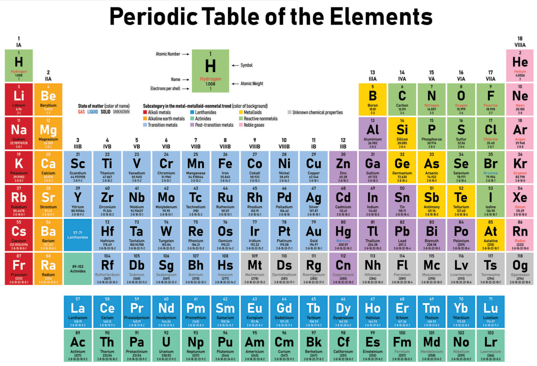
The Structure of Atoms and Periodic Trends
Chapter Six Part 2



CH 221
Professor Michael Russell

MAR *Last update: 4/29/24*

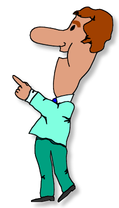
Arrangement of Electrons in Atoms

Electrons in atoms are arranged as

SHELLS (n)

SUBSHELLS (l)

ORBITALS (m_l)



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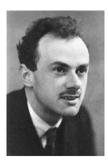
Arrangement of Electrons in Atoms

Each orbital can be assigned no more than 2 electrons!

This is tied to the existence of a 4th quantum number, the electron spin quantum number, m_s.

m_s arises naturally when relativity (Einstein) combined with quantum mechanics (Paul Dirac)


Paul Dirac

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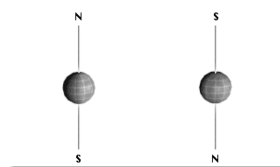
Electron Spin Quantum Number, m_s



Electron spin can be proven experimentally.
Two spin directions are given by m_s where m_s = $+^1/_2$ and $-^1/_2$.
Leads to magnetism in atoms and ions

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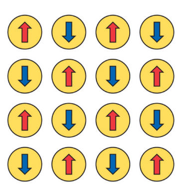
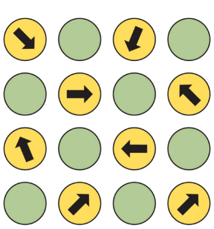
Magnetism

In diamagnetic systems, all electron spins are paired - no net magnetic moment.





In paramagnetic systems, unpaired spins present. Magnetic fields randomly arranged unless placed in an external magnetic field.

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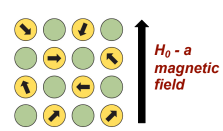
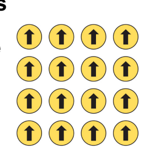
Magnetism

In ferromagnetic substances the orientations of magnetic fields from unpaired electrons are affected by spins from electrons around them.



When an external field is applied *and then removed*, the substance maintains the magnetic moment and becomes a permanent magnet.



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Electron Spin Quantum Number

Diamagnetic: NOT attracted to a magnetic field; spin paired.
Paramagnetic: substance is attracted to a magnetic field. Substance has unpaired electrons.

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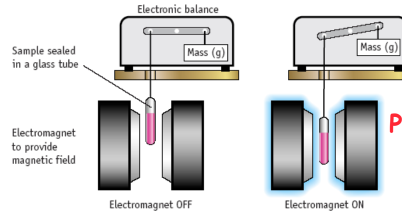
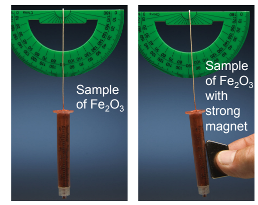


Measuring Paramagnetism

Paramagnetic: substance is attracted to a magnetic field. Substance has unpaired electrons.

