup>	Mg <sup>2+</sup>	3B	4B	5B	6B	7B	_	- 8B -	_	1B	2B	Al <sup>3+</sup>			S <sup>2-</sup>	Cl <sup>-</sup>	
3	K <sup>+</sup>	Ca <sup>2+</sup>														Se <sup>2-</sup>	Br <sup>-</sup>	
4	Rb <sup>+</sup>	Sr <sup>2+</sup>														Te <sup>2-</sup>	I-	
5	Cs <sup>+</sup>	Ba <sup>2+</sup>											,					

## **Electron Configuration of Anions in Their Ground State**

- Anions are formed when nonmetal atoms gain enough electrons to have eight valence electrons.
  - Filling the s and p sublevels of the valence shell
- The sulfur atom has six valence electrons.

S atom = 
$$1s^22s^22p^63s^23p^4$$

 To have eight valence electrons, sulfur must gain two more.

$$S^{2-}$$
 anion =  $1s^22s^22p^63s^23p^6$ 

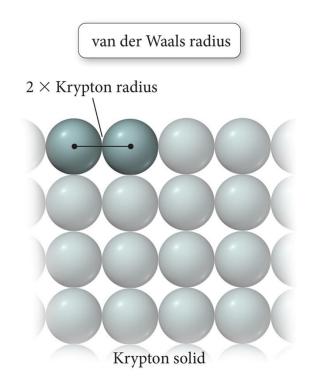
## **Electron Configuration of Cations in Their Ground State**

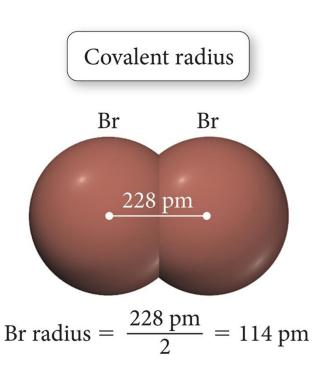
- Cations are formed when a metal atom loses all its valence electrons, resulting in a new lower energy level valence shell.
  - However, the process is always endothermic.
- The magnesium atom has two valence electrons. Mg atom =  $1s^22s^22p^63s^2$
- When magnesium forms a cation, it loses its valence electrons.

 $Mg^{2+}$  cation =  $1s^22s^22p^6$ 

## **Trend in Atomic Radius: Main Group**

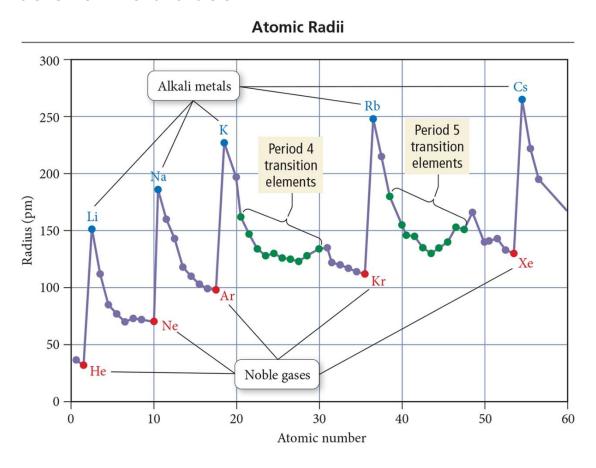
- There are several methods for measuring the radius of an atom, and they give slightly different numbers.
  - Van der Waals radius = nonbonding
  - Covalent radius = bonding radius
  - Atomic radius is an average radius of an atom based on measuring large numbers of elements and compounds.





