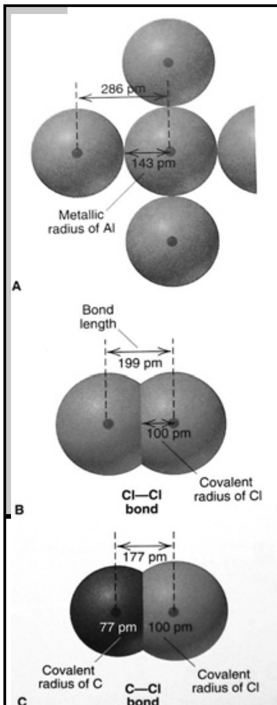
TRENDS OF CHEMICAL AND PHYSICAL PROPERTIES IN PERIODIC TABLE

Sixth Course (General Chemistry)
by Dr. Istadi



Trends in Atomic Size

- All physical and chemical behavior of the elements is based ultimately on the electron configurations of their atom
- Sometimes atomic size is defined in terms of how closely one atom lies next to another.
- Because atoms do not have hard surfaces, the size of an atom in a compound depends somewhat on the atoms near it.
- ==> *atomic size varies slightly from subtance to substance*
- The metallic radius is one-half the distance between nuclei of adjacent atoms in a crystal of the element
- The covalent radius is one-half the distance between nuclei of identical covalently bonded atoms

Trends Among the Main-Group Elements

- Atomic size greatly influences other atomic properties and is critical to understanding element behavior
- **Changes in *n***: As the principal quantum number (*n*) increases, the probability that the outer electrons will spend more time farther from the nucleus increases as well ==> *the atoms are larger*
- **Changes in Z_{eff}**: As the effective nuclear charge (Z_{eff}) – the positive charge "felt" by an electron – increases, outer electrons are pulled closer to the nucleus ==> the atoms are smaller

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- The net effect of these influences depends on shielding of the increasing nuclear charge by inner electrons:
  - ***Down a group, n dominates***: As we move down a main group, each member has one more level of inner electrons that shield the outer electrons very effectively. *Atomic radius generally increases in a group from top to bottom*
  - ***across a period, Z_{eff} dominates***. As we move across a period of main-group elements, electrons are added to the same outer level, so the shielding by inner electrons does not change. Because outer electrons shield each other poorly, Z_{eff} on the outer electrons rises significantly, so they are pulled closer to the nucleus. *Atomic radius generally decreases in a period from left to right*.

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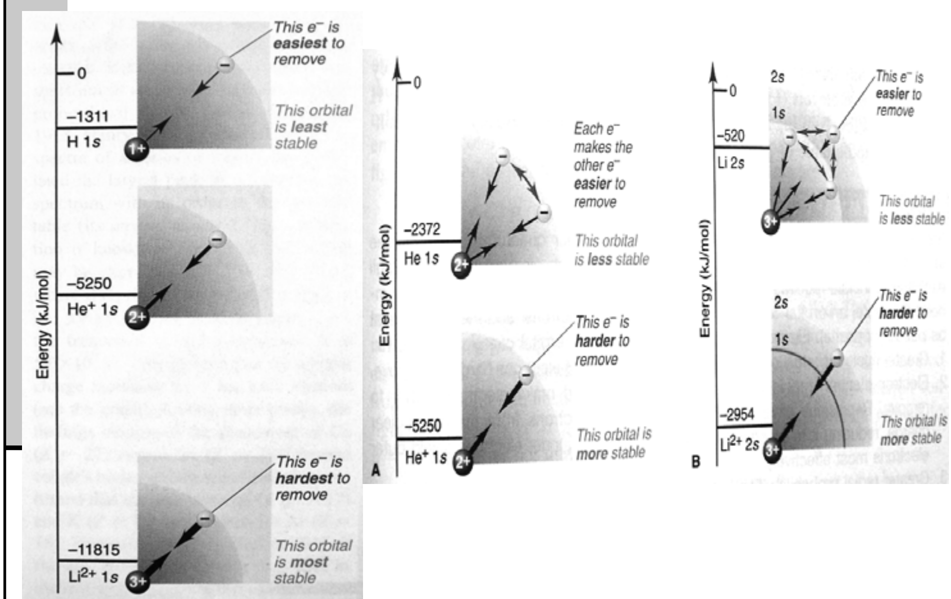