Diamagnetic: NOT attracted to a magnetic field



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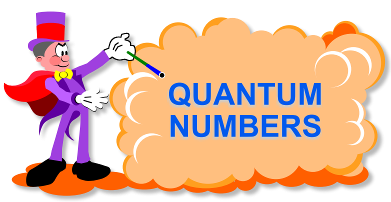

n --->	shell	1, 2, 3, 4, ...
l --->	subshell	0, 1, 2, ... (n - 1)
m_l --->	orbital	-l ... 0 ... +l
m_s --->	electron spin	$+^1/_2$ and $-^1/_2$

See: Quantum Numbers Handout

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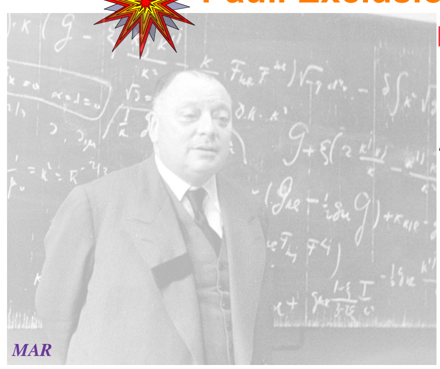
Pauli Exclusion Principle



No two electrons in the same atom can have the same set of 4 quantum numbers.

That is, each electron has a unique address which will consist of its own values of n, l, m_l and m_s.

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Wolfgang Pauli

Electrons in Atoms - the Pauli Exclusion Principle

When **n = 1**, *then* **l = 0** *and* **m_l = 0**
this shell has a **single orbital (1s)** *to which*
2e- *can be assigned*

n = 1, l = 0, m_l = 0, m_s = +1/2 - this is electron #1
n = 1, l = 0, m_l = 0, m_s = -1/2 - this is electron #2

When **n = 2**, *then* **l = 0** *(s)*, **1** *(p)*

2s orbital	**2e-**
three 2p orbitals	**6e-**
TOTAL =	**8e-**

"No two electrons in the same atom can have the same set of 4 quantum numbers."

electron number	n	l	m_l	m_s	
1	2	0	0	1/2	2s
2	2	0	0	-1/2	2s
3	2	1	-1	1/2	2p
4	2	1	-1	-1/2	2p
5	2	1	0	1/2	2p
6	2	1	0	-1/2	2p
7	2	1	+1	1/2	2p
8	2	1	+1	-1/2	2p

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Electrons in Atoms

When **n = 3**, *then* **l = 0** *(s)*, **1** *(p)*, **2** *(d)*

3s orbital	**2e-**
three 3p orbitals	**6e-**
five 3d orbitals	**10e-**
TOTAL =	**18e-**

Each electron has its own set of four quantum numbers!

Wolfgang Pauli

electron number	n	l	m_l	m_s	
1	3	0	0	1/2	3s
2	3	0	0	-1/2	3s
3	3	1	-1	1/2	3p
4	3	1	-1	-1/2	3p
5	3	1	0	1/2	3p
6	3	1	0	-1/2	3p
7	3	1	+1	1/2	3p
8	3	1	+1	-1/2	3p
9	3	2	-2	1/2	3d
10	3	2	-2	-1/2	3d
11	3	2	-1	1/2	3d
12	3	2	-1	-1/2	3d
13	3	2	0	1/2	3d
14	3	2	0	-1/2	3d
15	3	2	+1	1/2	3d
16	3	2	+1	-1/2	3d
17	3	2	+2	1/2	3d
18	3	2	+2	-1/2	3d

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Electrons in Atoms

electron number

	n	l	m_l	m_s	
1	4	0	0	1/2	4s
2	4	0	0	-1/2	4s
3	4	1	-1	1/2	4p
4	4	1	-1	-1/2	4p
5	4	1	0	1/2	4p
6	4	1	0	-1/2	4p
7	4	1	+1	1/2	4p
8	4	1	+1	-1/2	4p
9	4	2	-2	1/2	4d
10	4	2	-2	-1/2	4d
11	4	2	-1	1/2	4d
12	4	2	-1	-1/2	4d
13	4	2	0	1/2	4d
14	4	2	0	-1/2	4d
15	4	2	+1	1/2	4d
16	4	2	+1	-1/2	4d
17	4	2	+2	1/2	4d
18	4	2	+2	-1/2	4d

When **n = 4**, **l = 0**(*s*), **1**(*p*), **2**(*d*), **3**(*f*)

