

3.1 Hydrogen Spectrum

Light is electromagnetic radiation that can be produced at different energy levels.

High energy light has a short wavelength (λ) and a high frequency (f, ν) (gamma rays, x-rays, ultraviolet). Low energy light has a long wavelength and a low frequency (infrared, radio waves).

These levels come in a spectrum of wavelengths and frequencies.

$$c = \lambda f, \quad c = \text{speed of light}$$

Light emitted from a hot object has light at many different frequencies (depending of the motion of the atoms in the object).

Light that has all the frequencies forms a continuous spectrum (all “colours” no gaps).

It was found that light from an electrically excited atom did not form a continuous spectrum. It emitted a line spectrum.

These lines are caused by the energy absorbed or emitted by an electron in an atom.

An electron moving towards the nucleus emits energy (light), and electron moving away from the nucleus absorbs energy (light).

The energies of these lines are specific to atoms and compounds. (This is how atoms in stars can be identified.)

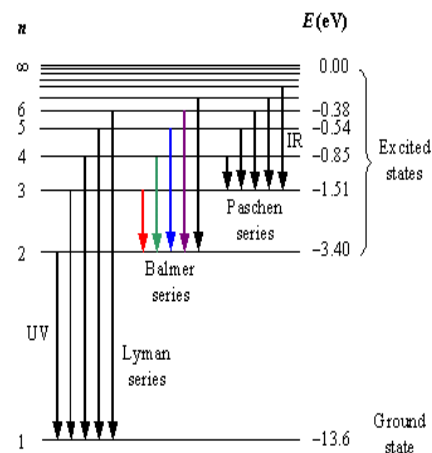
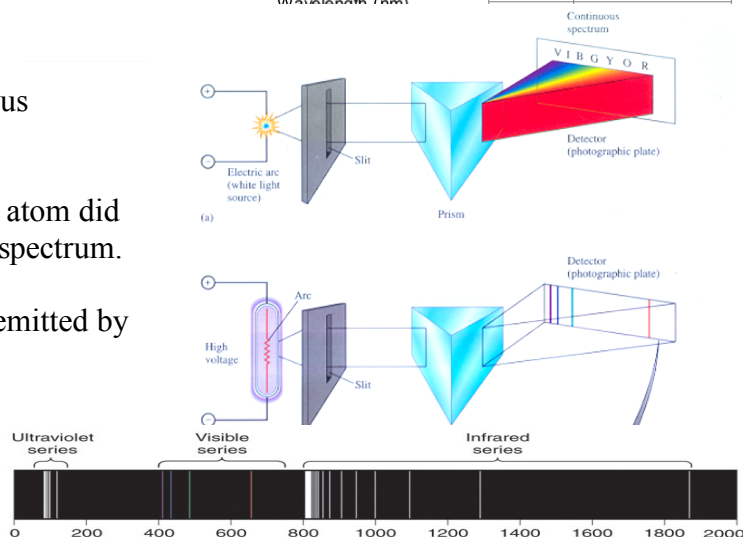
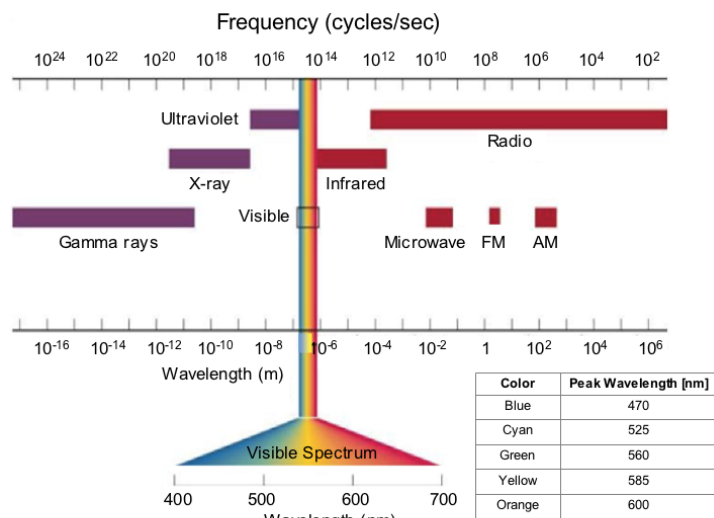
The energy is proportional to the frequency of the light

$$E = hf$$

Neils Bohr suggested that the specific energies could be explained if the electrons could only move to specific orbits around the atom and that these orbits had specific energies.

