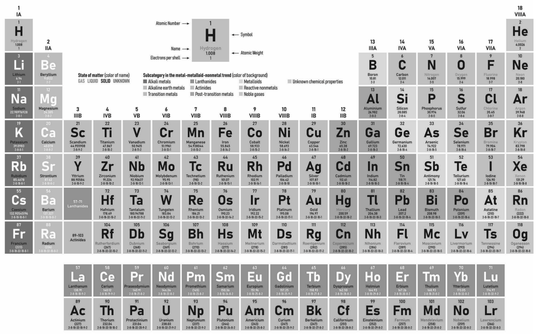
The Structure of Atoms and Periodic Trends
Chapter Six Part 2

Periodic Table of the Elements



CH 221
Professor Michael Russell

MAR *Last update: 4/29/24*

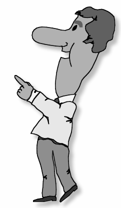
Arrangement of Electrons in Atoms

Electrons in atoms are arranged as

SHELLS (n)

SUBSHELLS (l)

ORBITALS (m_l)



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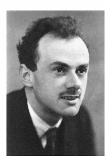
Arrangement of Electrons in Atoms

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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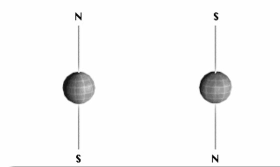

Electron Spin Quantum Number, m_s

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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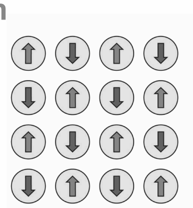
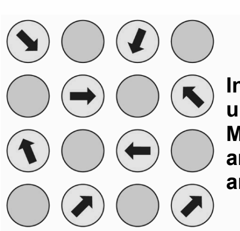
Magnetism

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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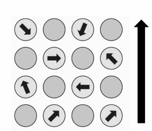
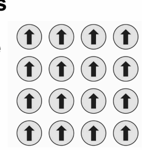
Magnetism

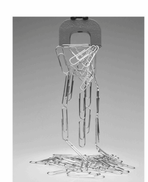
In ferromagnetic substances the orientations of magnetic fields from unpaired electrons are affected by spins from electrons around them.



H_0 - a magnetic field

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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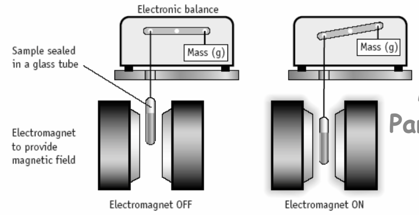
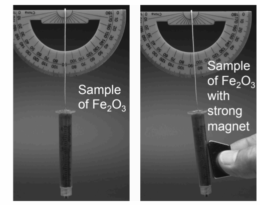


Measuring Paramagnetism

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

Diamagnetic: NOT attracted to a magnetic field



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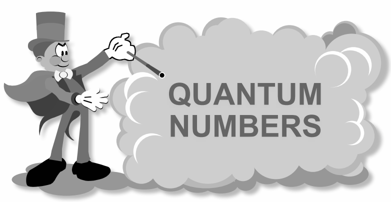

n	---> shell	1, 2, 3, 4, ...
l	---> subshell	0, 1, 2, ... (n - 1)
m_l	---> orbital	-l ... 0 ... +l
m_s	---> electron spin	$+^1/_2$ and $-^1/_2$

See: Quantum Numbers Handout

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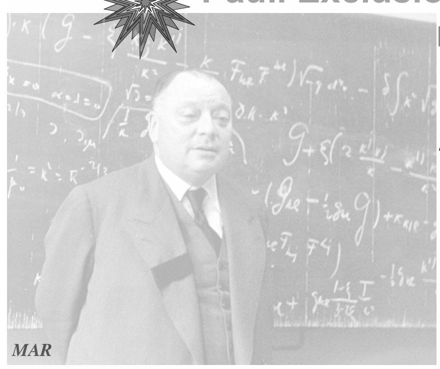
Pauli Exclusion Principle



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	½	4s
2	4	0	0	-½	4s
3	4	1	-1	½	4p
4	4	1	-1	-½	4p
5	4	1	0	½	4p
6	4	1	0	-½	4p
7	4	1	+1	½	4p
8	4	1	+1	-½	4p
9	4	2	-2	½	4d
10	4	2	-2	-½	4d
11	4	2	-1	½	4d
12	4	2	-1	-½	4d
13	4	2	0	½	4d
14	4	2	0	-½	4d
15	4	2	+1	½	4d
16	4	2	+1	-½	4d
17	4	2	+2	½	4d
18	4	2	+2	-½	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	½	4f
20	4	3	-3	-½	4f
21	4	3	-2	½	4f
22	4	3	-2	-½	4f
23	4	3	-1	½	4f
24	4	3	-1	-½	4f
25	4	3	0	½	4f
26	4	3	0	-½	4f
27	4	3	+1	½	4f
28	4	3	+1	-½	4f
29	4	3	+2	½	4f
30	4	3	+2	-½	4f
31	4	3	+3	½	4f
32	4	3	+3	-½	4f

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Distribution of Electrons in Shells

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.