4s orbital	**2e-**
three 4p orbitals	**6e-**
five 4d orbitals	**10e-**
seven 4f orbitals	**14e-**
TOTAL =	**32e-**

electron number

	n	l	m_l	m_s	
19	4	3	-3	1/2	4f
20	4	3	-3	-1/2	4f
21	4	3	-2	1/2	4f
22	4	3	-2	-1/2	4f
23	4	3	-1	1/2	4f
24	4	3	-1	-1/2	4f
25	4	3	0	1/2	4f
26	4	3	0	-1/2	4f
27	4	3	+1	1/2	4f
28	4	3	+1	-1/2	4f
29	4	3	+2	1/2	4f
30	4	3	+2	-1/2	4f
31	4	3	+3	1/2	4f
32	4	3	+3	-1/2	4f

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Electron Shell (n)	Subshells Available	Orbitals Available ($2\ell + 1$)	Number of Electrons Possible in Subshell [$2(2\ell + 1)$]	Maximum Electrons Possible for nth Shell ($2n^2$)
1	*s*	1	2	2
2	*s*	1	2	8
	p	3	6	
3	*s*	1	2	18
	p	3	6	
	d	5	10	
4	*s*	1	2	32
	p	3	6	
	d	5	10	
	f	7	14	
5	*s*	1	2	50
	p	3	6	
	d	5	10	
	f	7	14	
	*g**	9	18	
6	*s*	1	2	72
	p	3	6	
	d	5	10	
	*f**	7	14	
	*g**	9	18	
	*h**	11	22	

*These orbitals are not used in the ground state of any known element.

Distribution of Electrons in Shells

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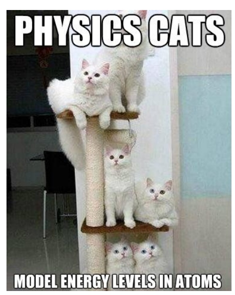
Assigning Electrons to Atoms

Electrons generally assigned to orbitals of successively higher energy.

For H atoms, E = - Rhc(1/n²). E depends only on n.

For many-electron atoms, energy depends on both n and l... introducing the "n + l" rule



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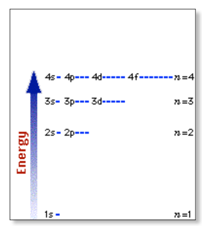
Assigning Electrons to Subshells



In H atom all subshells of same n have same energy.

In many-electron atom:

a) subshells increase in energy as value of n + l increases. (The *important* n + l rule)

b) for subshells of same n + l, subshell with lower n is lower in energy.

See Electron Configurations Handout

Using the n + l rule assumes zero point energy - the lowest energy state possible, or ground state

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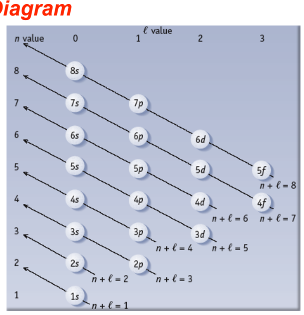
An Aufbau Diagram



Electron Filling Order

Aufbau comes from a German word meaning "building up", formulated by Bohr and Pauli in 1920s

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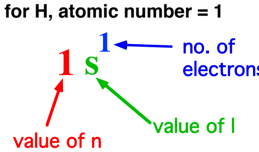
Writing Atomic Electron Configurations

Two ways of writing configs. One is called the spectroscopic or "spdf" notation.

SPECTROSCOPIC NOTATION for H, atomic number = 1



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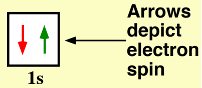
Writing Atomic Electron Configurations

Two ways of writing configs. Other is called the **orbital box notation**.

ORBITAL BOX NOTATION for He, atomic number = 2

$1s^2$



One electron has n = 1, l = 0, m_l = 0, m_s = + 1/2

Other electron has n = 1, l = 0, m_l = 0, m_s = - 1/2

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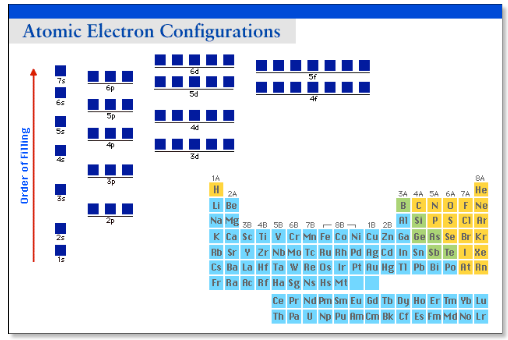

