Electronic Configuration

- The electrons are configured (distributed) into "orbitals," which represent energy levels
- Electrons are able to move from one orbital (energy level) to another by emission or absorption of a quantum of energy, in the form of a photon
- Knowledge of the electron configuration of different atoms is useful in understanding the structure of the periodic table of elements
- The concept is also useful for describing the chemical bonds that hold atoms together
- In bulk materials this same idea helps explain the peculiar properties of lasers and semiconductors

Electron Configuration

- According to quantum mechanics each electron is described by 4 Quantum numbers
  - Principal Quantum Number (n)
  - Angular Momentum Quantum Number (l)
  - Magnetic Quantum Number (m_l)
  - Spin Quantum Number (m_s)

The first 3 quantum numbers define the wave function of the electron's atomic orbital, i.e., it size and general energy level

The fourth quantum number refers to the

Spin Orientation

of the 2 electrons that occupy an atomic orbital

Electronic Configuration

- Quantum Numbers and Atomic Orbitals
  - The **Principal Quantum Number (n)** represents the “Shell Number” in which an electron “resides”
    - It represents the relative size of the orbital
    - Equivalent to periodic chart Period Number
    - Defines the principal energy of the electron
    - The smaller “n” is, the *smaller* the orbital size
    - The smaller “n” is, the *lower* the electron energy
    - n can have any positive value from

      1, 2, 3, 4 … ∞

      (Currently, n = 7 is the maximum known)

Quantum Theory of The Atom

- Quantum Numbers and Atomic Orbitals (Con't)
  - The Angular Momentum Quantum Number (l) distinguishes "sub shells" within a given shell
    - Each main "shell," designated by quantum number "n," is subdivided into:

$$l = n - 1 \text{ "sub shells"}$$

    - (l) can have any integer value from 0 to n - 1
    - The different "l" values correspond to the s, p, d, f designations used in the electronic configuration of the elements

Letter	s	p	d	f
l value	0	1	2	3

Quantum Theory of The Atom

- Quantum Numbers and Atomic Orbitals (Con't)
  - The Magnetic Quantum Number (m_l) defines atomic orbitals within a given sub-shell
    - Each value of the angular momentum number (l) determines the number of atomic orbitals
    - For a given value of "l," m_l can have any integer value from $-l$ to $+l$

$$m_l = -l \text{ to } +l \qquad (-2 \;\; -1 \;\; 0 \;\; +1 \;\; +2)$$

    - Each orbital has a different shape and orientation (x, y, z) in space
    - Each orbital within a given angular momentum number sub shell (l) has the same energy

Quantum Theory of The Atom

- Quantum Numbers and Atomic Orbitals (Con't)
  - The Spin Quantum Number (m_s) refers to the two possible spin orientations of the electrons residing within a given atomic orbital
    - Each atomic orbital can hold only two (2) electrons
    - Each electron has a "spin" orientation value
    - The spin values must oppose one another
    - The possible values of m_s spin values are:

$$+1/2 \quad \text{and} \quad -1/2$$

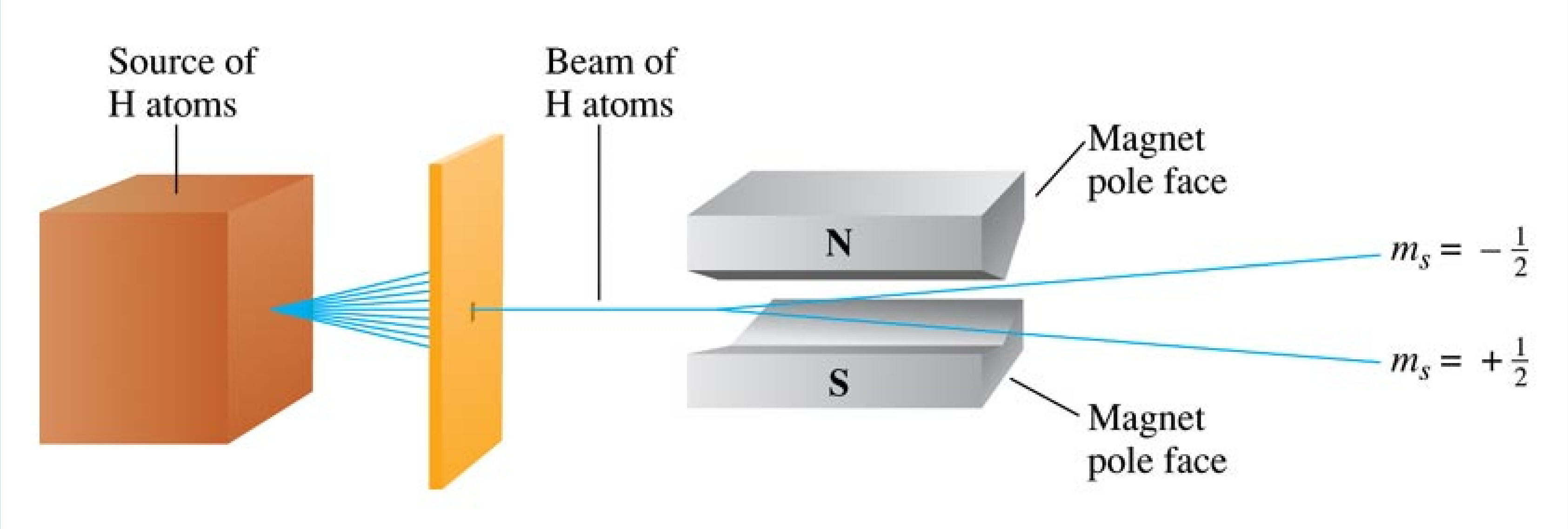
Electronic Configuration

- Quantum Numbers and Atomic Orbitals (Con't)
  - The Magnetic Quantum Number (m_l) defines the atomic <u>orbitals</u> within a given sub-shell
    - <u>Each value</u> of the angular momentum number (l) determines the <u>number</u> of atomic orbitals
    - For a given value of "l," m_l can have any integer value from $-l$ to $+l$

$$m_l = -l \text{ to } +l$$

    - Each orbital has a different shape and orientation (x, y, z) in space
    - Each orbital within a given angular momentum number sub shell (l) has the same energy

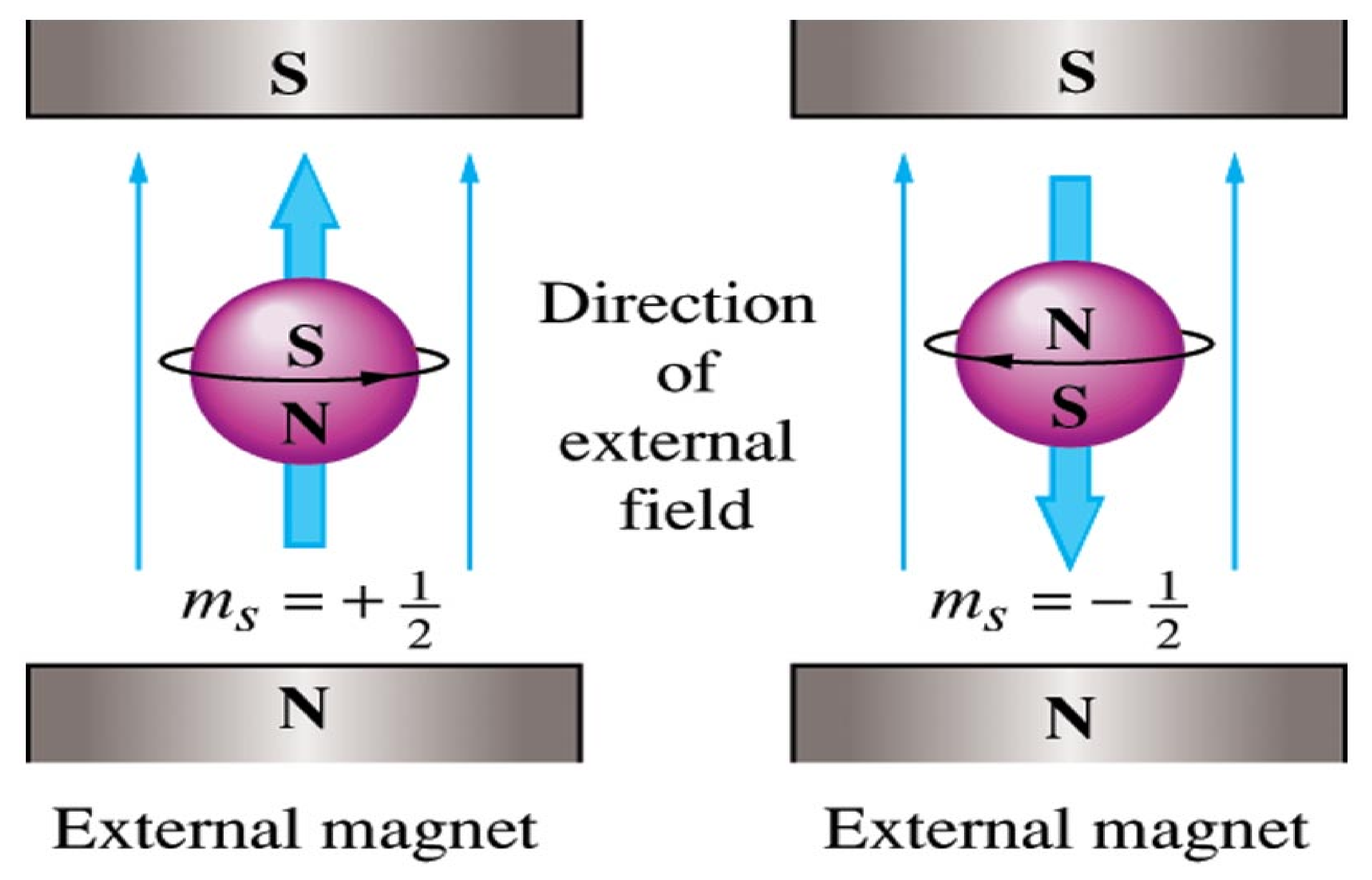
Stern-Gerlach Experiment



A beam of H atoms can be separated into 2 beams of opposite electron spin in a magnetic field