## **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



## **Shielding and Effective Nuclear Charge**

## Electron config.

## **Z**<sub>eff</sub> (Slater's rules)

Li 
$$(1s)^2(2s)^1$$

$$3 - [2(0.85)] = 1.30$$

Be 
$$(1s^2)(2s)^{2-1=1}$$

$$4 - [2(0.85) + 1(0.35)] = 1.95$$

B 
$$(1s)^2(2s2p)^{3-1=2}$$

$$5 - [2(0.85) + 2(0.35] = 2.60$$



C 
$$(1s)^2(2s2p)^{4-1=3}$$

$$6 - [2(0.85) + 3(0.35] = 3.25$$



N 
$$(1s)^2(2s2p)^{5-1=4}$$

$$7 - [2(0.85) + 4(0.35)] = 3.90$$



O 
$$(1s)^2(2s2p)^{6-1=5}$$

$$8 - [2(0.85) + 5(0.35)] = 4.55$$

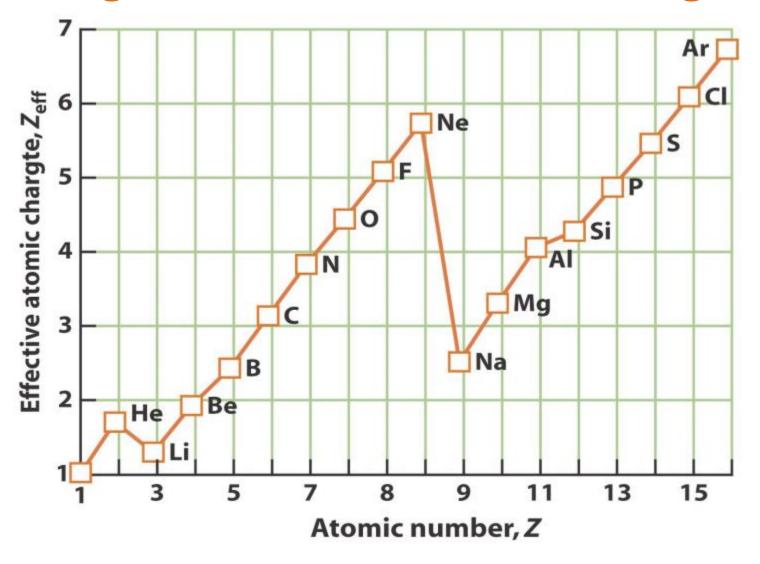
$$F (1s)^2 (2s2p)^{7-1=6}$$

$$9 - [2(0.85) + 6(0.35)] = 5.20$$

Ne 
$$(1s)^2(2s2p)^{8-1=7}$$

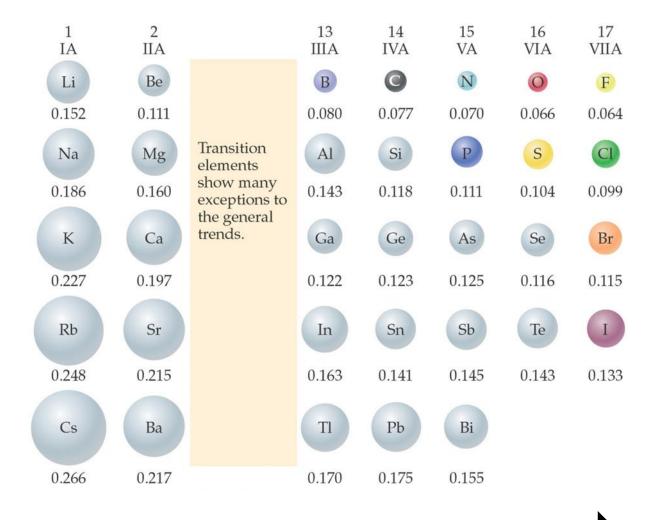
$$10 - [2(0.85) + 7(0.35)] = 5.85$$