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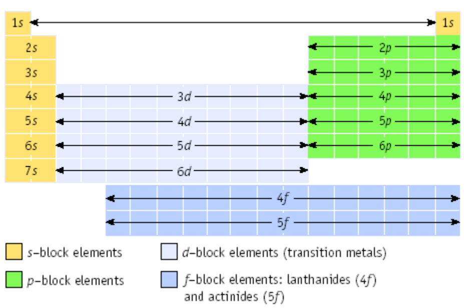
Atomic Electron Configurations Diagram

Electron Configurations and the Periodic Table



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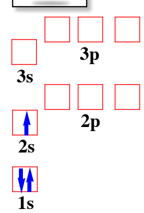
Lithium

Group 1A

Atomic number = 3

$1s^2 2s^1$ ---> 3 total electrons

paramagnetic



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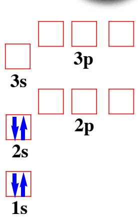
Beryllium

Group 2A

Atomic number = 4

$1s^2 2s^2$ ---> 4 total electrons

diamagnetic



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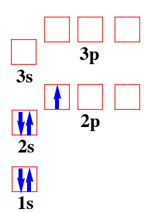
Boron

Group 3A

Atomic number = 5

$1s^2 2s^2 2p^1$ ---> 5 total electrons

paramagnetic



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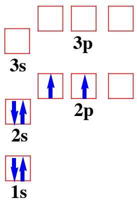
Carbon

Group 4A
Atomic number = 6
1s^2 2s^2 2p^2 --->
6 total electrons
paramagnetic



Friedrich Hund

Here we see for the first time **HUND'S RULE**. When placing electrons in a set of orbitals having the same energy, we place them singly as long as possible.

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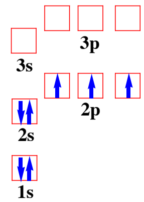
Nitrogen

Group 5A
Atomic number = 7
1s^2 2s^2 2p^3 --->
7 total electrons
paramagnetic



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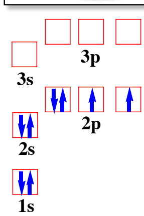
Oxygen

Group 6A
Atomic number = 8
1s^2 2s^2 2p^4 --->
8 total electrons
paramagnetic



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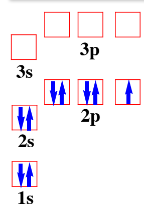
Fluorine

Group 7A
Atomic number = 9
1s^2 2s^2 2p^5 --->
9 total electrons
paramagnetic



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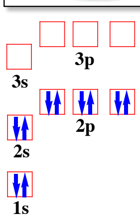
Neon

Group 8A
Atomic number = 10
1s^2 2s^2 2p^6 --->
10 total electrons
diamagnetic



Note that we have reached the end of the 2nd period, and the 2nd shell is full!

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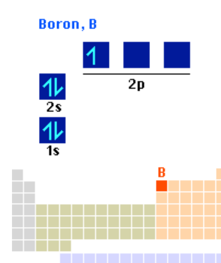
Electron Configurations of p-Block Elements



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Sodium

Group 1A
Atomic number = 11
$1s^2 2s^2 2p^6 3s^1$ or
"neon core" + $3s^1$
[Ne] $3s^1$ *(uses noble gas notation)*
And: we have begun a new period!

All Group 1A elements have [core]ns^1 configurations.

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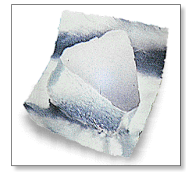
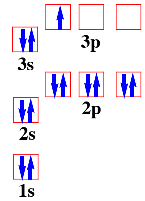
Aluminum



Group 3A
Atomic number = 13
$1s^2 2s^2 2p^6 3s^2 3p^1$ *or*
[Ne] $3s^2 3p^1$

All* Group 3A elements have [core] $ns^2 np^1$ configurations where n is the period number.