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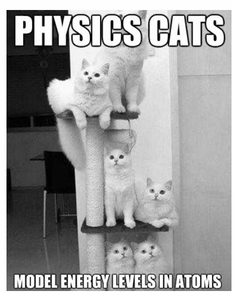
Assigning Electrons to Atoms

Electrons generally assigned to orbitals of successively higher energy.

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

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



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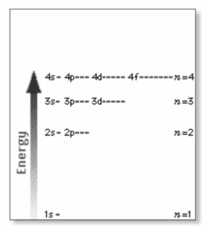
Assigning Electrons to Subshells



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 <u>Electron Configurations Handout</u>

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

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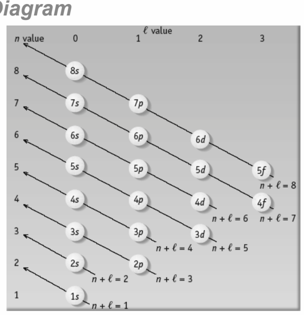
Electron Filling Order

An *Aufbau* Diagram



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

$1s^1$

1 = value of n; s = value of l; superscript 1 = no. of electrons

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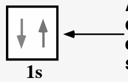
Writing Atomic Electron Configurations

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

ORBITAL BOX NOTATION for He, atomic number = 2

$1s^2$



Arrows depict electron spin

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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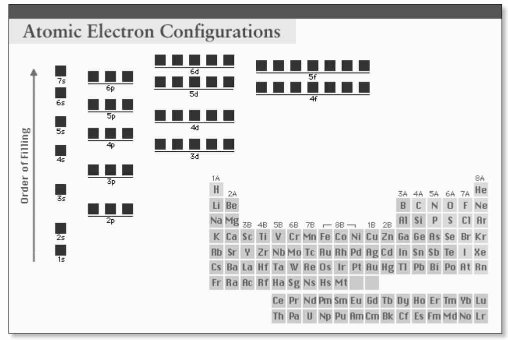

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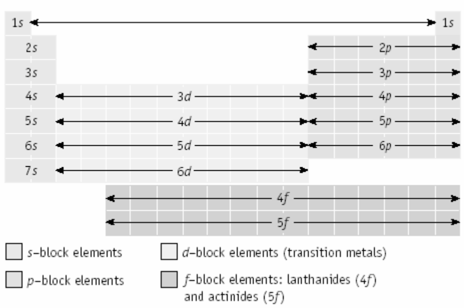
Atomic Electron Configurations Diagram

Electron Configurations and the Periodic Table



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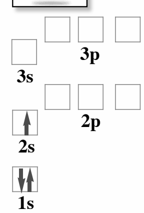
Lithium

Group 1A

Atomic number = 3

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

paramagnetic



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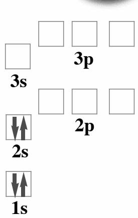
Beryllium

Group 2A

Atomic number = 4

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

diamagnetic



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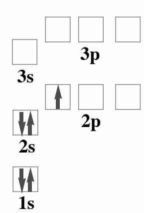
Boron

Group 3A

Atomic number = 5

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

paramagnetic



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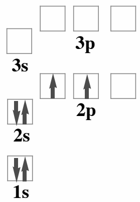
Carbon

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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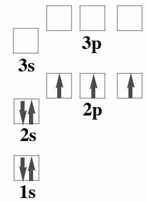
Nitrogen

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



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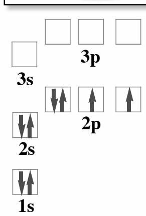
Oxygen

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



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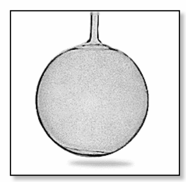
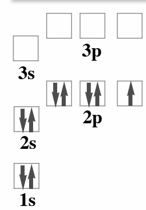


Fluorine

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



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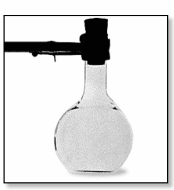
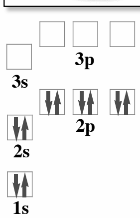