This is the basis of the Bohr Model of the atom: First level can hold 2 electrons, the second and third levels can hold 8 electrons. (This model will become more complex)

The transitions from 6-2, 5-2, 4-2, 3-2 happen to be in the visible spectrum.



Energy levels of the hydrogen atom with some of the transitions between them that give rise to the spectral lines indicated

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The energy levels begin to converge as they get farther from the nucleus.

An electron that falls from level 3 to level 1 will release a specific energy light (red)

3 to 1 will be slightly more energy, (blue)

4 to 1 will be slightly more energy, (violet)

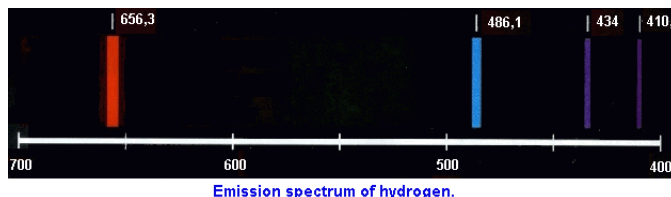
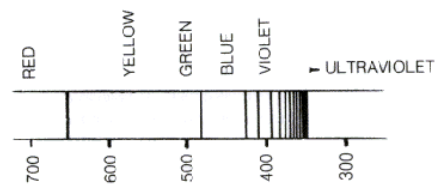
5 to 1 will be slightly more energy, (violet)

6 to 1 will be slightly more, (near UV)

7 to 1 and higher begin to converge.

3.1 Hydrogen Spectrum

Here is a partial spectrum of hydrogen:



There will be one set of converging lines for level 1.

There will be a different set of lines for the drop to each level.

Changes between the higher levels of the hydrogen atom have very low energies.

If an electron is given enough energy to go above the top level, it will leave the atom, forming an ion.

Follow Up Problems 7.1, 2

Problems 7.1, 2, 11, 18, 19a, 20, 22

3.2 Electrons Around Atoms

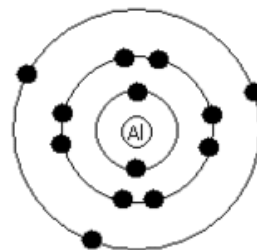
Simplified Bohr Model:

Electrons are in orbitals (shells) around the nucleus.

First orbital can hold 2 electrons

Second and third hold 8, fourth can hold 18.

Bohr diagrams show the electrons:



A more sophisticated model depends on quantum mechanics, primarily electrons behave like waves.

To orbit the nucleus the electron must establish a standing wave.

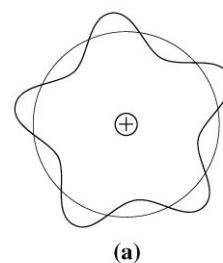
Standing waves can only exist in whole number steps.

In an atom, the different standing waves form different orbitals.

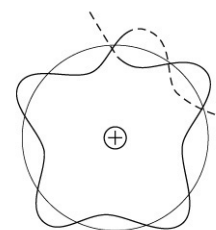
Here is a simple representation of the fifth harmonic around an atom. (top)

The four and a half harmonic will cancel itself out. Electrons are not in the business of spontaneously disappearing.

In a 3 dimensional atom, the actual shapes of the standing waves are quite complicated. As the waves get to higher harmonics, there are more possible shapes for the standing wave.