* *some have $(n-1)d^{10}$ as well*

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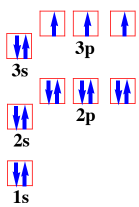
Phosphorus

Group 5A
Atomic number = 15
$1s^2 2s^2 2p^6 3s^2 3p^3$ *or*
[Ne] $3s^2 3p^3$

All* Group 5A elements have [core] $ns^2 np^3$ configurations where n is the period number.



* *some have $(n-1)d^{10}$ also*

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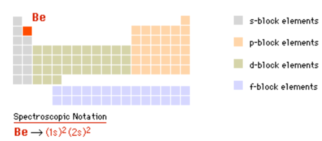
Relationship of Electron Configuration and Region of the Periodic Table



Gray = s block
Orange = p block
Green = d block
Violet = f block

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Transition Metals

All transition metals have the configuration [core]$ns^x(n - 1)d^y$ and so are "d-block" elements.


Chromium


Iron


Copper

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Fourth Period Electron Configurations

K	$1s^22s^22p^63s^23p^64s^1$	or [Ar]$4s^1$
Ca	$1s^22s^22p^63s^23p^64s^2$	or [Ar]$4s^2$
Sc	$1s^22s^22p^63s^23p^64s^23d^1$	or [Ar]$4s^23d^1$
Ti	$1s^22s^22p^63s^23p^64s^23d^2$	or [Ar]$4s^23d^2$
V	$1s^22s^22p^63s^23p^64s^23d^3$	or [Ar]$4s^23d^3$
Cr	$1s^22s^22p^63s^23p^64s^13d^5$	or [Ar]$4s^13d^5$
Mn	$1s^22s^22p^63s^23p^64s^23d^5$	or [Ar]$4s^23d^5$
Cu	$1s^22s^22p^63s^23p^64s^13d^{10}$	or [Ar]$4s^13d^{10}$

Note: *exceptions!*

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Electron Configuration Anomalies

Cr $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$ or $[Ar]4s^1 3d^5$

Cu $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$ or $[Ar]4s^1 3d^{10}$

Chromium, copper and other elements do not follow the *n* + *l* filling orders

Anomalies arise from stability associated with half-filled and completely filled d-subshells.

Know how n + l rule works, and know that anomalies exist on the periodic table

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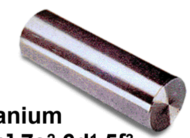
Lanthanides and Actinides

All these elements have the configuration
$[core]ns^x(n - 1)d^y(n - 2)f^z$
and so are "f-block" elements

Exceptions exist:

Cerium
$[Xe]\ 6s^2\ 5d^1\ 4f^1$
$[Xe]\ 6s^2\ 4f^2$ expected



Uranium
$[Rn]\ 7s^2\ 6d^1\ 5f^3$
$[Rn]\ 7s^2\ 5f^4$ expected

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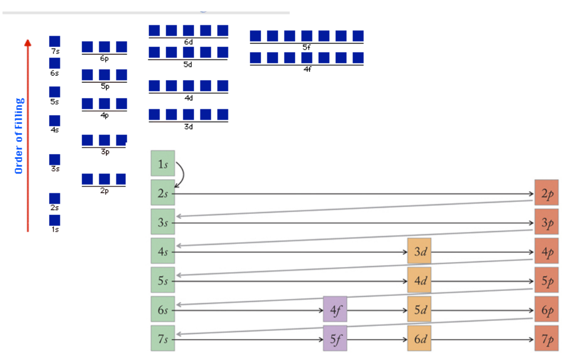

Electron Configurations Filling Order

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Transition Metals

Iron:
Zinc:
Technetium:
Niobium:
Osmium:
Meitnerium:

notice f orbitals in 6th period & beyond

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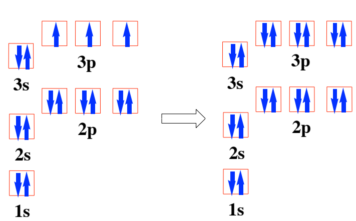
Anion Configurations

To form *anions* from elements add 1 or more e- using normal n + l rules

P $[Ne]\ 3s^2\ 3p^3$ + 3e- → P^{3-} $[Ne]\ 3s^2\ 3p^6$



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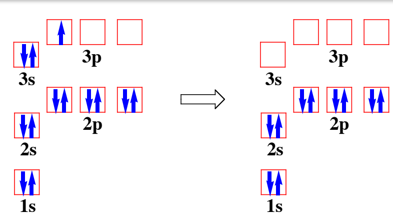
Cation Configurations

To form cations from elements remove 1 or more e- from subshell of highest n [or highest (n + l)].