m_s (–1/2) electrons have a slightly greater energy than m_s (+1/2) electrons

Representation of electron spin

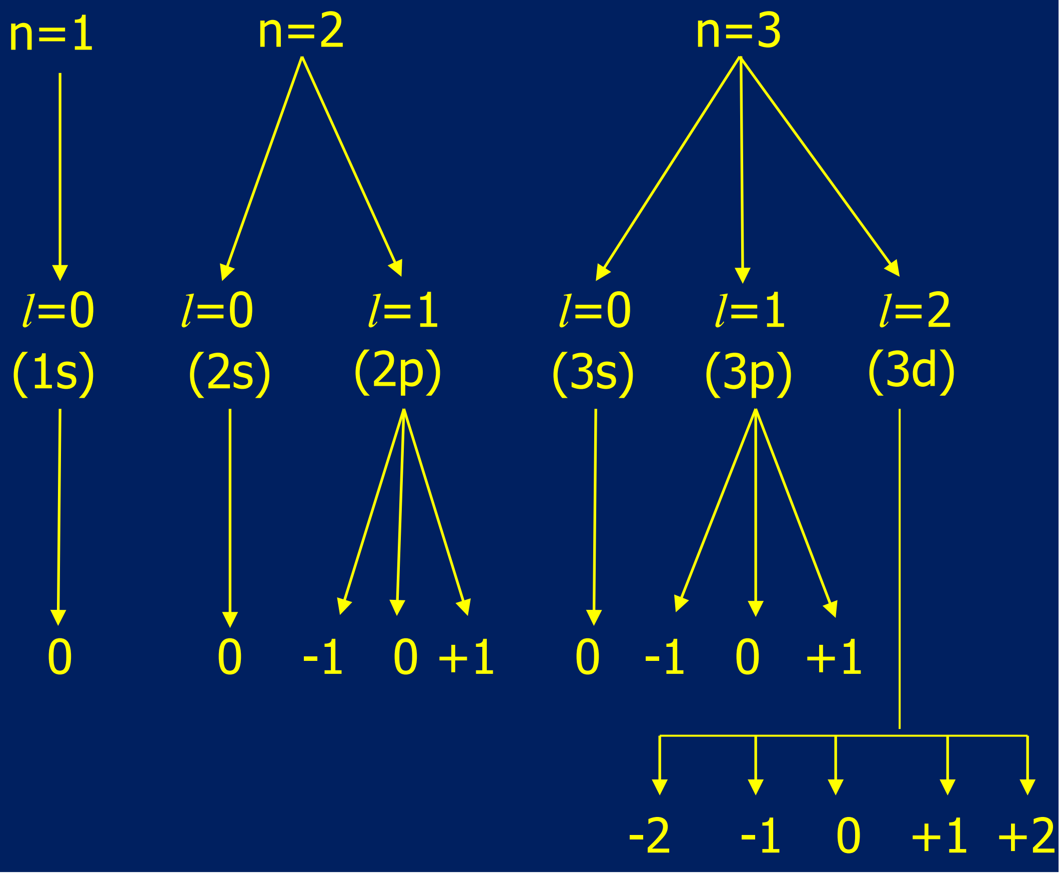


A spinning charged particle aligns in a magnetic field depending on spin state

Summary of Quantum Numbers

Name	**Symbol**	**Permitted Values**	**Property**
principal	n	positive integers (1, 2, 3, …)	orbital energy (size)
angular momentum	l	integers from $0 \rightarrow n - 1$	orbital shape The l values 0, 1, 2, and 3 correspond to *s*, *p*, *d*, *f* orbitals, respectively
magnetic	m_l	integers from $-l \rightarrow 0 \rightarrow +l$	orbital orientation
spin	m_s	+1/2 ↑ or – 1/2 ↓	direction of e^- spin

Summary of Quantum Numbers



Name, Symbol (Property)	**Allowed Values**	**Quantum Numbers**
Principal, n (size, energy)	Positive integer (1, 2, 3, ...)	n=1 n=2 n=3
Angular momentum, l (shape)	$l = 0 \rightarrow n-1$ 0(s), 1(p), 2(d), 3(f)	l=0 (1s) l=0 (2s), l=1 (2p) l=0 (3s), l=1 (3p), l=2 (3d)
Magnetic, m_l (orientation)	$-l,\ldots,0,\ldots,+l$	0 0; -1 0 +1 0; -1 0 +1; -2 -1 0 +1 +2

Electron Configuration

- An **electron configuration** of an atom is a particular distribution of electrons among available sub shells
  - The configuration notation lists the subshell symbols (s, p, d, f…) sequentially with a superscript indicating the number of electrons occupying that subshell
  - Ex: lithium (Period (n) = 2, Atomic No 3) has

2 electrons in the "1s" sub shell

1 electron in the "2s" sub shell

$1s^2\ 2s^1$

Fluorine (Period (n) 2, Atomic No 9) has

2 electrons in the "1s" sub shell

2 electrons in the "2s" sub shell

5 electrons in the "2p" subshell

$1s^2\ 2s^2\ 2p^5$

Electron Configuration

- A unique set of the first 3 quantum numbers (n, l, m_l) defines an "Orbital"
- An orbital can contain a maximum of 2 electrons, each with a different "spin" (+1/2 or -1/2)
- An **orbital diagram** is notation used to show how the orbitals of a sub shell are occupied by electrons
  - Each orbital is represented by a circle
  - Each orbital can have a maximum of 2 electrons
  - Each group of orbitals is labeled by its

    Sub Shell Notation (s, p, d, f)
  - Electrons are represented by arrows:

    up (↑) for $m_s = +1/2$ and down (↓) for $m_s = -1/2$

The Pauli Exclusion Principle

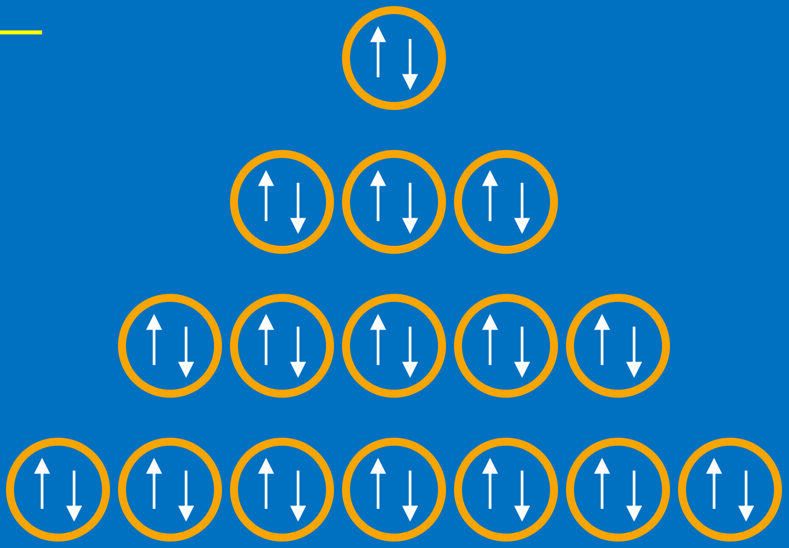
- The **Pauli Exclusion Principle**
  - No two electrons in an atom can have the same four quantum numbers
  - An orbital (unique combination of n, l, m_l) can hold, at most, two electrons
  - Two electrons in the same Orbital have opposite spins

$+1/2 \uparrow \quad -1/2 \downarrow$

The Pauli Exclusion Principle

- The maximum number of electrons and their orbital diagrams are:

Sub Shell	No. Orbitals	Values ($-l$ to $+l$)	Max No. Electrons
s (l = 0)	1	(0)	2
p (l = 1)	3	(-1, 0, +1)	6
d (l =2)	5	(-2,-1,0,+1,+2)	10
f (l =3)	7	(-3,-2,1,0,+1,+2,+3)	14



Practice Problem

If the l quantum number is 3, what are the possible values of m_l?

Ans: m_l can have any integer value from $-l$ to $+l$

Since $l = 3$

m_l = -3 -2 -1 0 +1 +2 +3

Practice Problem

State which of the following sets of quantum numbers would be possible and which impossible for an electron in an atom?

a. $n = 0$, $l=0$, $m_l = 0$, $m_s = +1/2$

b. $n = 1$, $l=0$, $m_l = 0$, $m_s = +1/2$

c. $n = 1$, $l=0$, $m_l = 0$, $m_s = -1/2$

d. $n = 2$, $l=1$, $m_l = -2$, $m_s = +1/2$

e. $n = 2$, $l=1$, $m_l = -1$, $m_s = +1/2$

Ans:		
	Possible	b c e
	Impossible	a "n" must be positive 1, 2, 3...
	Impossible	d m_l can only be -1 0 +1

Configurations and the Periodic Table

Condensed Electronic Configurations

	Full Electronic Configuration	Condensed Electronic Configuration
Helium	$1s^2$	[He] 2 e^-
Neon	$1s^2\underline{\mathbf{2s^2 2p^6}}$	[Ne] 10 e^-
Argon	$1s^2 2s^2 2p^6\underline{\mathbf{3s^2 3p^6}}$	[Ar] 18 e^-
Krypton	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}\underline{\mathbf{4s^2 4p^6}}$	[Kr] 36 e^-
Xenon	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}\underline{\mathbf{5s^2 5p^6}}$	[Ze] 54 e^-
Beryllium	$1s^2\underline{\mathbf{2s^2}}$	[He] $\underline{\mathbf{2s^2}}$ 4 e-
Magnesium	$1s^2 2s^2 2p^6\underline{\mathbf{3s^2}}$	[Ne] $\underline{\mathbf{3s^2}}$ 12 e-
Calcium	$1s^2 2s^2 2p^6 3s^2 3p^6\underline{\mathbf{4s^2}}$	[Ar] $\underline{\mathbf{4s^2}}$ 20 e-
Sodium Ion	(Na) $1s^2 2s^2 2p^6 3s^1 \rightarrow$ (Na^+) $1s^2 2s^2 2p^6 + 1e^-$	[Ne] + $1e^-$

Electron Configuration

- Quantum Number n = 1 (Period 1)

  l values = 0 to (n-1) = 0 to (1 -1) = 0 ∴ l = 0 (s orbital)

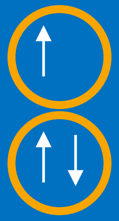
  m_l values = $-l, \ldots 0, \ldots +l$ = 0 (1 s orbital)

  m_s values = -1/2 & +1/2 = (2 e^- per orbital)

Z = 1 Hydrogen $1s^1$

Z = 2 Helium $1s^2$

1s orbital



Thus, for n = 1 there is one orbital (s) which can accommodate 2 elements – Hydrogen & Helium

Electron Configuration

- Quantum Number n = 2 (Period 2)

  l values = 0 to (n-1) = 0 to (2-1) = 0 to 1 $\therefore$ l = 0(s), 1(p)