## **Shielding and Effective Nuclear Charge**



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

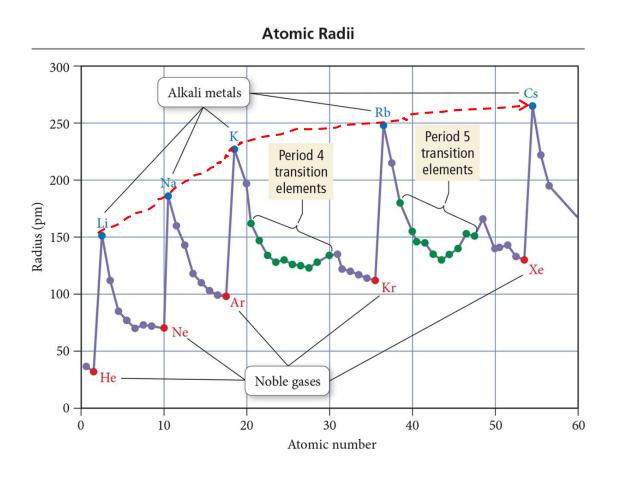
## **Periodic Trends in Atomic Radius**



#### **DECREASE**

## **Trend in Atomic Radius: Main Group**

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



## Shielding and Effective Nuclear Charge

#### Electron config.

### **Z**<sub>eff</sub> (Slater's rules)

1 IA Li 0.152

Li 
$$(1s)^2(2s)^1$$

$$3 - [2(0.85)] = 1.30$$

Na

Na 
$$(1s)^2(2s2p)^8(3s)^1$$

$$11 - [2(1) + 8(0.85)] = 2.2$$

0.186

K

$$K (1s)^2 (2s2p)^8 (3s3p)^8 (4s)^1$$

$$19 - [2(1) + 8(1) + 8(0.85] = 2.2$$

0.227

Rb  $(1s)^2(2s2p)^8(3s3p3d)^{18}(4s4p)^8(5s)^1 37 - [2(1)+8(1)+18(1)+8(0.85)] = 2.2$ 

0.248

Cs

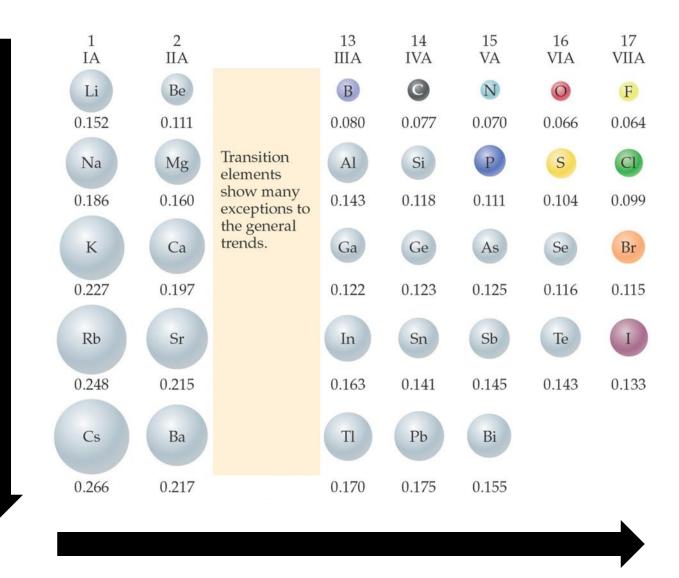
Cs  $(1s^2)(2s^22p^6)(3s^23p^63d^{10})(4s^24p^64d^{10})(5s^25p^6)(6s^1)$ 