Al $[Ne]\ 3s^2\ 3p^1$ - 3e- → Al^{3+} [Ne]



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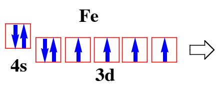
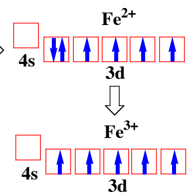
Ion Configurations

For transition metals, remove ns electrons and then (n - 1) electrons.

Fe [Ar] $4s^2 3d^6$ ---> Fe^{2+} [Ar] $3d^6$ ---> Fe^{3+} [Ar] $3d^5$





To form cations, always remove electrons of highest n value first!

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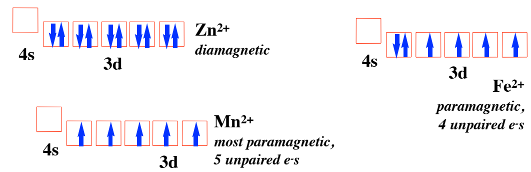
Magnetic Properties

<u>Magnetic properties</u> of ions assist us with charges

DIAMAGNETIC ions have no unpaired electrons.
Ions with unpaired electrons are PARAMAGNETIC.

As number of unpaired electrons increases, the degree of paramagnetism also increases



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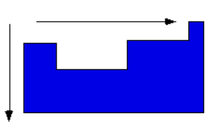
Periodic Trends

CH 221 Q&D Guide to Periodic Trends:

- **Atomic** and **ionic size**: **increase left** *and* **down**
- **Ionization energy** *and* **Electron affinity**: **increase right** and **up**
- *See <u>Periodic Trends Handout</u>*

Electrons held more tightly

Larger orbitals. Electrons held less tightly.



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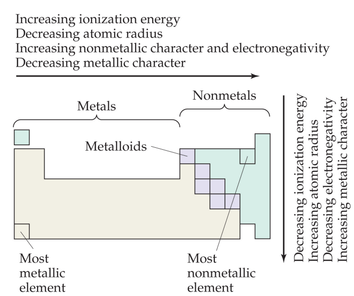
CH 221 Periodic Trends "Cheat Sheet"



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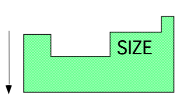
Atomic Size



Size increases as you go down a group.

Because electrons are added further from the nucleus, there is less attraction.

Size increases as you go left across a period.

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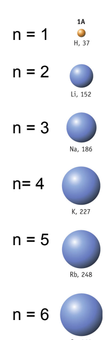
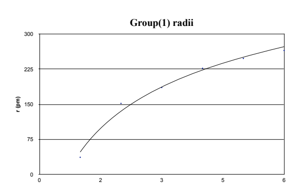


Moving **down** group IA, the atomic radii **increase** with the principle quantum number



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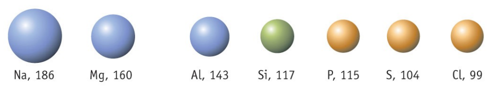
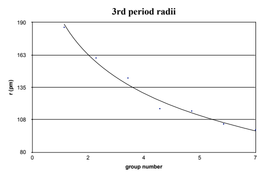


Moving **across** the 3rd period we see the atomic radii of the elements **decrease**.

Atomic **radii** *generally* **increase** going **right to left** on the periodic table.



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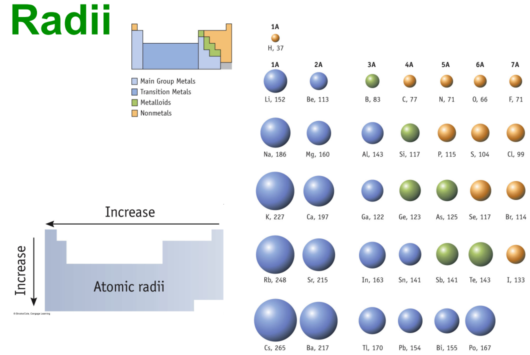
Atomic Radii



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Ion Sizes

Li,152 pm
3e and 3p

Does the size go up or down when losing an electron to form a cation?