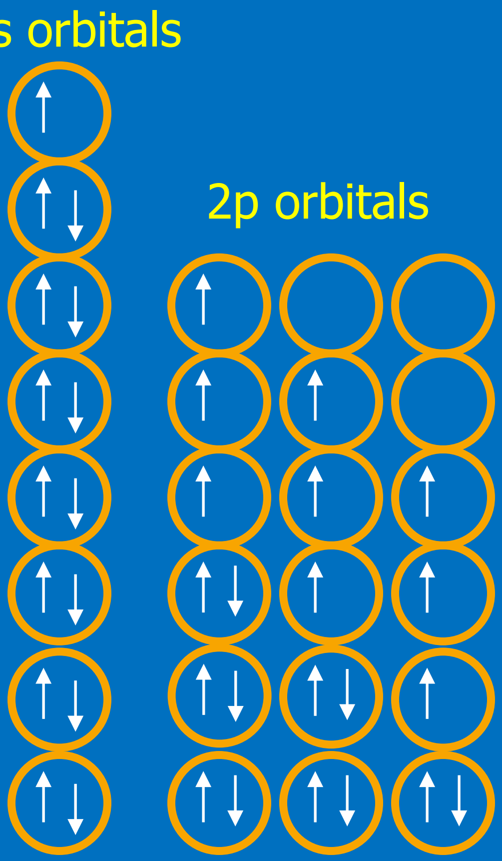
  For l = 0 (s) m_l = $-l$ $0 + l$ = 0 (one 2s orbital, 2 electrons)

  m_s values = -1/2 & +1/2

  For l = 1 (p) m_l = -1 0 +1 (three 2p orbitals, 6 electrons)

  m_s values = -1/2 & +1/2 in each orbital

Z=3	**Lithium**	**$1s^2 2s^1$**	**or**	**$[He]2s^1$**
Z=4	**Beryllium**	**$1s^2 2s^2$**	**or**	**$[He]2s^2$**
Z=5	**Boron**	**$1s^2 2s^2 2p^1$**	**or**	**$[He]2s^2 2p^1$**
Z=6	**Carbon**	**$1s^2 2s^2 2p^2$**	**or**	**$[He]2s^2 2p^2$**
Z=7	**Nitrogen**	**$1s^2 2s^2 2p^3$**	**or**	**$[He]2s^2 2p^3$**
Z=8	**Oxygen**	**$1s^2 2s^2 2p^4$**	**or**	**$[He]2s^2 2p^4$**
Z=9	**Fluorine**	**$1s^2 2s^2 2p^5$**	**or**	**$[He]2s^2 2p^5$**
Z=10	**Neon**	**$1s^2 2s^2 2p^6$**	**or**	**$[He]2s^2 2p^6$**



Electron Configuration

- With sodium (Z = 11), the <u>3s</u> sub shell begins to fill

Z=11 Sodium $1s^2 2s^2 2p^6 3s^1$ or [Ne]$3s^1$

Z=12 Magnesium $1s^2 2s^2 2p^6 3s^2$ or [Ne]$3s^2$

Starting with Z = 13, the <u>3p</u> sub shell begins to fill

Z=13 Aluminum $1s^2 2s^2 2p^6 3s^2 3p^1$ or [Ne]$3s^2 3p^1$

↓

Z=18 Argon $1s^2 2s^2 2p^6 3s^2 3p^6$ or [Ne]$3s^2 3p^6$

Electron Configuration

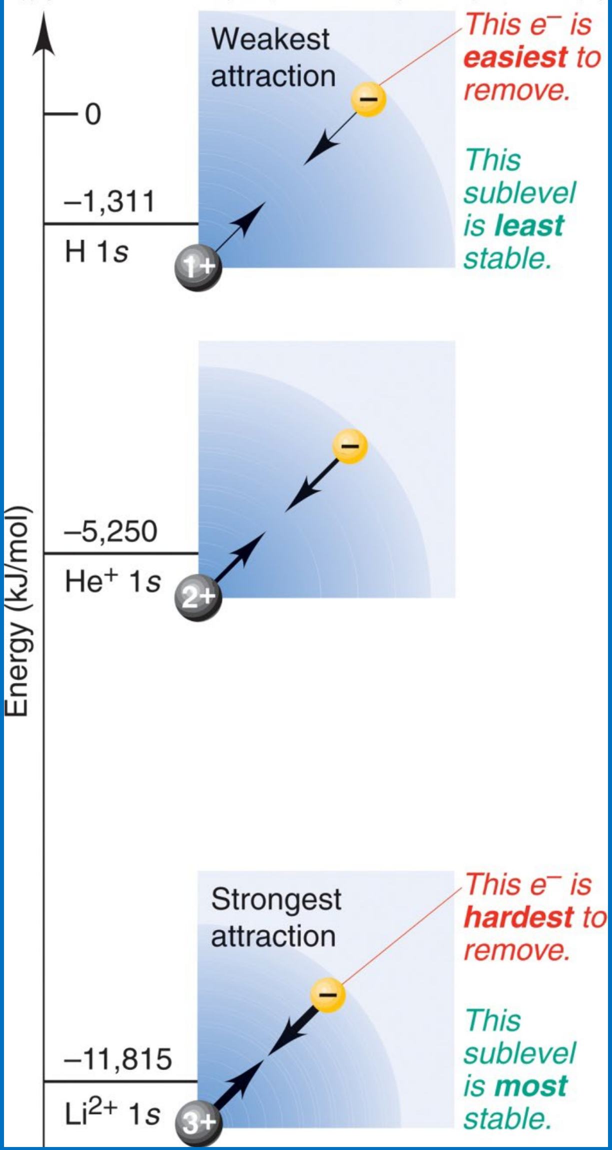
- Electrostatic Effects and Energy-Level Splitting
  - The principal quantum number (n) defines the energy level of an atom
    - The higher the “n” value, the higher the energy level
  - The unique values of the principal quantum numbers of multi-electron atoms (n, l, m_l) define a unique energy level for the orbital of a given electron
    - The energy of a given orbital depends mostly on the value of the principal quantum number (n), i.e. its size, and to a lesser degree on the shape of the orbital represented by the various values of the magnetic quantum number (l)

Electron Configuration

- The energy states of multi-electron atoms arise from 2 counteracting forces:
  - Nucleus – Positive protons attract Negative electrons
  - Electron – Negative electrons repulse each other
  - Nuclear protons create a pull (attraction) on electrons
  - Higher nuclear charge (Z) lowers orbital energy (stabilizes system) by increasing proton-electron attractions
    - The energy required to remove the 1s electron from Hydrogen (H), Z =1, is much less than the energy to remove the 1s electron from the Li^{2+} ion, Z = 3

Electron Configuration

- Effect of Nuclear Charge (Z) on Orbital Energy



Greater Nuclear Charge lowers orbital energy making it more difficult to remove the electron from orbit

The absolute value of the 1s orbital energy is related directly to Z^2

Energy required to remove 1s electron from H

1311 kJ/mol (Z= +1, Least stable)

Energy required to remove 1s electron from He^+

5250 kJ/mol (Z = +2)

Energy required to remove 1s electron from Li

11815 kJ/mol (Z = +3, Most stable)

Electron Configuration

- Shielding – Effect of Electron Repulsions on Orbital Energy
  - Electrons feel repulsion from other electrons somewhat shielding (counteracting) the attraction of the nuclear protons
  - Shielding (screening) lowers the full nuclear charge to an "Effective Nuclear Charge (Z_{eff})
  - The lower the Effective Nuclear Charge, the easier it is to remove an electron
    - It takes less than half as much energy to remove an electron from Helium (He) (2373 kJ/mol) than from He^+ (5250 kJ/mol) because the second electron in He repels the first electron and effectively shields the first electron from the full nuclear charge (lower Z_{eff})

Electron Configuration

- Penetration: Effects of orbital shape
  - The shape of an atomic orbital affects how close an electron moves closer to nucleus, i.e., the level of penetration
  - Penetration and the resulting effects of shielding on a atomic orbital causes the energy level (n) to be split into sublevels of differing energy representing the various values of the magnetic quantum number (l)
  - The lower the value of the magnetic quantum number (l), the more its electrons penetrate

Order of Sublevel Energies

s (l=0) < p(l=1) < d(l=2) < f(l=3)

  - Each of the orbitals for a given value of l (m_l = -1 0 +1) has the <u>same</u> energy

Aufbau Principle

- **Aufbau Principle** – scheme used to reproduce the ground state electron configurations of atoms by following the "building up" order based on relative energy levels of quantum subshells

- The "building up" order corresponds for the most part to *increasing energy* of the subshells

- By filling orbitals of the lowest energy first, you usually get the lowest total energy ("ground state") of the atom

Aufbau Principle

- Listed below is the order in which all the possible sub-shells fill with electrons

  Note the order does NOT follow a strict numerical subshell order

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s, 5f

You need not memorize this order

The next slide provides a pictorial providing an easier way of the viewing the 'build-up" order

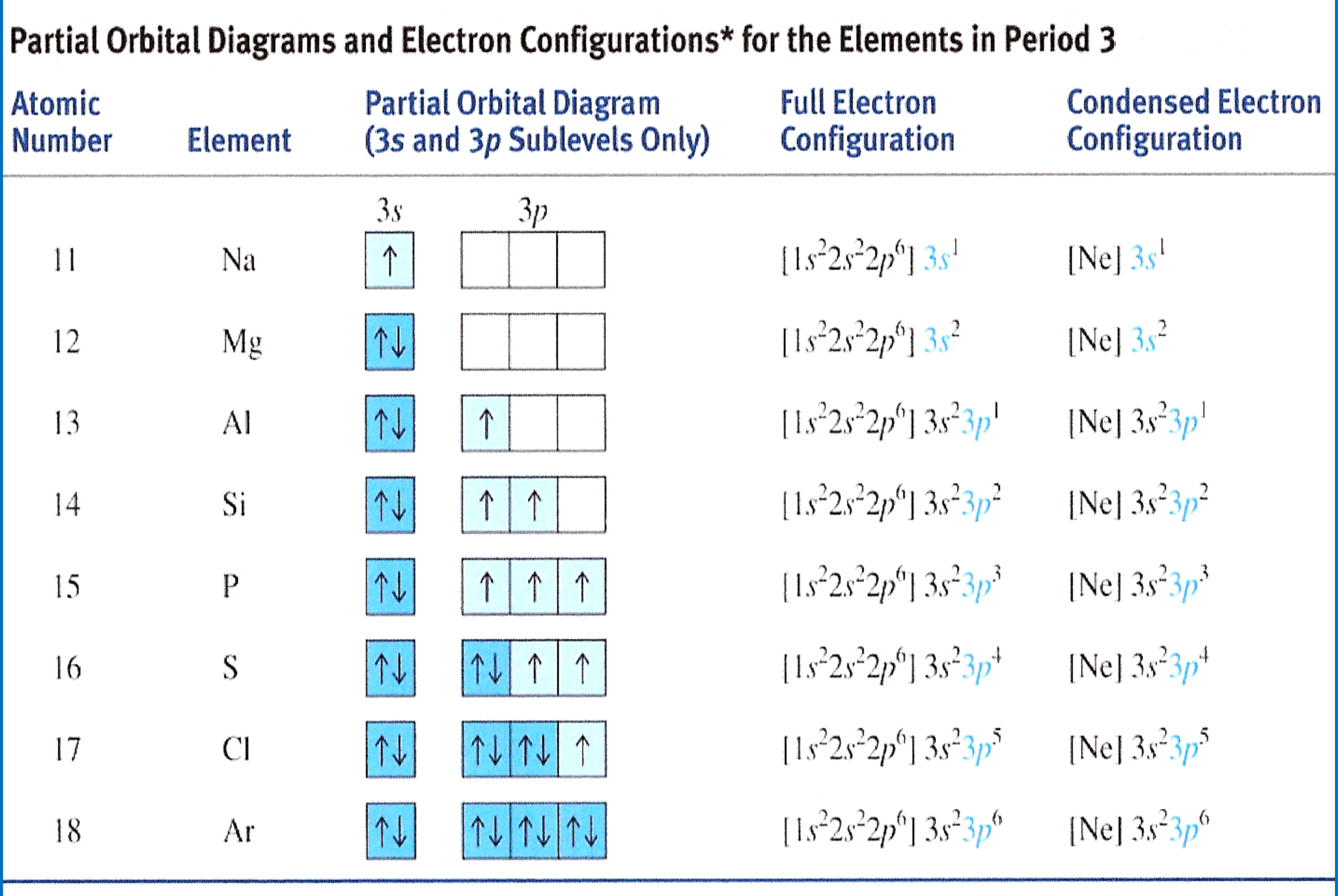
Aufbau Principle

- Every atom has an infinite number of possible electron configurations (electrons can be raised to any number of energy (n) levels)
  - The configuration associated with the lowest energy level of the atom is called the