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Trends Among the Transition Elements

- As we move **from left to right**, size shrinks through the first two or three transition elements because of the increasing nuclear charge.
- But, the size remains relatively constant because shielding by inner *d* electrons counteracts the usual increase in Z_{eff}.
- The shielding by *d* electrons causes a major size decrease from Group 2A(2) to Group 3A(13), the two main groups that flank the transition series.
- The size decrease in Periods 4,5, and 6 (with a transition series) is much greater than in Period 3 (without transition series). Because electrons in the *np* orbitals penetrate more than those in the (*n*-1)*d* orbitals, the first *np* electron (Group 3A(13)) feels a Z_{eff} that has been increased by the protons added to all the intervening transition elements

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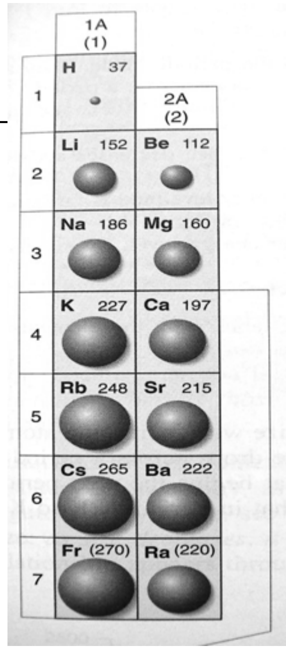
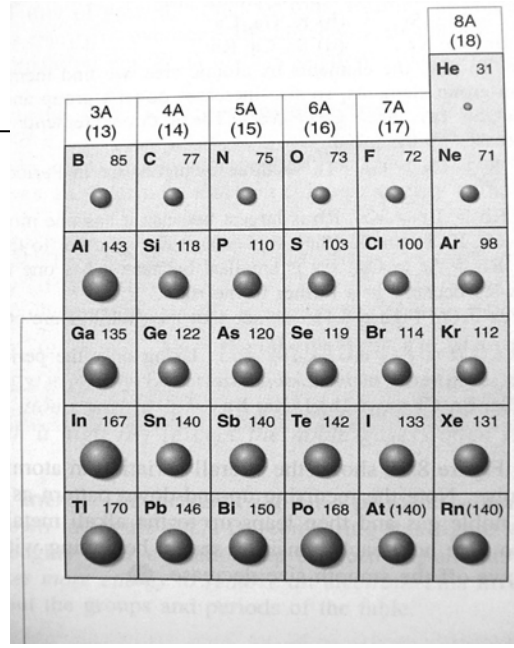
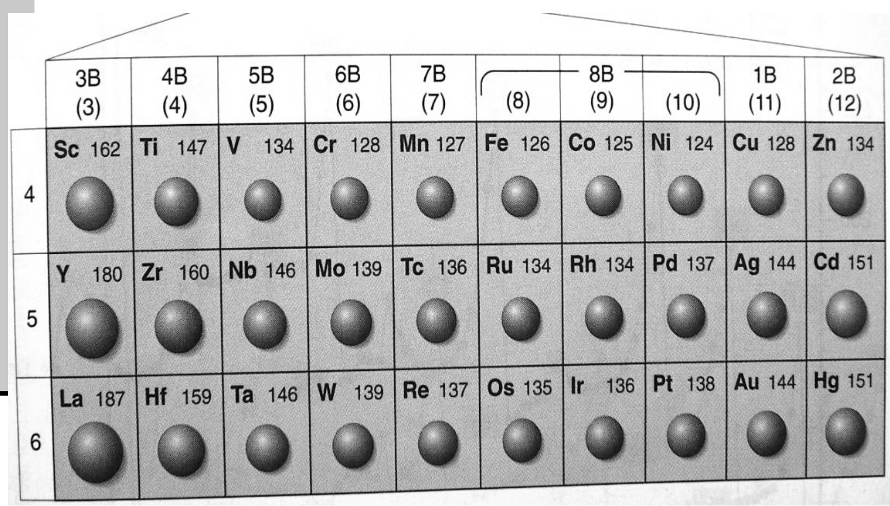