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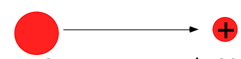
Ion Sizes



Li,152 pm
3e and 3p

Li^{+}, 60 pm
2e and 3 p

Forming a cation.

- **CATIONS are SMALLER than the atoms from which they come.**
- **The electron/proton attraction has increased, and so size DECREASES.**

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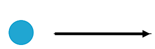
Ion Sizes



F,64 pm
9e and 9p

Does the size go up or down when gaining an electron to form an anion?

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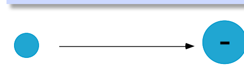
Ion Sizes



F,64 pm
9e and 9p

F^{-}, 136 pm
10 e and 9 p

Forming an anion.

- **ANIONS are LARGER than the atoms from which they come.**
- **The electron/proton attraction has decreased, and so size INCREASES.**
- **Trends in ion sizes are the same as atom sizes** *(but only compare cations to cations or anions to anions!)*

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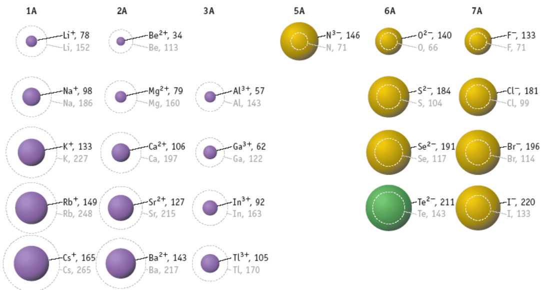
Trends in Ion Sizes



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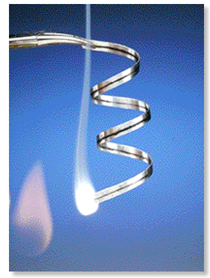
Redox Reactions



Why do metals lose electrons in their reactions?

Why does Mg form Mg^{2+} ions and not Mg^{3+}?

Why do nonmetals take on electrons?

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Ionization Energy

Mg (g) + 738 kJ ---> Mg^+ (g) + e-

Mg^+ (g) + 1451 kJ ---> Mg^{2+} (g) + e-

Mg^{2+} (g) + 7733 kJ ---> Mg^{3+} (g) + e-

Mg^+ has 12 protons and only 11 electrons. Therefore, IE for Mg^+ > Mg.

IE = energy required to remove an electron from an atom in the gas phase.

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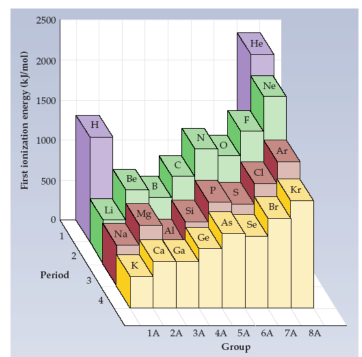
Trends in Ionization Energy



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Trends in Ionization Energy

Ionization Energy increases moving right across a period and up a group on the periodic table

Metals lose electrons more easily than nonmetals.

Metals are good reducing agents.

Nonmetals lose electrons with difficulty.

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Periodic Trend in the Reactivity of Alkali Metals with Water

Lithium

Sodium

Potassium

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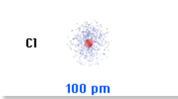
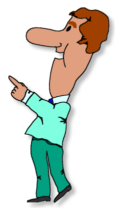
Electron Affinity

Nonmetlas tend to GAIN electrons to form anions.

Electron affinity is the energy involved when an atom gains an electron.

$A(g) + e^- \rightarrow A^-(g)$ E.A. = ΔE





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Trends in Electron Affinity

Electron Affinity increases as you move right across a period (EA becomes more negative).

Electron Affinity increases as you move up a group (EA becomes more negative).