    "ground state"
  - Other configurations correspond to

    "excited states"
  - Tables on the next 3 slides list the ground-state configurations of atoms up to krypton

Partial Orbital Diagrams

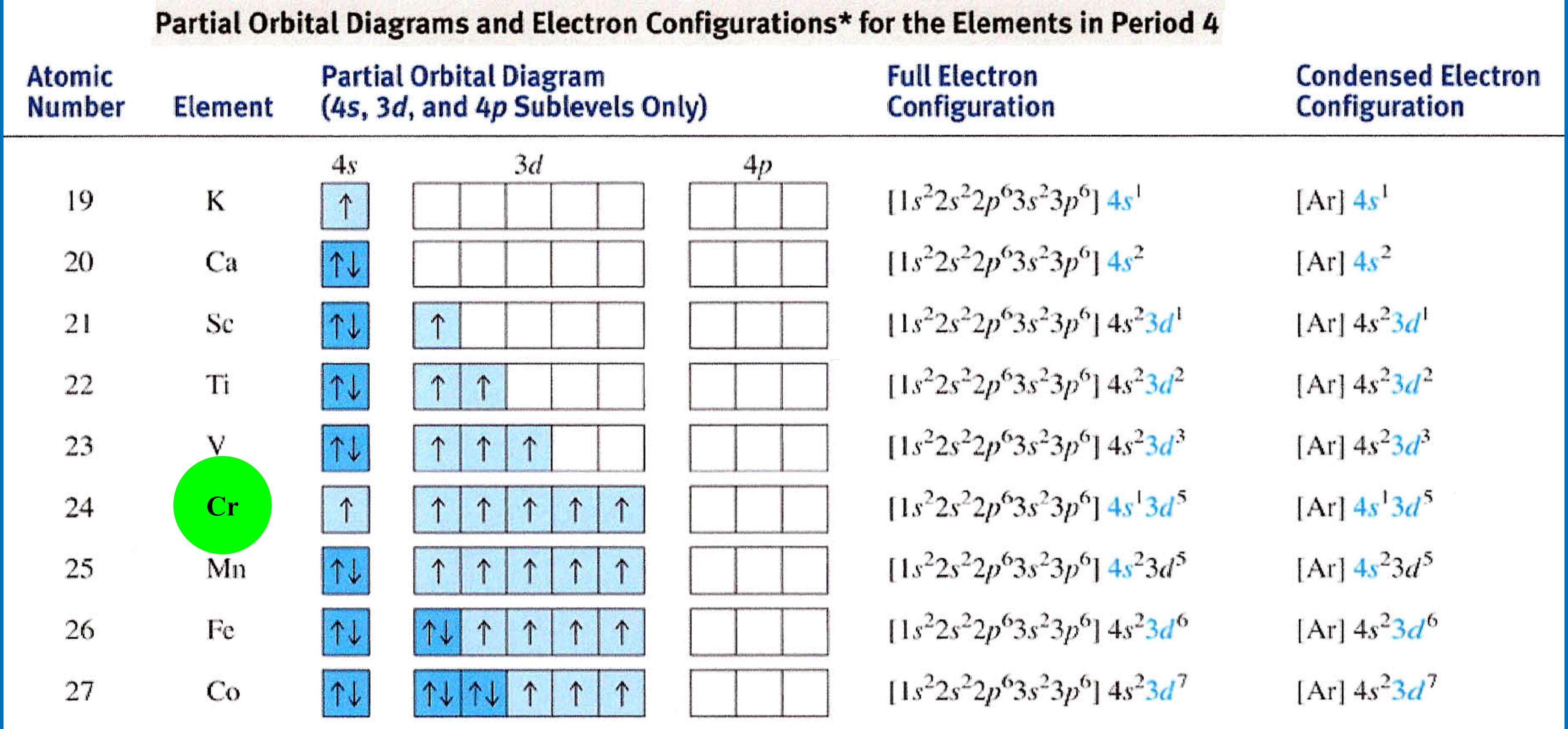


Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 3

Atomic Number	Element	Partial Orbital Diagram (3*s* and 3*p* Sublevels Only)				Full Electron Configuration	Condensed Electron Configuration
		3*s*	3*p*				
11	Na	↑				$[1s^2 2s^2 2p^6]\ 3s^1$	$[\mathrm{Ne}]\ 3s^1$
12	Mg	↑↓				$[1s^2 2s^2 2p^6]\ 3s^2$	$[\mathrm{Ne}]\ 3s^2$
13	Al	↑↓	↑			$[1s^2 2s^2 2p^6]\ 3s^2 3p^1$	$[\mathrm{Ne}]\ 3s^2 3p^1$
14	Si	↑↓	↑	↑		$[1s^2 2s^2 2p^6]\ 3s^2 3p^2$	$[\mathrm{Ne}]\ 3s^2 3p^2$
15	P	↑↓	↑	↑	↑	$[1s^2 2s^2 2p^6]\ 3s^2 3p^3$	$[\mathrm{Ne}]\ 3s^2 3p^3$
16	S	↑↓	↑↓	↑	↑	$[1s^2 2s^2 2p^6]\ 3s^2 3p^4$	$[\mathrm{Ne}]\ 3s^2 3p^4$
17	Cl	↑↓	↑↓	↑↓	↑	$[1s^2 2s^2 2p^6]\ 3s^2 3p^5$	$[\mathrm{Ne}]\ 3s^2 3p^5$
18	Ar	↑↓	↑↓	↑↓	↑↓	$[1s^2 2s^2 2p^6]\ 3s^2 3p^6$	$[\mathrm{Ne}]\ 3s^2 3p^6$

Partial Orbital Diagrams

- Chromium (Cr) relative to Vanadium (V)
- The Cr $4s^1$ subshell is filled <u>before</u> the 3d subshell is completed
- An $[Ar]3d^44s^2$ orbital configuration would be expected for ground state Cr, but the $[Ar]3d^54s^1$ orbital is lower in energy

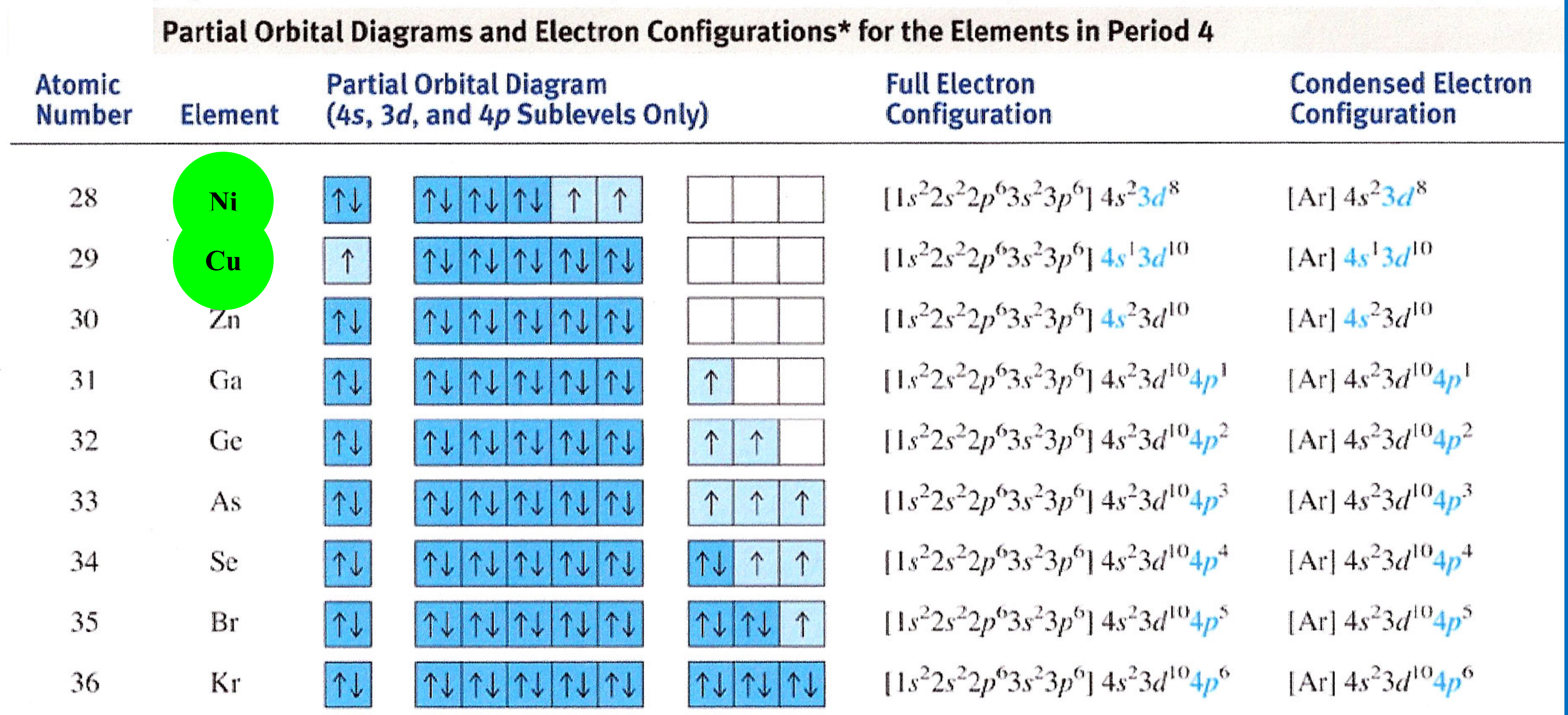


Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 4

Atomic Number	Element	Partial Orbital Diagram (4s, 3d, and 4p Sublevels Only) 4s	3d	4p	Full Electron Configuration	Condensed Electron Configuration
19	K	↑			$[1s^22s^22p^63s^23p^6]\ 4s^1$	$[Ar]\ 4s^1$
20	Ca	↑↓			$[1s^22s^22p^63s^23p^6]\ 4s^2$	$[Ar]\ 4s^2$
21	Sc	↑↓	↑		$[1s^22s^22p^63s^23p^6]\ 4s^23d^1$	$[Ar]\ 4s^23d^1$
22	Ti	↑↓	↑ ↑		$[1s^22s^22p^63s^23p^6]\ 4s^23d^2$	$[Ar]\ 4s^23d^2$
23	V	↑↓	↑ ↑ ↑		$[1s^22s^22p^63s^23p^6]\ 4s^23d^3$	$[Ar]\ 4s^23d^3$
24	Cr	↑	↑ ↑ ↑ ↑ ↑		$[1s^22s^22p^63s^23p^6]\ 4s^13d^5$	$[Ar]\ 4s^13d^5$
25	Mn	↑↓	↑ ↑ ↑ ↑ ↑		$[1s^22s^22p^63s^23p^6]\ 4s^23d^5$	$[Ar]\ 4s^23d^5$
26	Fe	↑↓	↑↓ ↑ ↑ ↑ ↑		$[1s^22s^22p^63s^23p^6]\ 4s^23d^6$	$[Ar]\ 4s^23d^6$
27	Co	↑↓	↑↓ ↑↓ ↑ ↑ ↑		$[1s^22s^22p^63s^23p^6]\ 4s^23d^7$	$[Ar]\ 4s^23d^7$