1A
(1)
2A
(2)
1
2
3
4
5
6
7
H 37
Li 152
Be 112
Na 186
Mg 160
K 227
Ca 197
Rb 248
Sr 215
Cs 265
Ba 222
Fr (270)
Ra (220)


8A
(18)
He 31
3A
(13)
4A
(14)
5A
(15)
6A
(16)
7A
(17)
B 85
C 77
N 75
O 73
F 72
Ne 71
Al 143
Si 118
P 110
S 103
Cl 100
Ar 98
Ga 135
Ge 122
As 120
Se 119
Br 114
Kr 112
In 167
Sn 140
Sb 140
Te 142
I 133
Xe 131
Tl 170
Pb 146
Bi 150
Po 168
At (140)
Rn (140)


3B
(3)
4B
(4)
5B
(5)
6B
(6)
7B
(7)
8B
(8)
(9)
(10)
1B
(11)
2B
(12)
4
5
6
Sc 162
Ti 147
V 134
Cr 128
Mn 127
Fe 126
Co 125
Ni 124
Cu 128
Zn 134
Y 180
Zr 160
Nb 146
Mo 139
Tc 136
Ru 134
Rh 134
Pd 137
Ag 144
Cd 151
La 187
Hf 159
Ta 146
W 139
Re 137
Os 135
Ir 136
Pt 138
Au 144
Hg 151

- The greatest change in size occurs in period 4, in which calcium (Ca, Z=20) is nearly 50% larger than gallium (Ga, Z=31).
- In fact, filling the *d* orbitals in the transition series causes such a major size contraction that gallium is slightly smaller than aluminum (Al, Z=13), even though Ga is below Al in the same group

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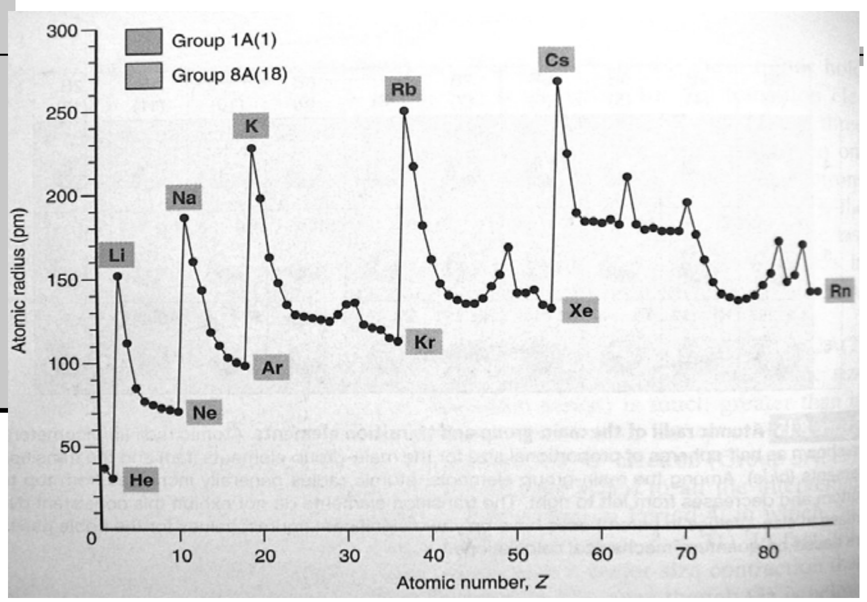
Periodicity of Atomic Radius



Trends in Ionization Energy (IE)