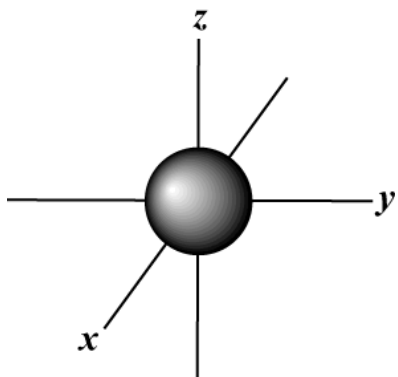


(a)



(b)

For the first level of the atom ($n = 1$), the shape of the orbital (shell) is a sphere. The letter “s” is used to designate this orbital.

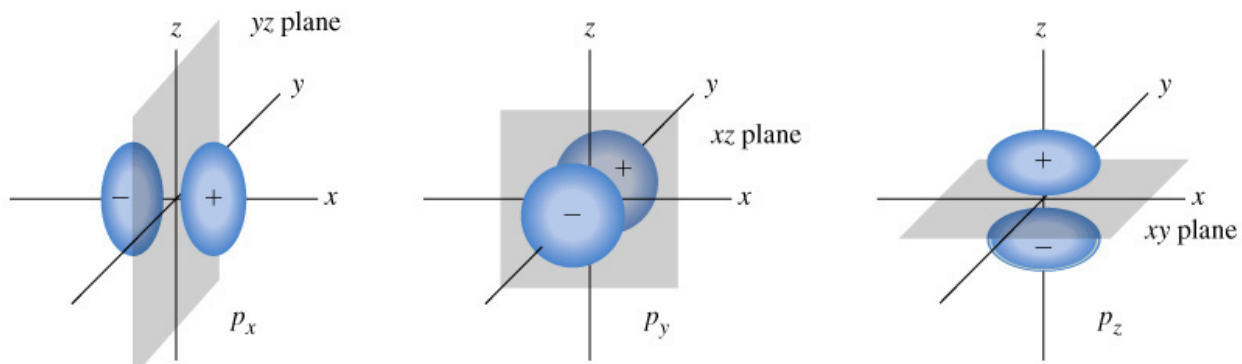


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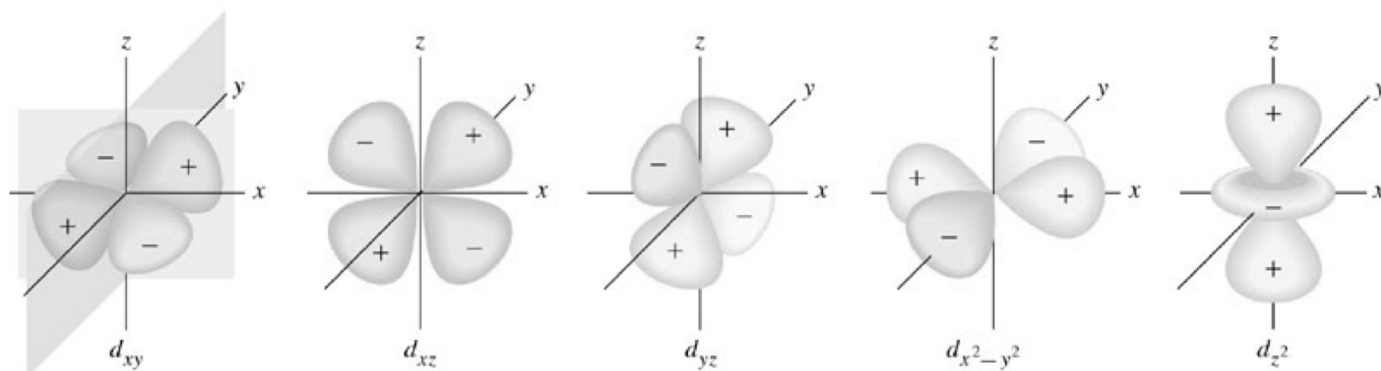
The second shell has a spherical orbital and three orbitals that have a dumbbell shape.