0.266

$$55 - [2(1) + 8(1) + 18(1) + 18(1) + 8(0.85] = 2.2$$

## **Periodic Trends in Atomic Radius**

**INCREASE** 



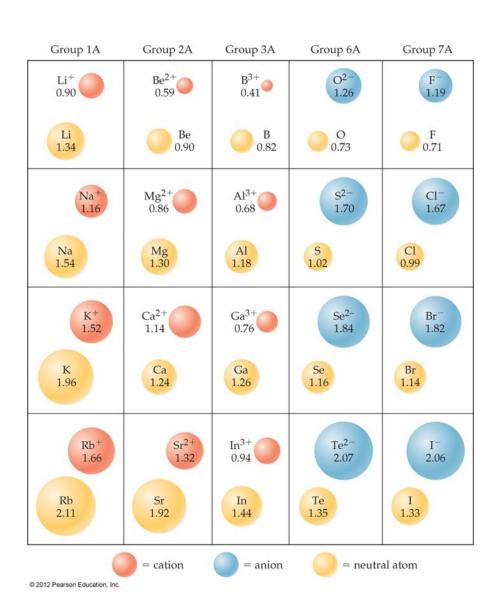
**DECREASE** 

#### **Trends in Ionic Radius**

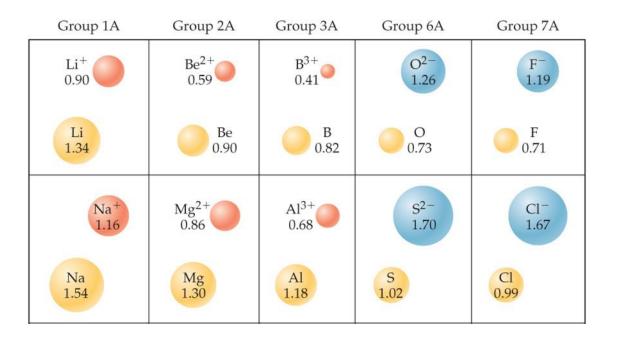
- lons in the same group have the same charge.
- Ion size increases down the column.
  - Higher valence shell, larger ion
- Cations are smaller than neutral atoms; anions are larger than neutral atoms.
- Cations are smaller than anions.
  - Except Rb<sup>+</sup> and Cs<sup>+</sup>, bigger or same size as F<sup>-</sup> and O<sup>2-</sup>
- 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

- Ionic size depends upon
  - The nuclear charge.
  - The number of electrons.
  - The orbitals in which electrons reside.
- Cations are smaller than their parent atoms
- Anions are larger than their parent atoms"



### Periodic Trends in Ionic Radius



- In an isoelectronic series, ions have the same number of electrons.
- Ionic size decreases with an increasing nuclear charge.

# **Explanation for the Trends in Anion Radius**

 When atoms form anions, electrons are added to the valence shell.

- These "new valence electrons" experience a smaller effective nuclear charge than the "old valence electrons," increasing the size.
- The result is that the anion is larger than the atom.

## **Explanation for the Trends in Anion Radius**

- Traversing down a group increases the n level, causing the anions to get larger.
- Traversing to the right across a period decreases the effective nuclear charge for isoelectronic anions, causing the anions to get larger.

## **Ionization Energy (IE)**

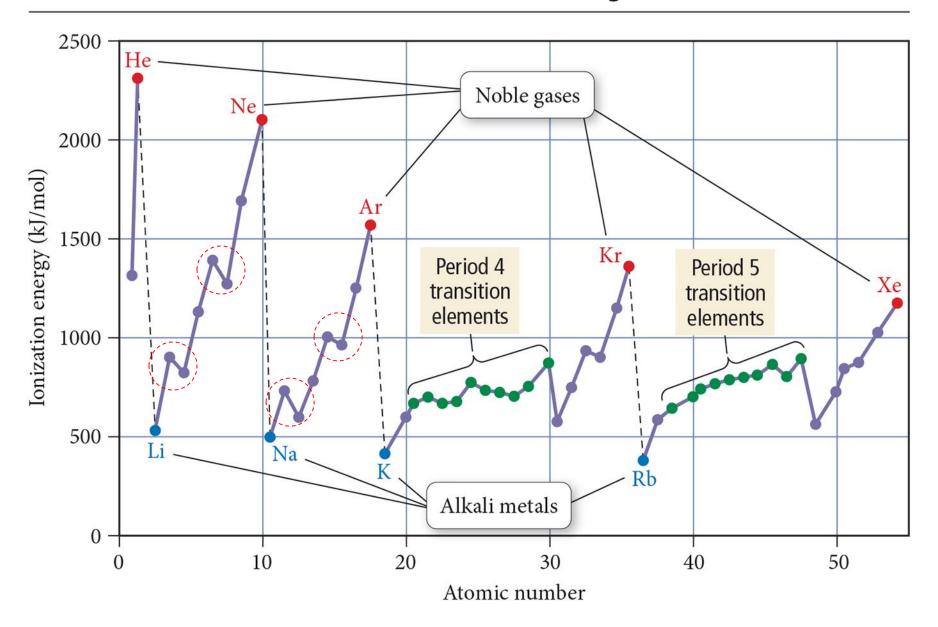
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- Minimum energy needed to remove an electron from an atom or ion
  - Gas state
  - Endothermic process
  - Valence electron easiest to remove, lowest IE
  - $M(g) + IE_1 \rightarrow M^{1+}(g) + 1 e^{-}$
  - $M^{+1}(g) + IE_2 \rightarrow M^{2+}(g)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