- **IE ionization** is the energy (in kJ) required for the complete removal of 1 mol of electrons from 1 mol of gaseous atoms or ions.
- Pulling an electron away from a nucleus ***requires*** energy to overcome the attraction.
- Because energy flows into the system, the ionization energy is always positive (like ΔH in endothermic reaction)
- In previous Section, the ionization energy of the H atom is the energy difference between n=1 and n= ∞ (completely removed)
- Many-electron atoms can lose more than one electron.
- The first ionization energy (IE_1) removes an outermost electron (highest energy sublevel) from the gaseous atom:
  - Atom (g) → ion^+ (g) + e^- $\Delta E = IE_1 > 0$

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- The second ionization energy (IE_2) removes a second electron. This electron is pulled away from a positively charged ion, so IE_2 is always larger than IE_1:

  Ion^+ (g) → ion^{2+} (g) + e^- $\Delta E = IE_2$ (always > IE_1)
- The first ionization energy is a key factor in an element's chemical reactivity, because atoms with a low IE_1 tend to form cations during reactions, whereas those with a high IE_1 (except the noble gases) often form anions.

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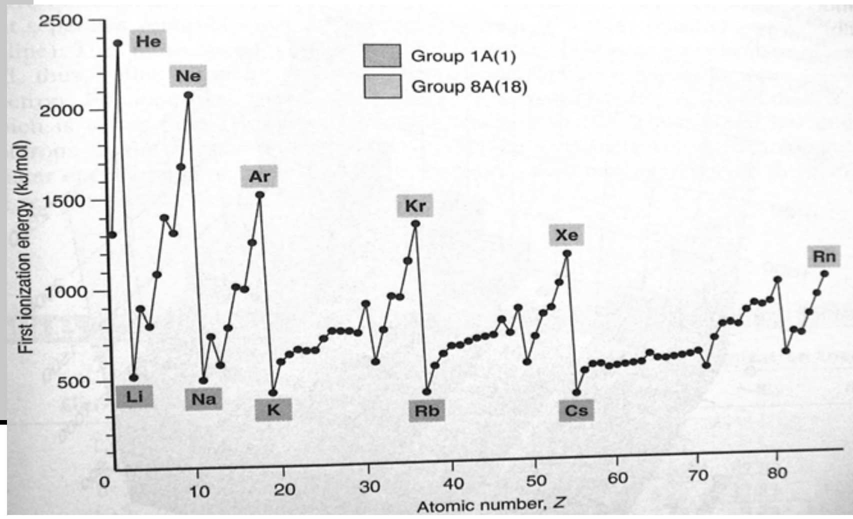
Variations in First Ionization Energy (IE1)



- Inverse relationship between IE_1 and atomic size: as size decreases, it takes more energy to remove an electron

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Down a Group

- As we move down a main group, the orbital's *n* value increases, and so does atomic size. ==> *the attraction between nucleus an electron lessens* ==> the electron easier to remove
- The Ionization Energy generally *decreases down a group*
- It is easier to remove an outer electron from an element in Period 6 than Period 2
- Significant exception: Group 3A(13) ==> *IE_1 decreases from B to Al, but not for the rest of the group*
- Why? Filling the *d* sublevels in Period 4,5,6 causes a greater than expected Z_{eff} which holds the outer electrons more tightly in the larger Group 3A members

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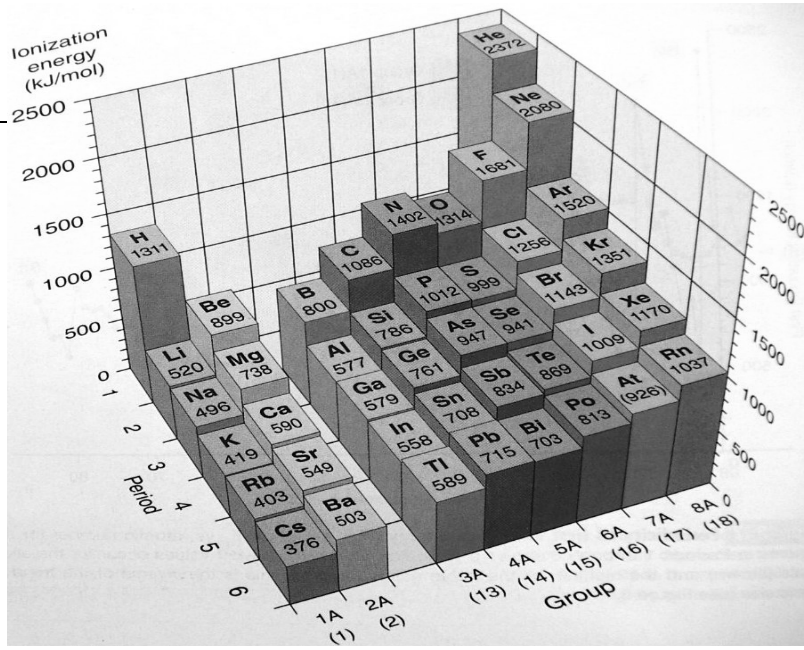