Neon

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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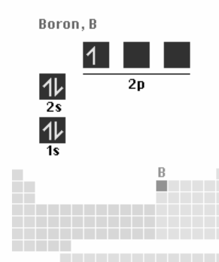
Electron Configurations of p-Block Elements



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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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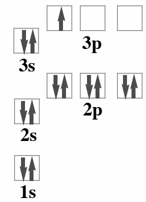
Aluminum

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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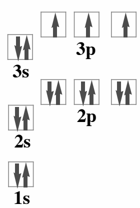
Phosphorus

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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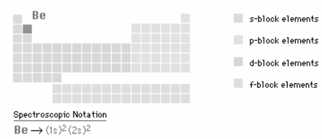
Relationship of Electron Configuration and Region of the Periodic Table



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

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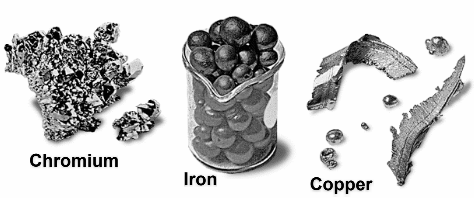
Transition Metals

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



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Fourth Period Electron Configurations

K	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$	or [Ar]$4s^1$
Ca	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2$	or [Ar]$4s^2$
Sc	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^1$	or [Ar]$4s^2 3d^1$
Ti	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$	or [Ar]$4s^2 3d^2$
V	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$	or [Ar]$4s^2 3d^3$
Cr	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$	or [Ar]$4s^1 3d^5$
Mn	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$	or [Ar]$4s^2 3d^5$
Cu	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^{10}$	or [Ar]$4s^1 3d^{10}$

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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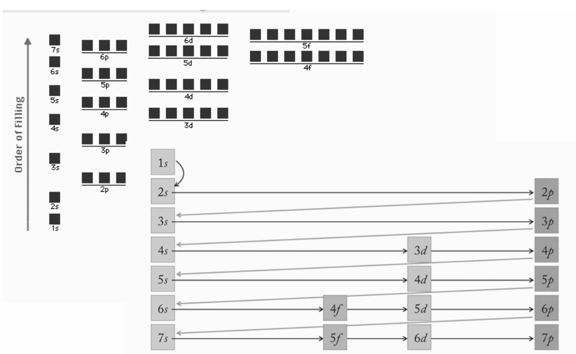

Electron Configurations Filling Order

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Transition Metals

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

notice f orbitals in 6th period & beyond

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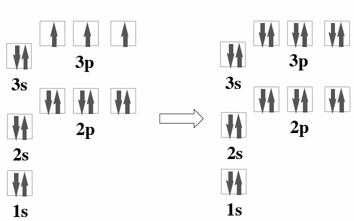
Anion Configurations

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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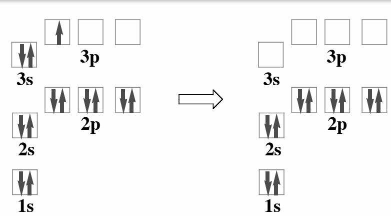
Cation Configurations

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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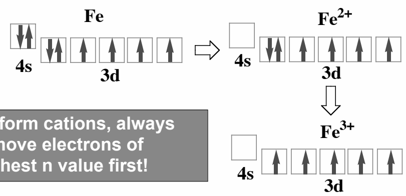
Ion Configurations

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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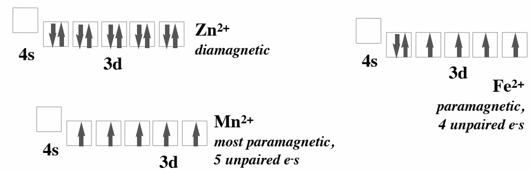
Magnetic Properties

Magnetic properties 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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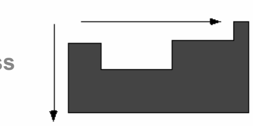
Periodic Trends

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 Periodic Trends Handout*



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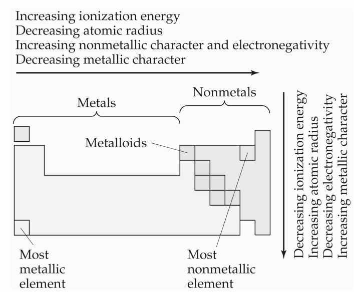
CH 221 Periodic Trends "Cheat Sheet"