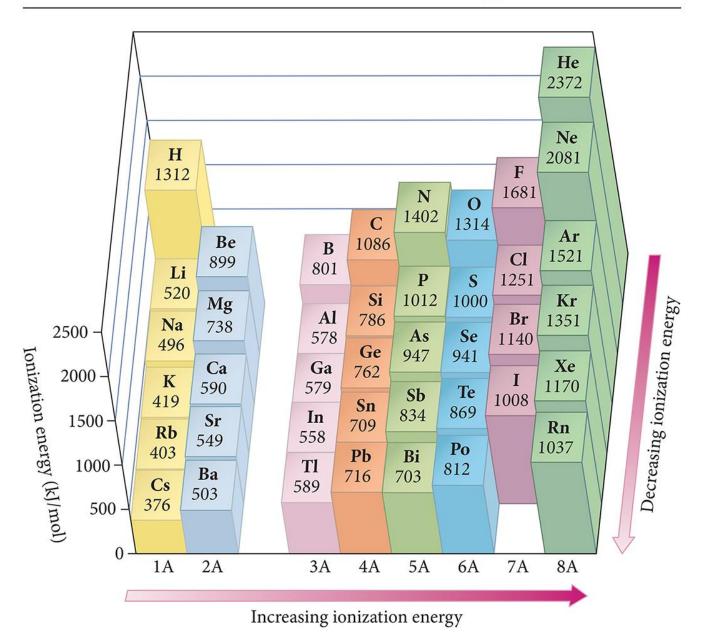
## **General Trends in First Ionization Energy**

- The larger the effective nuclear charge on the electron, the more energy it takes to remove it.
- The farther the most probable distance the electron is from the nucleus, the less energy it takes to remove it.
- First IE decreases down the group.
  - Valence electron farther from nucleus
- First IE generally increases across the period.
  - Effective nuclear charge increases

#### **First Ionization Energies**

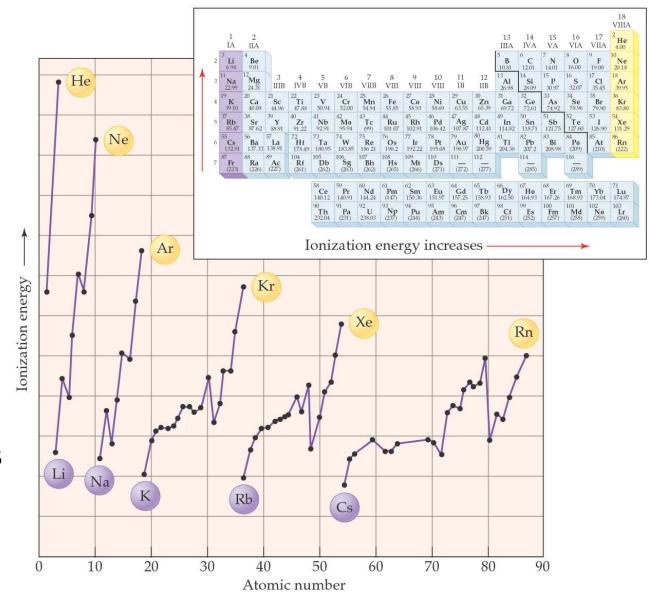


#### **Trends in First Ionization Energy**



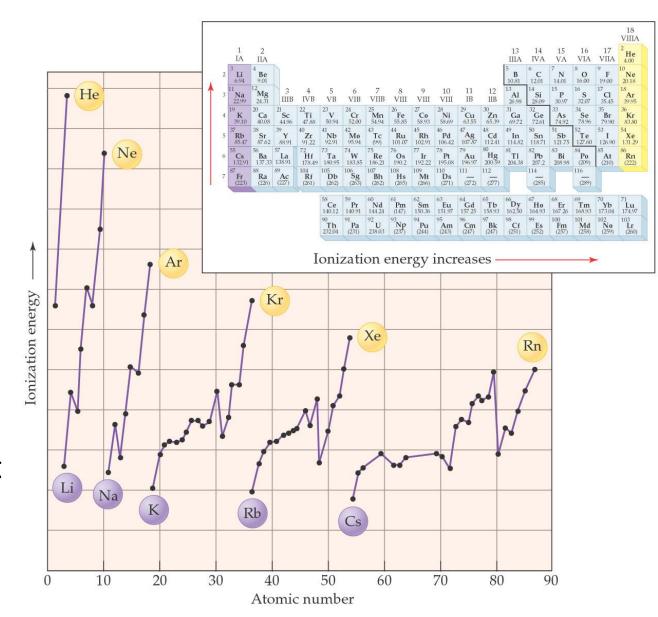
## **General Trends in First Ionization Energy**