Partial Orbital Diagrams

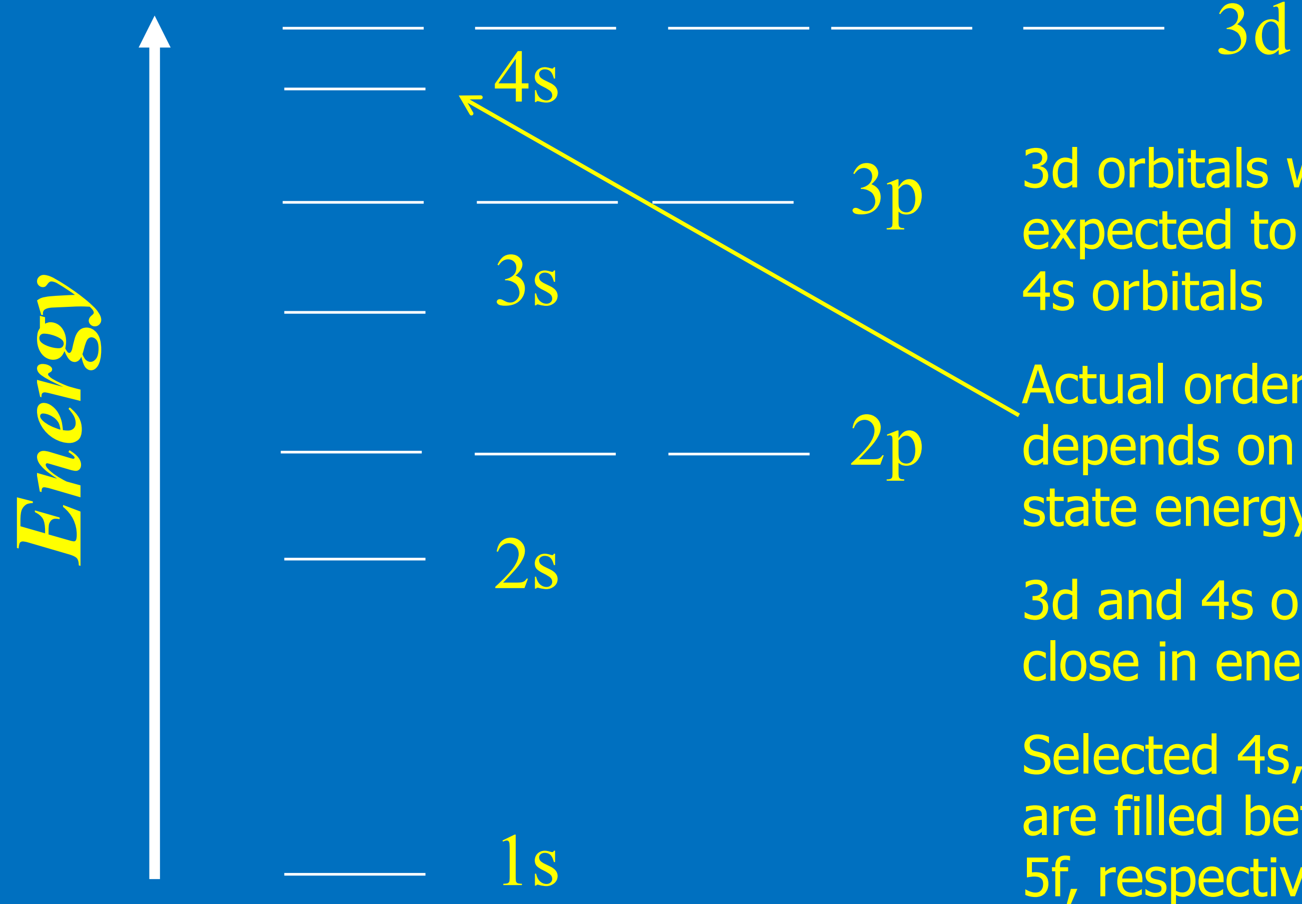
- Copper (Cu) relative to Nickel (Ni)
- Copper would be expected to have a ground state configuration of $[Ar]3d^94s^2$
- The $[Ar]3d^{10}4s^1$ configuration is actually lower in energy



Partial Orbital Diagrams and Electron Configurations* for the Elements in Period 4

Atomic Number	Element	Partial Orbital Diagram (4s, 3d, and 4p Sublevels Only)			Full Electron Configuration	Condensed Electron Configuration
28	Ni	↑↓	↑↓ ↑↓ ↑↓ ↑ ↑	□ □ □	$[1s^22s^22p^63s^23p^6]\ 4s^23d^8$	$[Ar]\ 4s^23d^8$
29	Cu	↑	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	□ □ □	$[1s^22s^22p^63s^23p^6]\ 4s^13d^{10}$	$[Ar]\ 4s^13d^{10}$
30	Zn	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	□ □ □	$[1s^22s^22p^63s^23p^6]\ 4s^23d^{10}$	$[Ar]\ 4s^23d^{10}$
31	Ga	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ □ □	$[1s^22s^22p^63s^23p^6]\ 4s^23d^{10}4p^1$	$[Ar]\ 4s^23d^{10}4p^1$
32	Ge	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ ↑ □	$[1s^22s^22p^63s^23p^6]\ 4s^23d^{10}4p^2$	$[Ar]\ 4s^23d^{10}4p^2$
33	As	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑ ↑ ↑	$[1s^22s^22p^63s^23p^6]\ 4s^23d^{10}4p^3$	$[Ar]\ 4s^23d^{10}4p^3$
34	Se	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑ ↑	$[1s^22s^22p^63s^23p^6]\ 4s^23d^{10}4p^4$	$[Ar]\ 4s^23d^{10}4p^4$
35	Br	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑	$[1s^22s^22p^63s^23p^6]\ 4s^23d^{10}4p^5$	$[Ar]\ 4s^23d^{10}4p^5$
36	Kr	↑↓	↑↓ ↑↓ ↑↓ ↑↓ ↑↓	↑↓ ↑↓ ↑↓	$[1s^22s^22p^63s^23p^6]\ 4s^23d^{10}4p^6$	$[Ar]\ 4s^23d^{10}4p^6$

Orbital Energy Levels in Multi-electron Systems



3d orbitals would be expected to be filled before 4s orbitals

Actual order of filling depends on total ground state energy of the atom

3d and 4s orbitals are very close in energy

Selected 4s, 5s, 6s, 7s levels are filled before 3d, 4d, 4f, 5f, respectively

Configurations and the Periodic Table

- Electrons that *reside in the outermost shell* of an atom - or in other words, those electrons outside the “noble gas core” - are called *valence electrons*
  - These electrons are primarily involved in chemical reactions
  - Elements within a given group have the same valence shell configuration
  - This accounts for the similarity of the chemical properties among groups of elements

n = 2 Li – $2s^1$ Be – $2s^2$
n = 3 Na – $3s^1$ Mg – $3s^2$
n = 4 K – $4s^1$ Ca – $4s^2$
n = 5 Rb – $5s^1$ Sr – $5s^2$

Configurations and the Periodic Table

- Noble gas core: an inner shell configuration resembling one of the noble gases (He, Ne, Ar, Kr, Xn)

- Pseudo-noble gas core: noble gas core + (n-1)d^{10} electrons: Ex $Sn \rightarrow Sn^{+4}$

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

Configurations and the Periodic Table

- Configurations of Main Group Ions
  - Noble gases have filled outer energy levels (ns^2np^6), have very high Ionization Energies (IEs), and positive (endothermic) Electron Affinities (EAs); thus do not readily form ions
  - Elements in Groups 1A, 2A, 6A, 7A that readily form ions by gaining electrons (1A & 2A) or losing electrons (6A & 7A) attain a filled outer level conforming to a Noble Gas configuration
  - Such ions are said to be "Isoelectronic" with the nearest Noble gas configuration

$$\text{Na}\ (1s^22s^22p^63s^1) \rightarrow \text{Na}^+\ (1s^22s^22p^6)\ +\ 1e^-$$

Isoelectronic with [Ne] + $1e^-$

Configurations and the Periodic Table

- The energy needed to remove the electrons from metal in groups 1A, 2A, 6A, 7A, is supplied during exothermic reactions with nonmetals

- Attempts to remove more than 1 electron from group 1A or 2 electrons from group 2A metals would mean removing core (not valence) electrons requiring significantly more energy than is available from a reaction with a non-metal

Configurations and the Periodic Table

- The larger metals from Groups 3A, 4A, and 5A form cations through a different process
- It would be energetically impossible for them to lose enough electrons to attain a noble gas configuration

  Ex: Tin (Sn), Z = 50 would have to lose 14 electrons (two 5p, ten 4d, two 5s) to be isoelectronic with Krypton: Z =36

- Instead, tin loses fewer electrons and still attains one or more stable pseudo-noble gas configurations

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

Stability comes from empty 5s & 5p sublevels

and a filled inner 4d sublevel (n-1)d^{10} configuration

Pseudo-Noble Gas Configuration

Practice Problem

Which of the following electron configurations represents an excited state?

a. He: $1s^2$

b. Ne: $1s^2\ 2s^2\ 2p^6$

c. Na: $1s^2\ 2s^2\ 2p^6\ 3s^1$

d. P: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^2\ 4s^1$

e. N: $1s^2\ 2s^2\ 2p^3$

Ans: d

Ground state for Phosphorus is:

$1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^3$

The 3p subshell would continue to fill before the 4s subshell would start to fill

Practice Problem

What is the electron configuration for the valence electrons of Technetium (Tc, Z = 43)?

a. $4d^5 5s^2$

b. $5s^2 5d^4$

c. $4s^2 4d^4$

d. $4d^6 5s^2$

e. $3d^4 4s^2$

Ans: a

$4d^5 5s^2$ 5 + 2 = 7 valence electrons

Technetium (atomic no. = 43 = 43 total electrons)

Practice Problem

What is the electron configuration for the valence electrons of Polonium (Po, Z=84)?