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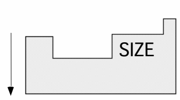
Atomic Size



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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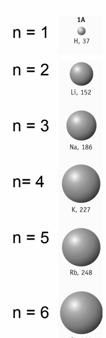
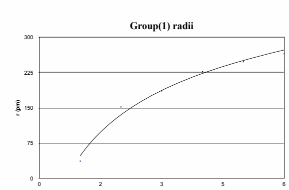


Moving down group IA, the atomic radii increase with the principle quantum number



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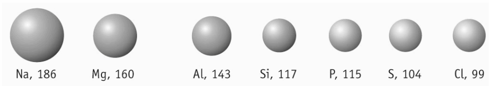
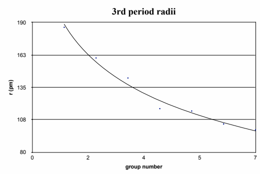


Moving **across** the 3rd period we see the atomic radii of the elements **decrease**.

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



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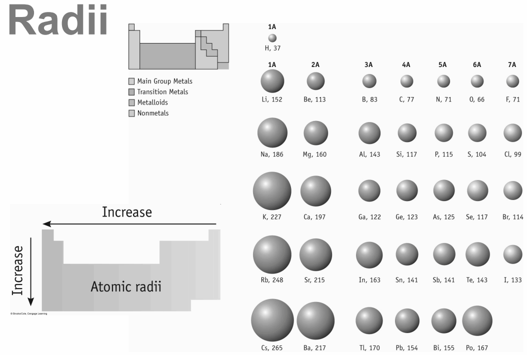
Atomic Radii



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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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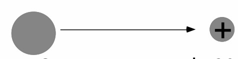
Ion Sizes



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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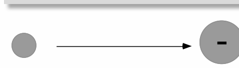
Ion Sizes



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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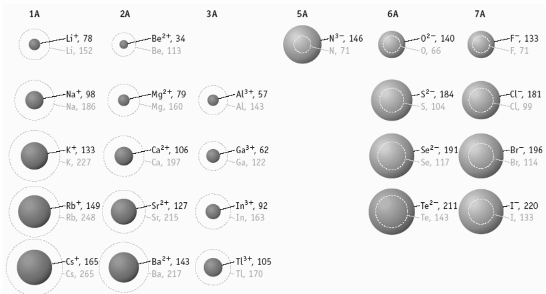
Trends in Ion Sizes



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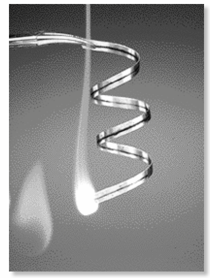
Redox Reactions



- 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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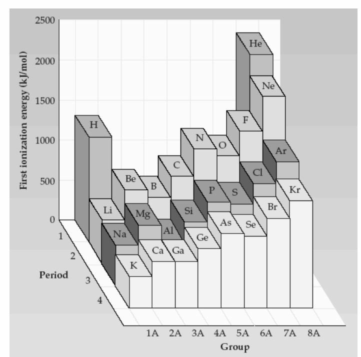
Trends in Ionization Energy



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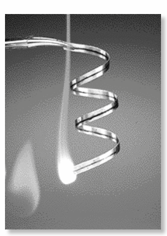
Trends in Ionization Energy

- 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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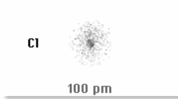
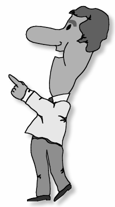
Electron Affinity

Nonmetlas tend to GAIN electrons to form anions.

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

A(g) + e- ---> 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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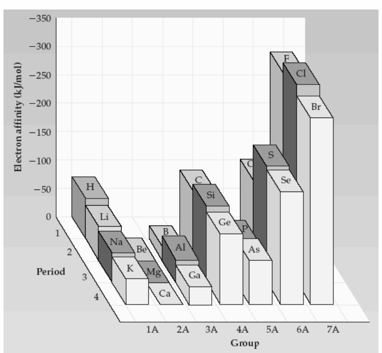
Trends in Electron Affinity



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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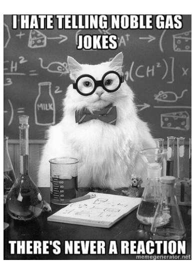
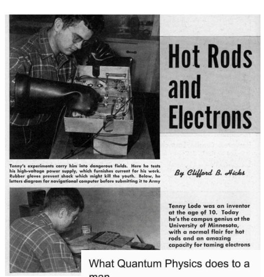


End of Chapter 6 Part 2



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