- Down a column, less energy is required to remove the first electron.
- In the same group, Z<sub>eff</sub> is the same, but the valence electrons are farther from the nucleus.



## **General Trends in First Ionization Energy**

- Across a row, it gets harder to remove an electron.
- As you go from left to right,  $Z_{\rm eff}$  increases.
- However, there are two apparent discontinuities in this trend.

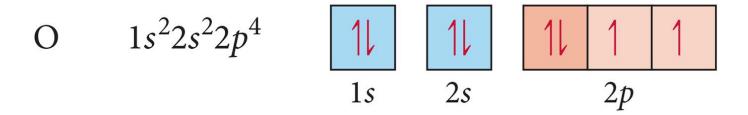


## **Exceptions in the First IE Trends**

- First ionization energy generally increases from left to right across a period.
- Except from 2A to 3A and 5A to 6A

# **Exceptions in the First Ionization Energy Trends, N and O**

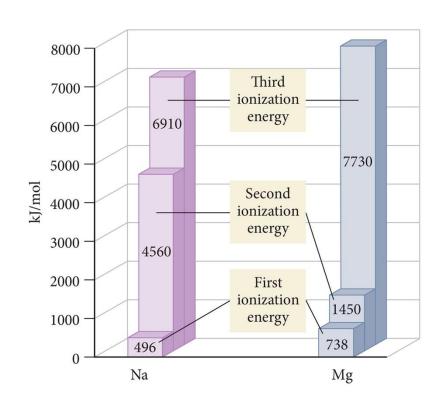
To ionize N, you must break up a half-full sublevel, which costs extra energy.



When you ionize O, you get a half-full sublevel, which costs less energy.

## **Trends in Successive Ionization Energies**

- Removal of each successive electron costs more energy.
  - Shrinkage in size due to having more protons than electrons
  - Outer electrons closer to the nucleus; therefore harder to remove
- There's a regular increase in energy for each successive valence electron.
- There's a large increase in energy when core electrons are removed.



# Trends in Second and Successive Ionization Energies

TABLE 8.1 Successive Ionization Energies for the Elements Sodium through Argon (kJ/mol)							
Element	IE <sub>1</sub>	IE <sub>2</sub>	IE <sub>3</sub>	IE <sub>4</sub>	IE <sub>5</sub>	IE <sub>6</sub>	IE <sub>7</sub>
Na	496	4560					
Mg	738	1450	7730		Core e	lectrons	
Al	578	1820	2750	11,600			
Si	786	1580	3230	4360	16,100		
Р	1012	1900	2910	4960	6270	22,200	
S	1000	2250	3360	4560	7010	8500	27,100
CI	1251	2300	3820	5160	6540	9460	11,000
Ar	1521	2670	3930	5770	7240	8780	12,000

## **Electron Affinity**

- Energy is released when a neutral atom gains an electron.
  - 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							8A
H -73	2A	3A	4A	5A	6A	7A	<b>He</b> >0
<b>Li</b> -60	<b>Be</b> >0	<b>B</b> -27	<b>C</b> -122	N >0	O -141	F -328	Ne >0
Na -53	<b>Mg</b> >0	Al -43	<b>Si</b> -134	<b>P</b> -72	S -200	<b>Cl</b> -349	<b>Ar</b> >0
<b>K</b> -48	<b>Ca</b> -2	<b>Ga</b> -30	<b>Ge</b> –119	<b>As</b> -78	<b>Se</b> -195	<b>Br</b> -325	<b>Kr</b> >0
<b>Rb</b> -47	<b>Sr</b> -5	In -30	<b>Sn</b> -107	<b>Sb</b> -103	<b>Te</b> -190	I -295	<b>Xe</b> >0