1A (1)	2A (2)	3A (13)	4A (14)	5A (15)	6A (16)	7A (17)	8A (18)
H −72.6							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 −2.4	Ga −28.9	Ge −119	As −78.2	Se −195	Br −325	Kr (+39)*
Rb −46.9	Sr −5.0	In −28.9	Sn −107	Sb −103	Te −190	I −295	Xe (+41)*
Cs −45.5	Ba −14	Tl −19.2	Pb −35.2	Bi −91.3	Po −183.3	At −270*	Rn (+41)*

*Calculated values.

Electron Affinity values (kJ/mol)

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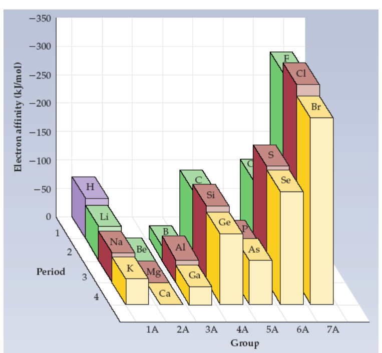
Trends in Electron Affinity



Notice:
$EA_{(F)} < EA_{(Cl)}$
unknown mechanism, electron repulsion? atom size?

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Implications of Periodic Trends

Useful in predicting reactivities, chemical formulas, etc.

Metals: **low ionization energy, give up electrons easily**
Nonmetals: **high electron affinity, love electrons from metals**

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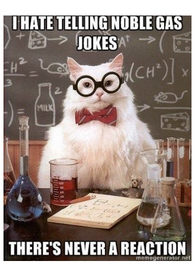
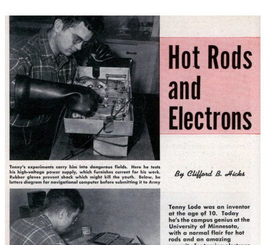


End of Chapter 6 Part 2



What Quantum Physics does to a man

See also:
- *Chapter Six Part 2 Study Guide*
- *Chapter Six Part 2 Concept Guide*
- *Important Equations (following this slide)*
- *End of Chapter Problems (following this slide)*

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Important Equations, Constants, and Handouts from this Chapter:

- **quantum numbers:** *know the origin and meaning of* **n, l, m_l, m_s**
- *understand* **paramagnetism** *and* **diamagnetism** *for atoms and ions*
- *know* **"nl" notation** *(4s, 3d, etc.) and the* **"n + l" rule** *for energy*
- *know how the* **Pauli Exclusion Theory** *and* **Hund's Rule** *apply towards electrons in orbitals; know the* **Aufbau Principle**
- *know how to* **create electron configurations** *for* **neutral atoms** *and also* **cations** *and* **anions using both orbital box** *and* **spectroscopic notation**
- *know the* **periodic trends** *for* **size**, **ion size**, **ionization energy** *and* **electron affinity**

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End of Chapter Problems: *Test Yourself*

1. Depict the electron configuration for arsenic (As) using *spdf* notation.
2. Using orbital box diagrams and/or noble gas notation, depict the electron configurations of the following: (a) V, (b) V^{2+}, and (c) V^{5+}. Are any of the ions paramagnetic? How many unpaired electrons are in each species?
3. Arrange the following elements in order of increasing size: Al, B, C, K, and Na.
4. Name the element corresponding to each characteristic below.
   a. the element with the electron configuration $1s^22s^22p^63s^23p^3$
   b. the alkaline earth element with the smallest atomic radius
   c. the element with the largest ionization energy in Group 5A
   d. the element whose 2+ ion has the configuration $[Kr]4d^5$
   e. the element with the most negative electron affinity in Group 6A
   f. the element whose electron configuration is $[Ar]3d^{10}4s^2$

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End of Chapter Problems: *Answers*

1. $[Ar]3d^{10}4s^24p^3$ ***or*** $1s^22s^22p^63s^23p^63d^{10}4s^24p^3$
2. V: $[Ar]4s^23d^3$ (paramagnetic, 3 unpaired electrons); V^{2+}: $[Ar]3d^3$ (paramagnetic, 3 unpaired electrons); V5+: [Ar] (diamagnetic, 0 unpaired electrons);
3. C < B < Al < Na < K
4. a. P b. Be c. N d. Tc e. O f. Zn

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