a. $6s^2 6p^2$

b. $6s^2 5d^{10} 6p^4$

c. $6s^2 5d^{10} 6p^6$

d. $6s^2 6p^4$

e. $7s^2 6p^4$

Ans: b

$6s^2 5d^{10} 6p^4$ 2 + 10 + 4 = 16 valence electrons

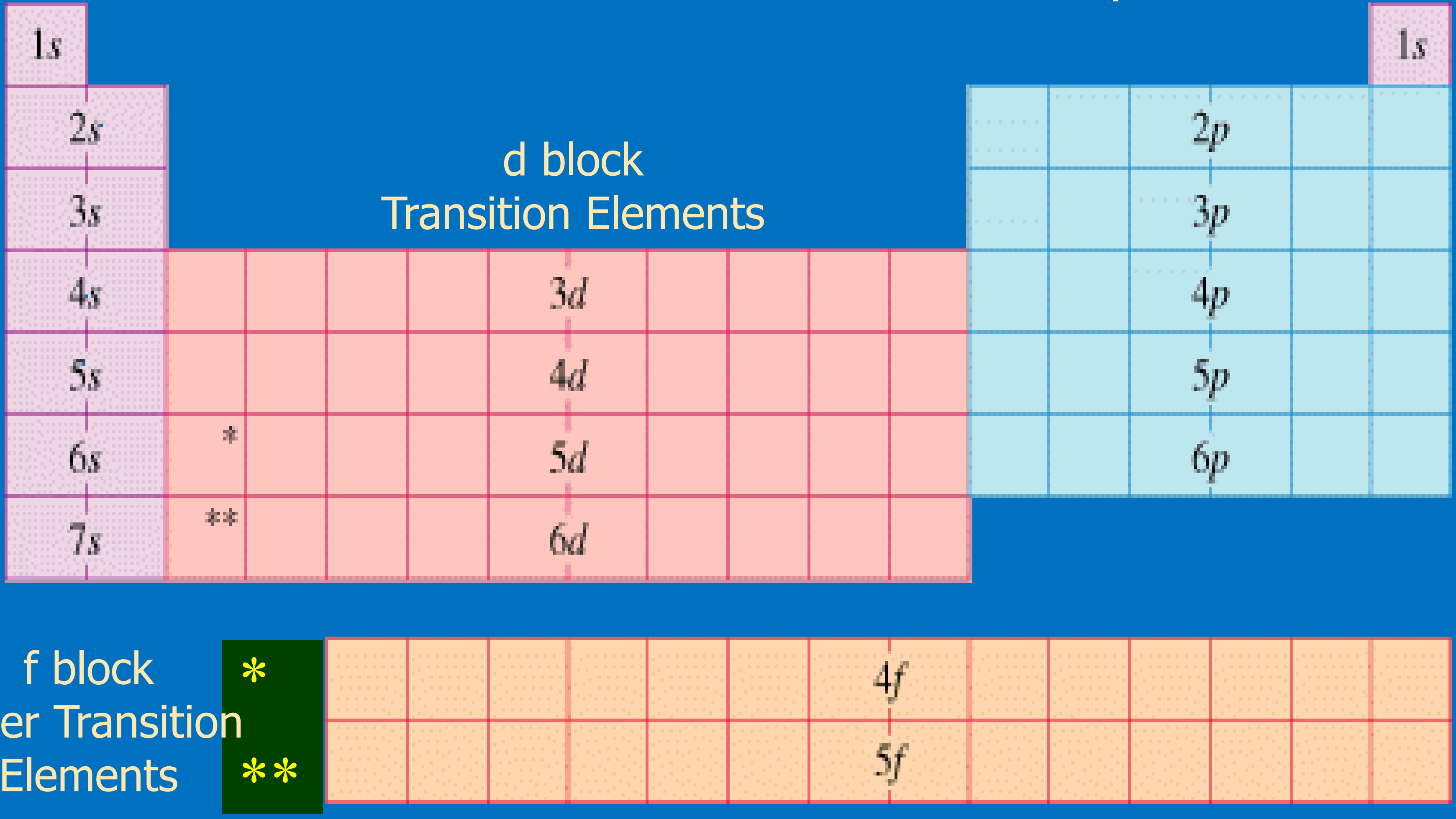
Polonium (atomic no. 84 = 84 total electrons)

Configurations and the Periodic Table

- The following slide illustrates how the periodic table provides a sound way to remember the Aufbau sequence
  - In many cases you need only the configuration of the outer electrons
  - You can determine this from their position on the periodic table
  - The total number of valence electrons for an atom equals its group (vertical column) number

Configurations and the Periodic Table

Main block = s + p blocks



s block

p block

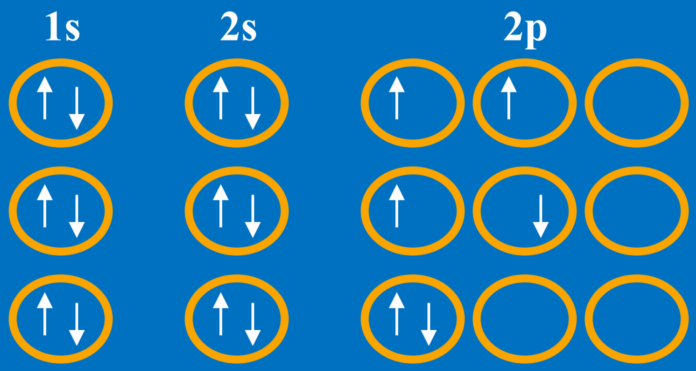
d block
Transition Elements

f block
Inner Transition
Elements

Orbital Diagrams

- Consider carbon (Z = 6) with the ground state configuration $1s^2 2s^2 2p^2$
  - Three possible arrangements are given in the following orbital diagrams.

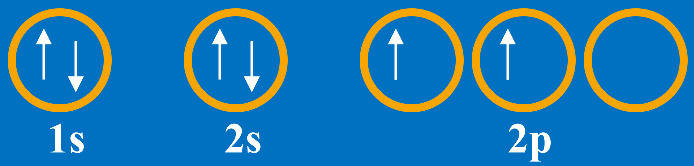
Diagram 1:
Diagram 2:
Diagram 3:



  - Each state has a different energy and different magnetic characteristics

Orbital Diagrams

- **Hund’s rule** states that the lowest energy arrangement (the “ground state”) of electrons in a sub-shell is obtained by putting electrons into separate orbitals of the sub shell with the same spin before pairing electrons
  - Looking at carbon again, we see that the ground state configuration corresponds to diagram 1 when following Hund’s rule

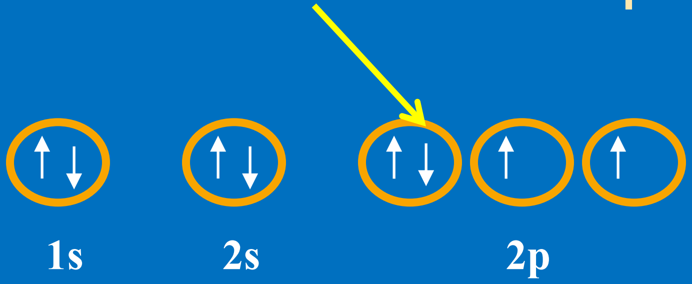


  - Note: The 2 e- in the 2p orbitals are shown as “up” arrows representing the +1/2 spin state, which has lower energy the -1/2 spine state

Orbital Diagrams

- To apply Hund's rule to Oxygen, whose ground state configuration is $1s^2 2s^2 2p^4$, place the first seven electrons as follows

  - The last electron is paired with one of the 2p electrons to give a doubly occupied orbital, i.e., a +½ spin state and a – ½ spin state



Summary

- Pauli Exclusion principle: no 2 e^-s in an atom can have the same four quantum numbers

- Aufbau Principle: obtain electron configurations of the ground state of atoms by successively filling subshells with electrons in a specific order

- Hunds Rule: the lowest energy arrangement of electrons in a subshell is obtained by putting electrons into separate orbitals of the subshell with the same spin before paring them

Recall: +1/2 spin has lower energy then -1/2 spin

Periodic Properties

- Two factors determine the size of an atom
  - One factor is the **principal quantum number, n**. The larger "n" is , the larger the size of the orbital
  - The other factor is the **effective nuclear charge** (slide 28)**,** which is the positive charge an electron experiences from the nucleus minus any "shielding effects" from intervening electrons
- The **Periodic Law** states that:

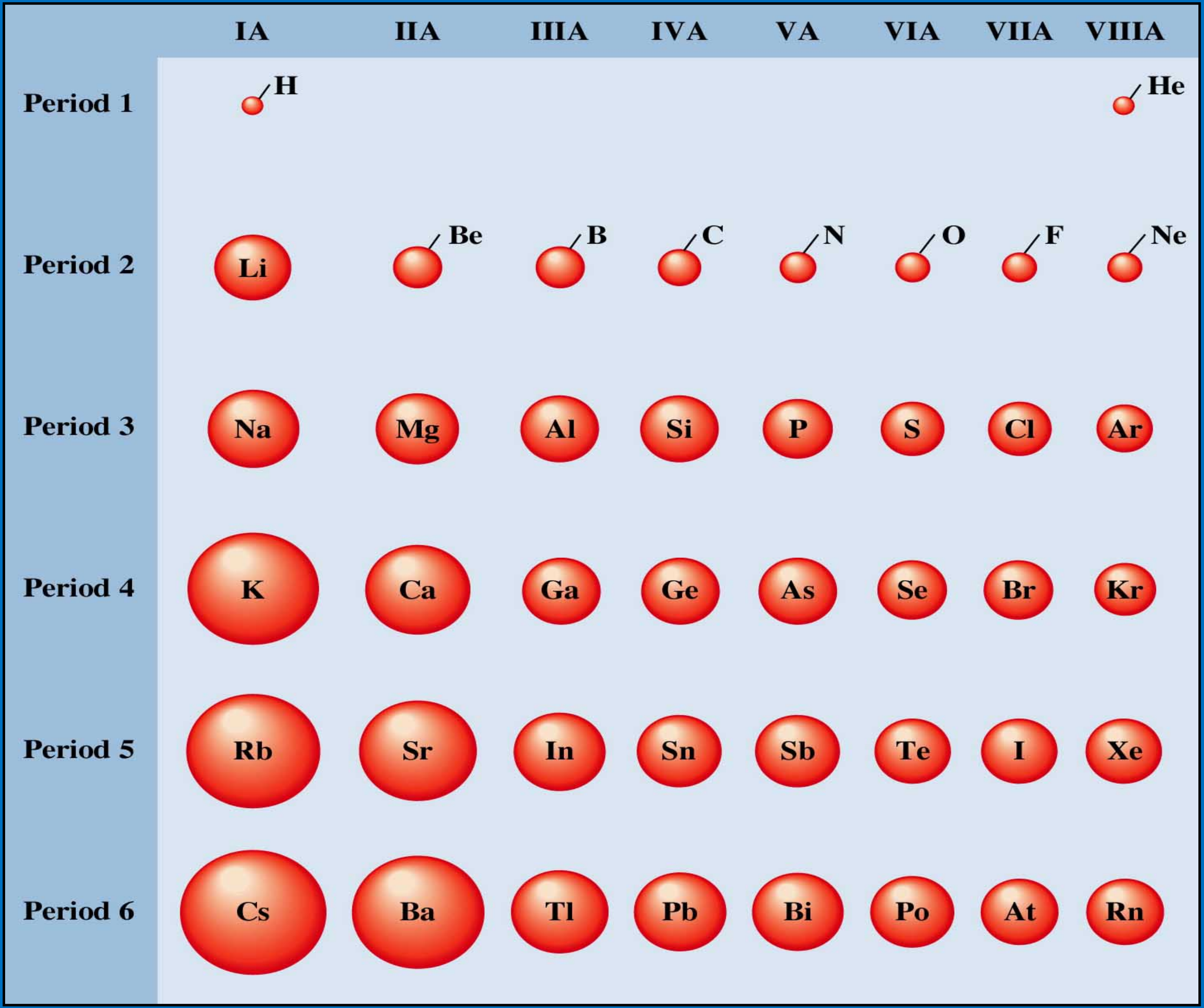
> When the elements are arranged by atomic number, their physical and chemical properties vary periodically – across the periodic chart row