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Across a Period

- As we move **from left to right** across a period, the orbital's n value stays the same ==> Z_{eff} *increases and atomic size decreases*
- ==> the attraction between nucleus and outer electrons increases ==> an electron harder to remove
- Ionization energy generally increases across a period
- It is easier to remove an outer electron from an alkali metal than from a noble gas

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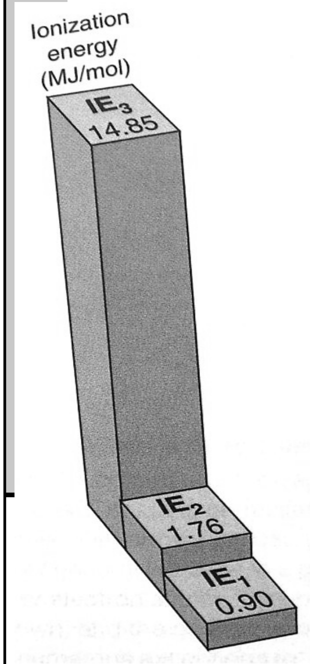

Variations in Successive Ionization Energies

- Succesive ionization energies (IE1, IE2, so forth) of a given element increase *because each electron is pulled away from an ion with a progressively higher positive charge.*
- However, this increase is not smooth, but includes an ***enormous jump***

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Table 8.5 Successive Ionization Energies of the Elements Lithium Through Sodium

Z	Element	Number of Valence Electrons	Ionization Energy (MJ/mol)*									
			IE_1	IE_2	IE_3	IE_4	IE_5	IE_6	IE_7	IE_8	IE_9	IE_{10}
3	Li	1	0.52	7.30	11.81							
4	Be	2	0.90	1.76	14.85	21.01						
5	B	3	0.80	2.43	3.66	25.02	32.82					
6	C	4	1.09	2.35	4.62	6.22	37.83	47.28				
7	N	5	1.40	2.86	4.58	7.48	9.44	53.27	64.36			
8	O	6	1.31	3.39	5.30	7.47	10.98	13.33	71.33	84.08		
9	F	7	1.68	3.37	6.05	8.41	11.02	15.16	17.87	92.04	106.43	
10	Ne	8	2.08	3.95	6.12	9.37	12.18	15.24	20.00	23.07	115.38	131.43
11	Na	1	0.50	4.56	6.91	9.54	13.35	16.61	20.11	25.49	28.93	141.37

CORE ELECTRONS

*MJ/mol, or megajoules per mole = 10^3 kJ/mol.

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Trends in Electron Affinity

- The **electron affinity (EA)** is the energy change (in kJ) accompanying the addition of 1 mol of electrons to 1 mol of gaseous atoms or ions.
- As with ionization energy, there is a first electron affinity, a second, and so forth
- The first Electron Affinity (EA_1) refers to the formation of 1 mol of monovalent gaseous anions:

  Atom (g) + e^- → ion^- (g) $\Delta E = EA_1$
- Energy is released when the first electron is added because it is attracted to the atom's nuclear charge.
- Thus, EA_1 is usually negative
- The second electron affinity (EA_2) is always positive because energy must be absorbed in order to overcome electrostatic repulsions and add another electron to a negative ion.