## **Properties of Metals and Nonmetals**

#### Metals

- Malleable and ductile
- Shiny, lustrous, reflect light
- Conduct heat and electricity
- Most oxides basic and ionic
- Form cations in solution
- Lose electrons in reactions—oxidized

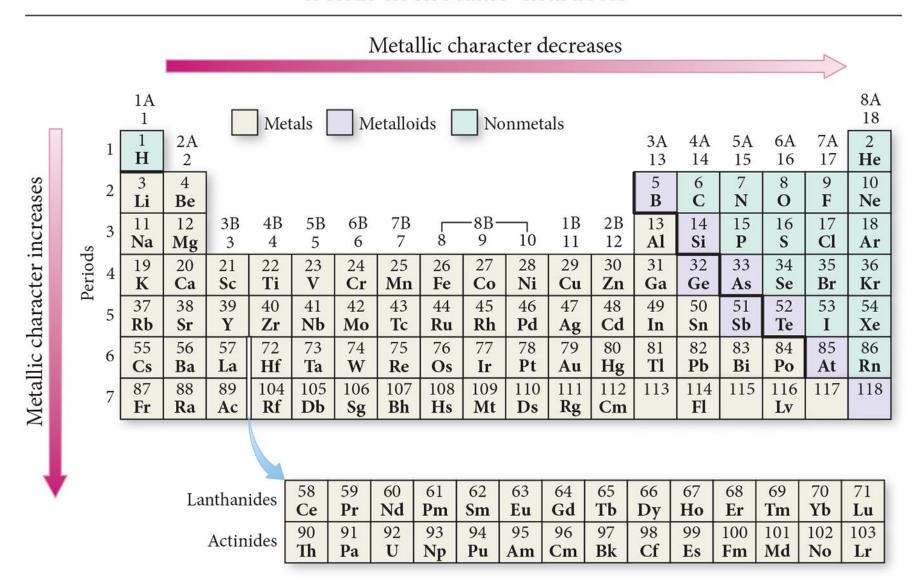
#### Nonmetals

- Brittle in solid state
- Dull, nonreflective solid surface
- Electrical and thermal insulators
- Most oxides are acidic and molecular
- Form anions and polyatomic anions
- Gain electrons in reactions—reduced

#### **Metallic Character**

- Metallic character is how closely an element's properties match the ideal properties of a metal.
  - More malleable and ductile, better conductors, and easier to ionize
- Metallic character decreases left to right across a period.
  - Metals found at the left of the period, and nonmetals to the right
- Metallic character increases down the column.
  - Nonmetals found at the top of the middle main-group elements, and metals found at the bottom

#### Trends in Metallic Character



# **Explanation for the Trends in Metallic Character**

- Metals generally have smaller first ionization energies, and nonmetals generally have larger electron affinities.
  - Except for the noble gases
- : quantum mechanics predicts the atom's metallic character should increase down a column because the valence electrons are not held as strongly.
- : quantum mechanics predicts the atom's metallic character should decrease across a period because the valence electrons are held more strongly and the electron affinity increases.

### **Trends in the Alkali Metals**

- Atomic radius increases down the column.
- Ionization energy decreases down the column.
- Very low ionization energies
  - Good reducing agents; easy to oxidize
  - Very reactive; not found uncombined in nature
  - React with nonmetals to form salts
  - Compounds generally soluble in water : found in seawater
- Electron affinity decreases down the column.
- Melting point decreases down the column.
  - All very low MP for metals
- Density increases down the column.
  - Except K
  - In general, the increase in mass is greater than the increase in volume.

## **Alkali Metals**

**TABLE 8.2** Properties of the Alkali Metals\* Melting Point (°C) **Element Electron Configuration** Atomic Radius (pm) IE<sub>1</sub> (kJ/mol) Density at 25 °C (g/cm<sup>3</sup>) 181 Li 152 520 0.535 [He] 2s1 102 [Ne] 3s1 186 496 0.968 Na 98 K [Ar] 4s<sup>1</sup> 227 419 0.856 39 Rb [Kr] 5s<sup>1</sup> 248 403 1.532 29 265 376 1.879 Cs [Xe] 6s1

#### Reactions of the Alkali Metals with Water







Lithium Sodium

Potassium

<sup>\*</sup>Francium is omitted because it has no stable isotopes.