Periodic Properties – Atomic Size

- Atomic Size, Ionization Energy, Electron Affinity
  - **Atomic radius**
    - Within each Period (across horizontal row), the atomic radius tends to decrease with increasing atomic number (nuclear charge more dominant than electron repulsion)
    - Within each Group (down a vertical column), the atomic radius tends to increase with increasing period number (electron repulsion dominates nuclear charge increase)

Periodic Properties – Atomic Size

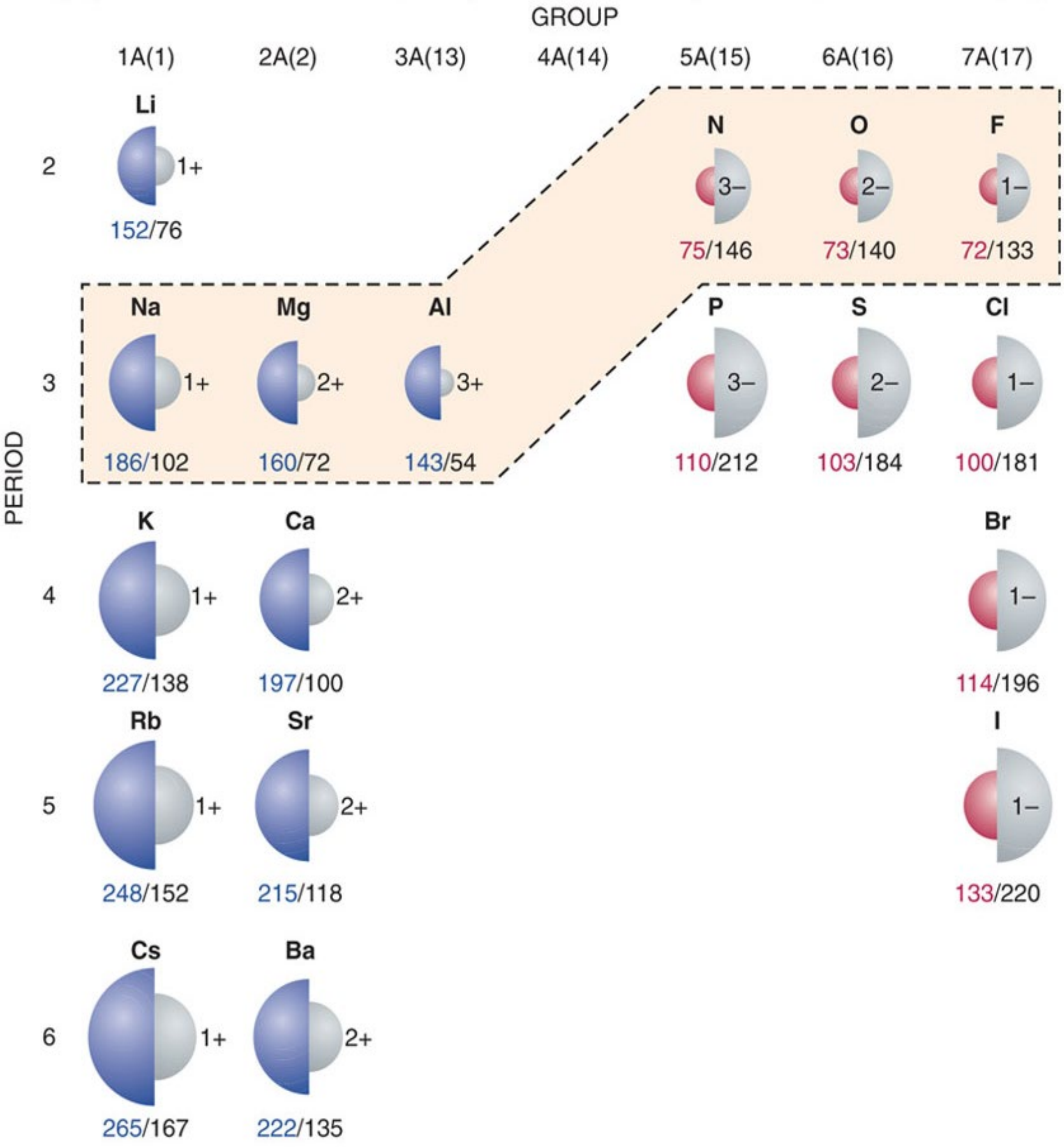
- Representation of atomic radii (covalent radii) of the main-group elements (neutral atoms)



Periodic Properties – Atomic Size

Elements vs Ions

- Ionic Size increase down a group
  - Number of energy levels increases
- Ionic Size becomes more complicated across a period
  - Decreases among cations
  - Increase dramatically with first anion
  - Decreases within anions



Periodic Properties – Atomic Size

- Ionic Size and Atomic Size
  - Cations are smaller than their parent atoms
    - Electrons are removed from the outer level
    - Resulting decrease in electron repulsions allows nuclear charge to pull remaining electrons closer
  - Anions are larger than their parent atoms
    - Electrons added to outer level
    - Resulting in increased electron repulsion allowing them to occupy more space

Periodic Properties – Ionization Energy

- **Ionization energy**
  - The **first ionization energy** of an atom is the minimal energy needed to remove the highest energy (outermost) electron from the neutral atom
  - For a Lithium atom, the first ionization energy is illustrated by:

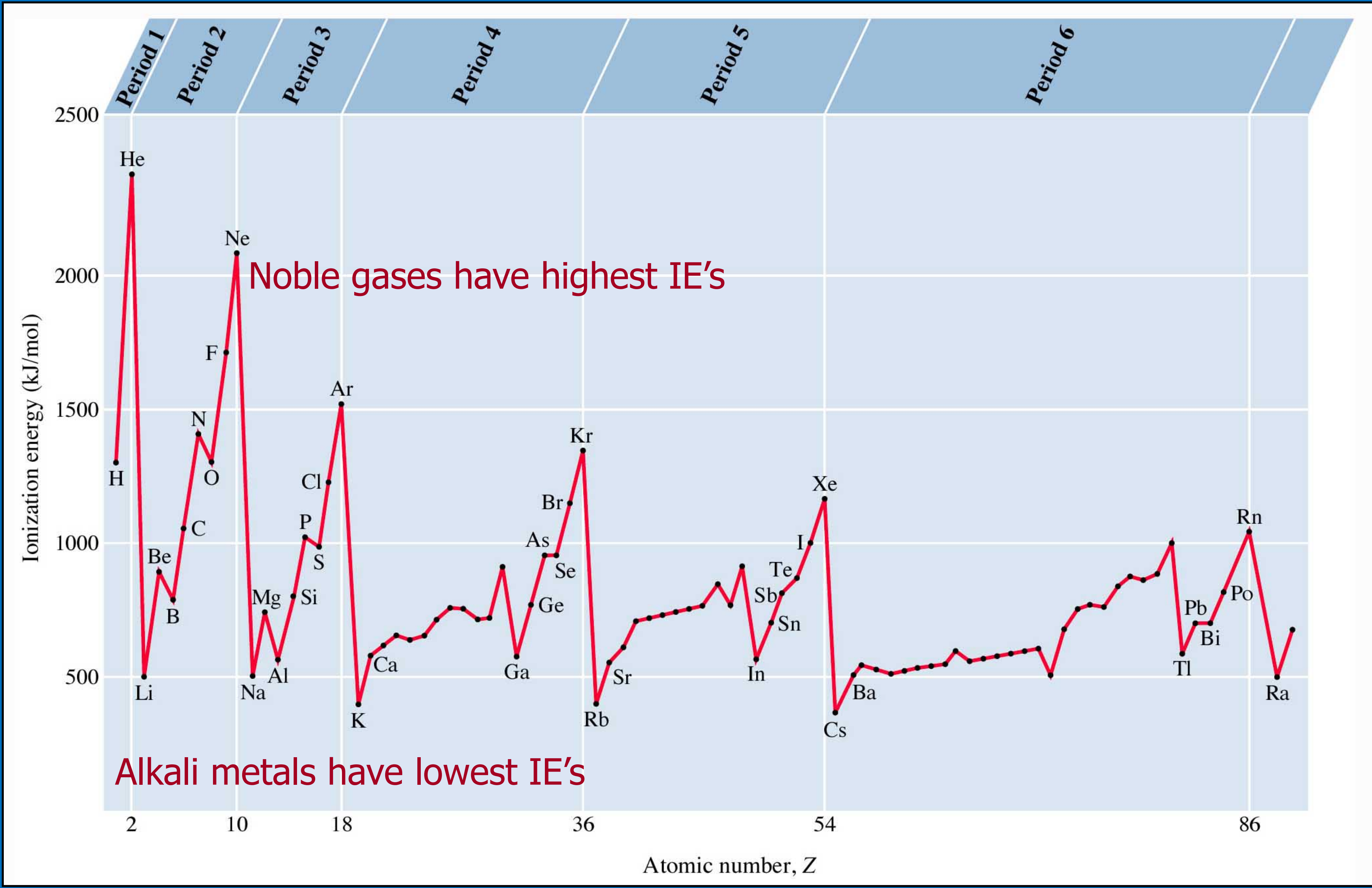
$\mathrm{Li}(1s^2 2s^1) \rightarrow \mathrm{Li}^+(1s^2) + e^-$ IE = 520 kJ/mol

Endothermic (requires energy input)

Periodic Properties – Ionization Energy

- **Ionization energy (IE)**
  - There is a general trend that ionization energies increase with atomic number within a given period
  - This follows the trend in size, as it is more difficult to remove an electron that is closer to the nucleus
  - For the same reason, we find that ionization energies, again following the trend in size, decrease descending down a column of elements