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Electron Affinities of the main-group elements

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)

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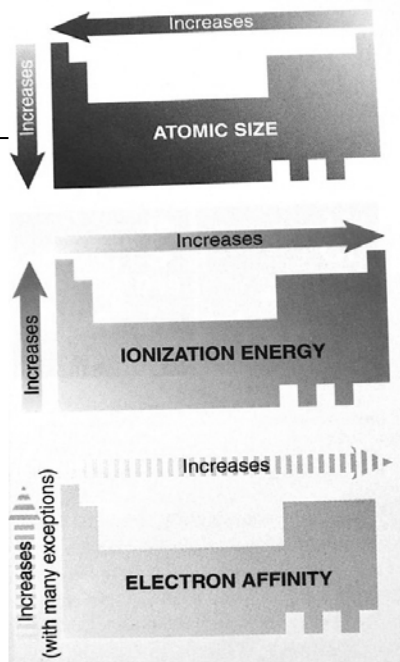
- Factors other than Z_{eff} and atomic size affect electron affinities ==> trends are not as regular as those for the previous two properties.
- We might expect electron affinities to decrease smoothly down a group (smaller negative number) *because the nucleus is farther away from an electron being added* ==> only Group 1A(1)
- We might also expect a regular increase in electron affinities across a period (larger negative number) because size decreases and the increasing Z_{eff} should attract the electron being added more strongly
- An overall left-to-right increase in magnitude is there, but we certainly **cannot say that it is a regular increase** ==> *arise from changes in sublevel energy and in electron-electron repulsion*

Relative Values of IE and EA

- **Reactive non metals**: the element in Group 6A(16) and especially those in Group 7A(17) (halogens) have high ionization energies and highly negative (exothermic) electron affinities. ==> *In their ionic compounds, they form negative ions*
- **Reactive Metals**: The element in Groups 1A(1) and 2A(2) have low ionization energies and slightly negative (exothermic) electron affinities. Both groups lose electrons readily but attract them only weakly ==> *in their ionic compounds, they form positive ions*.
- **Noble Gases**: The elements in Group 8A(18) have very high ionization energies and slightly positive (endothermic) electron affinities ==> *this elements tend not to lose or gain electrons*



Comparisons

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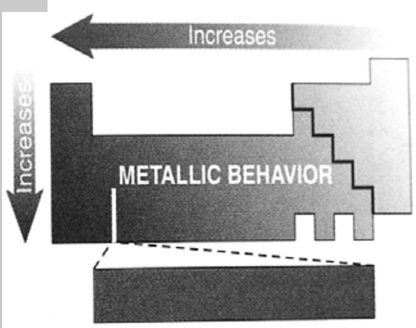
Trends in Metallic Behavior



- Metals are located in the left and lower three-quarters of the periodic table, and tend to lose electrons to nonmetals
- Nonmetals are located in the upper right quarter of the table, and tend to gain electrons from metal
- Metalloids are located in the region between the other two classes and have properties between them as well
- Thus, metallic behavior decreases left to right and increases top to bottom in the periodic table

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Relative Tendency to Lose Electron

- Metals tend to lose electrons during chemical reactions because they have low ionization energies compared to nonmetals
- As we move across a period, it becomes more difficult to lose an electron (IE increases) and easier to gain one (EA becomes more negative)
- Therefore, with regard to monatomic ions, **elements at the left tend to form cations and those at the right tend to form anions**

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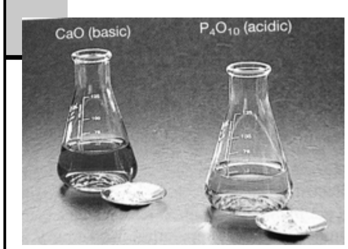
Acid-Base Behavior of the Element Oxide

- Metals are also distinguished from nonmetals by the acid-base behavior of their oxides in water:
  - Most main-group metals transfer electrons to oxygen, so their oxides are ionic. In water, these oxides act as bases, producing OH^- ions and reacting with acids.
  - Nonmetals share electrons with oxygen, so nonmetal oxides are covalent. In water, they act as acids, producing H^+ ions and reacting with bases.