## **Trends in the Halogens**

- Atomic radius increases down the column.
- Ionization energy decreases down the column.
- Very high electron affinities
  - Good oxidizing agents; easy to reduce
  - Very reactive; not found uncombined in nature
  - React with metals to form salts
  - Compounds generally soluble in water : found in seawater

## **Trends in the Halogens**

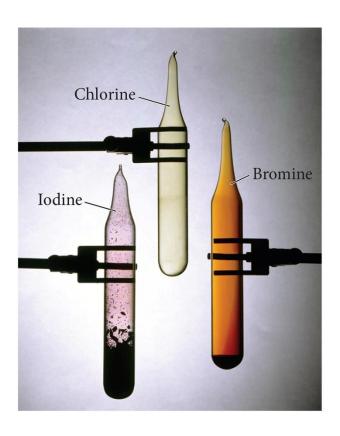
- Reactivity increases down the column.
- They react with hydrogen to form HX, acids.
- Melting point and boiling point increase down the column.
- Density increases down the column.
  - In general, the increase in mass is greater than the increase in volume.

# **Halogens**

**TABLE 8.3** Properties of the Halogens\*

Element	Electron Configuration	Atomic Radius (pm)	EA (kJ/mol)	Melting Point (°C)	Boiling Point (°C)	Density of Liquid (g/cm³)
F	[He] 2s <sup>2</sup> 2p <sup>5</sup>	72	-328	-219	-188	1.51
CI	[Ne] 3s <sup>2</sup> 3p <sup>5</sup>	99	-349	-101	-34	2.03
Br	[Ar] 4s <sup>2</sup> 4p <sup>5</sup>	114	-325	-7	59	3.19
1	[Kr] 5s <sup>2</sup> 5p <sup>5</sup>	133	-295	114	184	3.96

<sup>\*</sup>At is omitted because it is rare and radioactive.



## Reactions of Alkali Metals with Halogens

 Alkali metals are oxidized to the 1+ ion.

 Halogens are reduced to the 1- ion.

- The ions then attach together by ionic bonds.
- The reaction is exothermic.



### Reactions of Alkali Metals with Water

- Alkali metals are oxidized to the 1+ ion.
- H<sub>2</sub>O is split into H<sub>2</sub>(g) and OH<sup>-</sup> ion.
- The Li, Na, and K are less dense than the water, so they float on top.
- The ions then attach together by ionic bonds.
- The reaction is exothermic, and often the heat released ignites the H<sub>2</sub>(g).

Reactions of the Alkali Metals with Water







Lithium Sodium

Potassium

### **Trends in the Noble Gases**

- Atomic radius increases down the column.
- Ionization energy decreases down the column.
  - Very high IE
- Very unreactive
  - Only found uncombined in nature
  - Used as "inert" atmosphere when reactions with other gases would be undesirable

### **Trends in the Noble Gases**

- Melting point and boiling point increase down the column.
  - All gases at room temperature
  - Very low boiling points
- Density increases down the column.
  - In general, the increase in mass is greater than the increase in volume.

## **Noble Gases**

Element	Electron Configuration	Atomic Radius (pm)**	IE <sub>1</sub> (kJ/mol)	Boiling Point (K)	Density of Gas (g/L at STP)
Не	1s <sup>2</sup>	32	2372	4.2	0.18
Ne	[He] 2s <sup>2</sup> 2p <sup>6</sup>	70	2081	27.1	0.90
Ar	[Ne] 3s <sup>2</sup> 3p <sup>6</sup>	98	1521	87.3	1.78
Kr	[Ar] 4s <sup>2</sup> 4p <sup>6</sup>	112	1351	119.9	3.74
Xe	[Kr] 5s <sup>2</sup> 5p <sup>6</sup>	130	1170	165.1	5.86

<sup>\*</sup>Radon is omitted because it is radioactive.

<sup>\*\*</sup>Since only the heavier noble gases form compounds, covalent radii for the smaller noble gases are estimated.