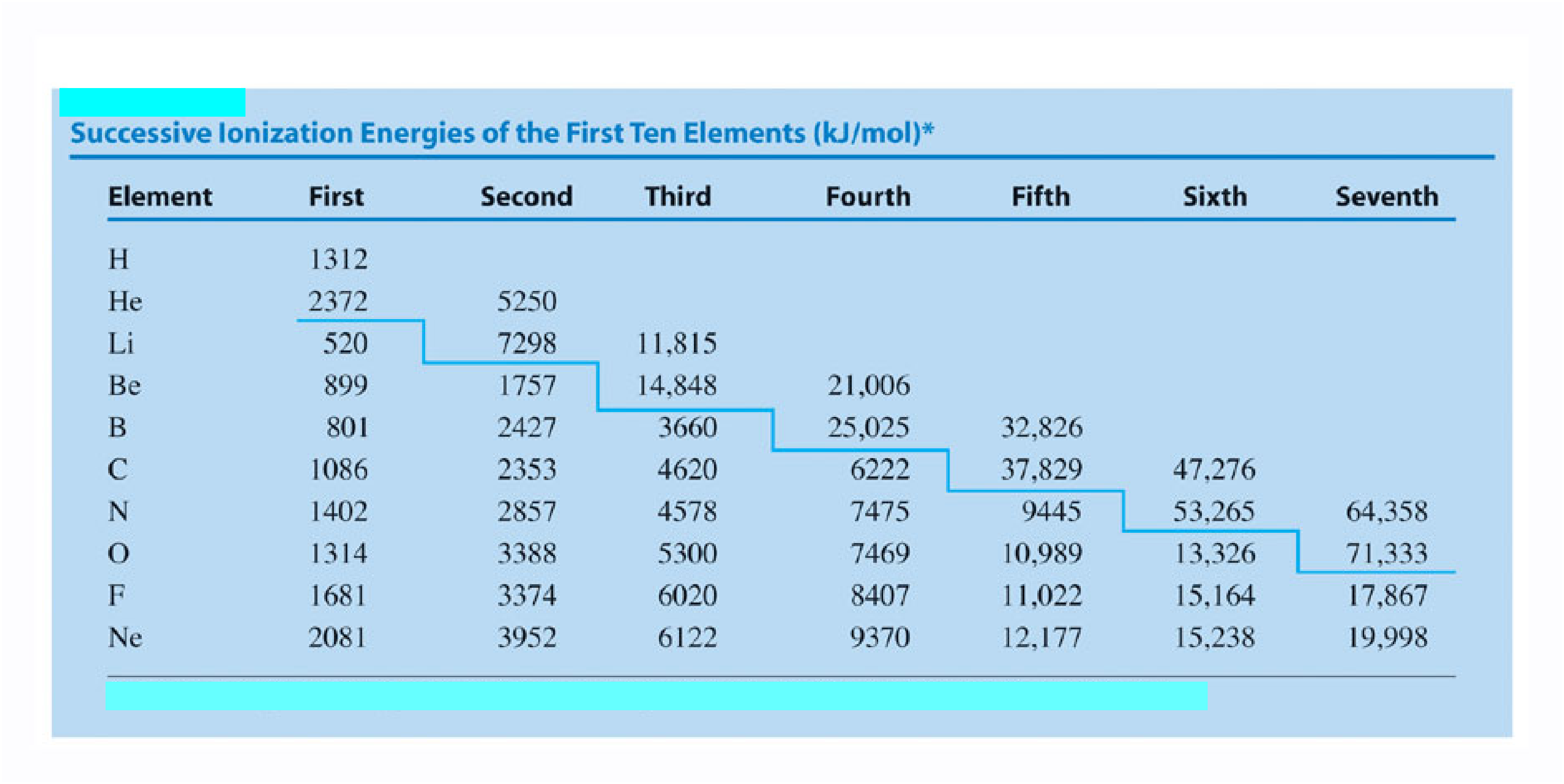
Ionization Energy vs Atomic Number



Noble gases have highest IE's

Alkali metals have lowest IE's

Periodic Properties – Ionization Energy



Successive Ionization Energies of the First Ten Elements (kJ/mol)*

Element	First	Second	Third	Fourth	Fifth	Sixth	Seventh
H	1312						
He	2372	5250					
Li	520	7298	11,815				
Be	899	1757	14,848	21,006			
B	801	2427	3660	25,025	32,826		
C	1086	2353	4620	6222	37,829	47,276	
N	1402	2857	4578	7475	9445	53,265	64,358
O	1314	3388	5300	7469	10,989	13,326	71,333
F	1681	3374	6020	8407	11,022	15,164	17,867
Ne	2081	3952	6122	9370	12,177	15,238	19,998

Ionization Energies to the “Right” of the a vertical line correspond to removal of electrons from the “Core” of the atom

Periodic Properties – Ionization Energy

- **Ionization energy (IE)**
  - The electrons of an atom can be removed successively
  - The energies required at each step are known as the **first** ionization energy, the **second** ionization energy, and so forth
  - Successive Ionization Energies increase because each electron is pulled away from an ion with a progressively higher positive charge, i.e., a more effective nuclear charge

Exceptions to Ionization Energy Trends

- A IIIA element , such as Boron ($2s^22p^1$), has a smaller ionization energy (IE) than the preceding IIA element Beryllium ($2s^2$) because one np electron is more easily removed than the second ns electron

- A VIA element, such as oxygen ($2s^22p^4$), has smaller ionization Energy than the preceding VA element nitrogen ($2s^22p^3$). As a result of repulsion it is easier to remove an electron from the doubly occupied 2p orbital of the VI element that from a singly occupied p orbital of the preceding VA element

Nitrogen $2s^22p^3$ Oxygen $2s^22p^4$

Periodic Properties – Electron Affinity

- **Electron Affinity (EA):** the energy change for the process of adding an electron to a neutral atom in the gaseous state to form a negative ion, i.e., an Anion
  - 1st Electron Affinity – Formation of 1 mole of monovalent (1^-) gaseous ions

    $$\text{Atoms(g)} + e^- \rightarrow \text{ion}^-\text{(g)} \quad \Delta E = EA_1$$

  - For the formation of the Chloride ion (Cl^-) from the Chlorine atom, the first electron affinity is illustrated by:

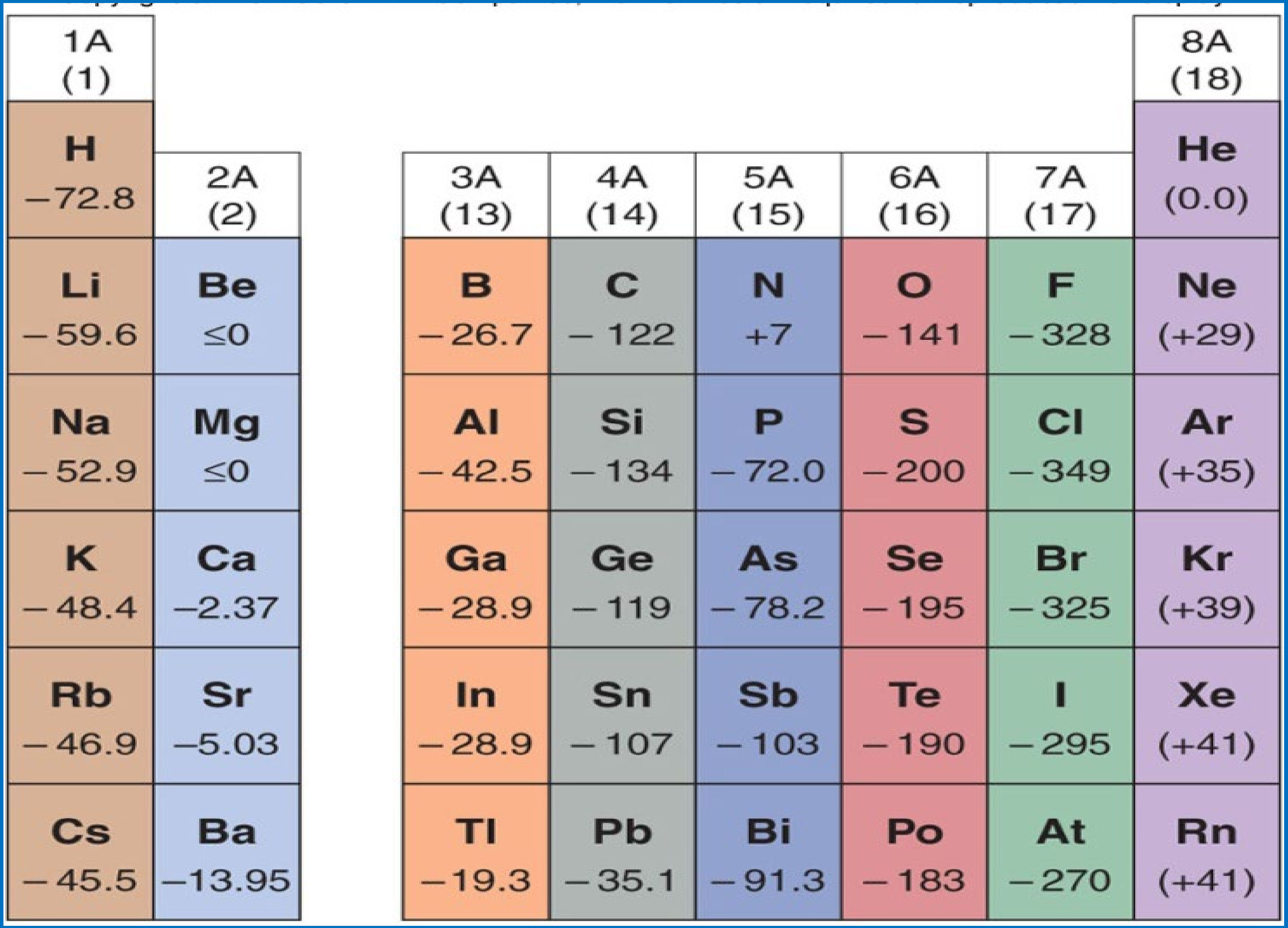
$$\mathbf{Cl([Ne]3s^2 3p^5) + e^- \rightarrow Cl^-([Ne]3s^2 3p^6)}$$

Electron Affinity = EA_1 = –349 kJ/mol
Exothermic (releases energy)

Periodic Properties – Electron Affinity

- **Electron Affinity (EA)**
  - The more negative the electron affinity, the more stable the negative ion that is formed
  - Broadly speaking, the general trend goes from lower left to upper right as electron affinities become more negative
  - Highest electron affinities occur for halogens, F and Cl
  - Negative values indicate that energy is released when the Anion forms
  - Note: Electron Affinity is not the same as Electronegativity
    See (Chap 9) – bonded atom attracting shared electron pair

Periodic Properties – Electron Affinity



1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
H −72.8							**He** (0.0)
Li −59.6	**Be** ≤0	**B** −26.7	**C** −122	**N** +7	**O** −141	**F** −328	**Ne** (+29)
Na −52.9	**Mg** ≤0	**Al** −42.5	**Si** −134	**P** −72.0	**S** −200	**Cl** −349	**Ar** (+35)
K −48.4	**Ca** −2.37	**Ga** −28.9	**Ge** −119	**As** −78.2	**Se** −195	**Br** −325	**Kr** (+39)
Rb −46.9	**Sr** −5.03	**In** −28.9	**Sn** −107	**Sb** −103	**Te** −190	**I** −295	**Xe** (+41)
Cs −45.5	**Ba** −13.95	**Tl** −19.3	**Pb** −35.1	**Bi** −91.3	**Po** −183	**At** −270	**Rn** (+41)

Periodic Properties – Atomic Size

- Atomic Size
  - Atomic Size (neutral atoms & ions) increases down a main group
  - Atomic Size (neutral atoms & ions) decreases across a Period
  - Atomic Size remains relatively constant across a transition series
- Ionization Energy
  - First Ionization Energy (remove outermost e-) is inversely related to atomic size
  - 1st Ionization Energy decreases down a group
  - 1st Ionization Energy increases across period
  - Successive IEs show very large increases after 1st electron is removed
- Electron Affinity
  - Similar patterns (with many exceptions) to ionization Energy (lower left to upper right)
  - Highest electron affinities occur for halogens, F and Cl