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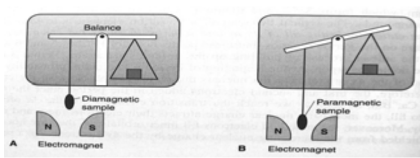
Magnetic Properties of Transition Metal Ions

- Only chemical species (atoms, ions, or molecules) with one or more unpaired electrons are affected by the external field.
- Example: unpaired ==> Ag(Z=47) [Kr] $5s^1$ $4d^{10}$
- paired ==> Cd ==> [Kr] $5s^2$ $4d^{10}$
- A species with **unpaired electrons** exhibits **paramagnetism** (it is attracted by an external magnetic field)
- A species with all **electrons paired** exhibits **diamagnetism** (it is not attracted by a magnetic field)
- Many transition metals and their compounds are paramagnetic because their atoms and ions have unpaired electrons



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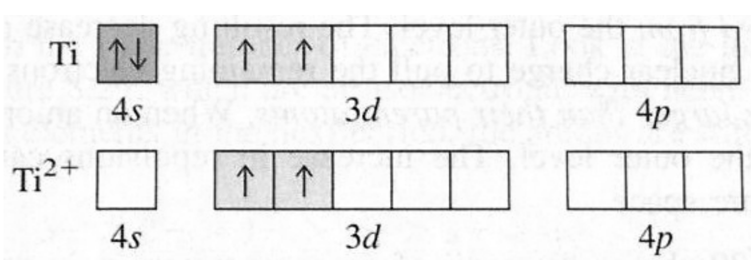
- Titanium ==> [Ar] $4s^2$ $3d^2$ ===> paramagnetic
- The electrons of highest n value are lost first:

  Ti ([Ar] $4s^2$ $3d^2$) → Ti^{2+} ([Ar] $3d^2$) + $2e^-$

- The partial orbital diagrams are:



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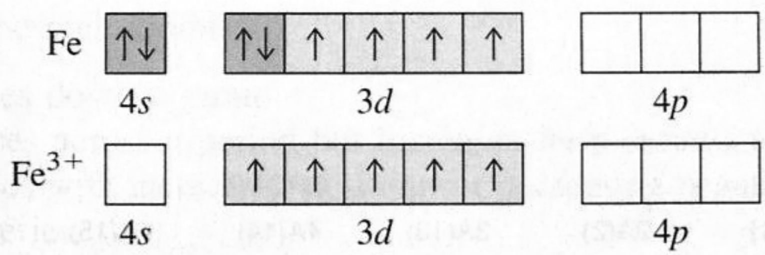
- An increase in paramagnetism occurs when iron metal (Fe) forms Fe^{3+} compounds.
- This fact is consistent with Fe losing its 4s electrons and one of its paired 3d electrons

$$Fe\ ([Ar]\ 4s^2 3d^6) \longrightarrow Fe^{3+}\ ([Ar]\ 3d^5) + 3e^-$$



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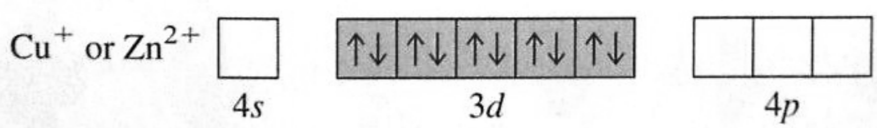
- Copper (Cu) is paramagnetic, but Zinc (Zn) is diamagnetic, as are the Cu^+ and Zn^{2+} ions
- The two ions are isoelectronic:

$$Cu\ ([Ar]\ 4s^1 3d^{10}) \longrightarrow Cu^+\ ([Ar]\ 3d^{10}) + e^-$$
$$Zn\ ([Ar]\ 4s^2 3d^{10}) \longrightarrow Zn^{2+}\ ([Ar]\ 3d^{10}) + 2e^-$$



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