They are designated $2s$, $2p_x$, $2p_y$, and $2p_z$.

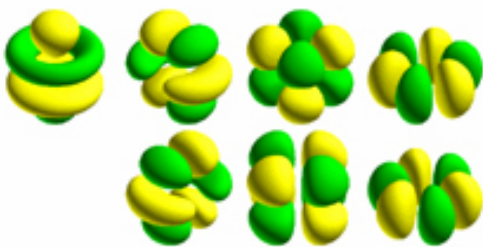
You need to know the shapes of these orbitals.



The third orbitals has $3s$, $3p$, and $3d$ shapes.



There is also a $4f$ set:



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Each sub-orbital can hold two electrons.

The 1s can hold 2 electrons

The 2s can hold 2 electrons, and the 2p can hold 6 electrons (two in each of p_x , p_y , p_z).

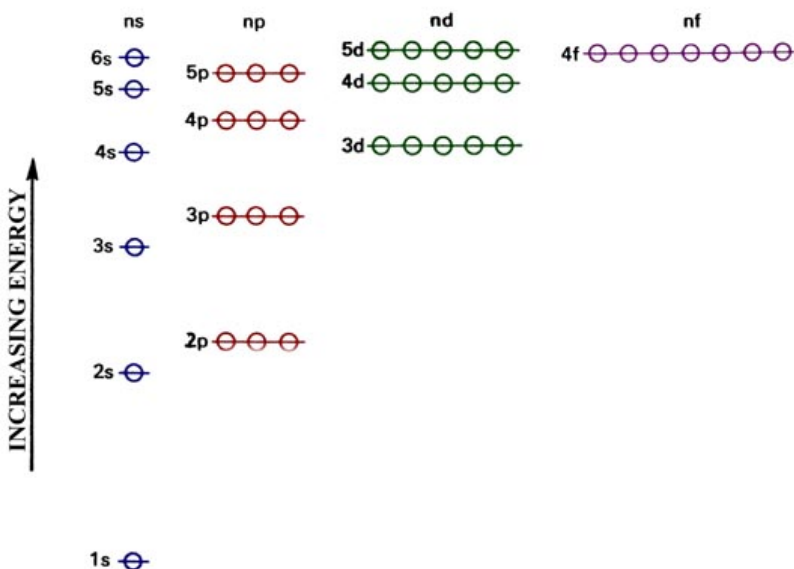
As orbitals get farther from the nucleus, they have a higher energy.

The Aufbau principle shows us the order to fill the orbitals.

The principle is that the lowest energy orbitals are filled first.

Aufbau is German for “build up.”

The energy levels of the different orbitals are given in the chart below. This is a complicated chart, but the order can be found on the periodic table.



The order of filling these orbitals is given on the periodic table.

Electrons are placed in the lowest orbitals first. Once they are full, then the next level is filled.

Electrons behave like magnets. If two electrons are in the same sub-orbital one is placed “spin up” the other “spin down.”

If three electrons are placed in the 2p orbitals, 1 is placed in each of p_x , p_y , and p_z . All are placed in the same direction. (Hund’s Rule). The notation is $2p^3$

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Ex 1:

Sketch the electron diagram and write the notation for:

a) Li

b) O

c) Cl

d) Fe

e) Sn²⁺

Now use shorthand for d) and e)

The lowest energy arrangement of electrons will be the most stable.

Notice the energy increase after each of the noble gasses.

A filled sub-orbital is more stable than a partially filled sub-orbital.

To add electrons to a noble gas would cause a great increase in energy.

This is why noble gasses are stable.

Two exceptions to note are the ground states of chromium and copper.

Cr is $4s^1 3d^5$.

Cu is $4s^1 3d^{10}$.

When an orbital is full or half full it gains some stability. Taking one electron from the 4s makes the 3d full or half full. Overall the atom is more stable this way.

Follow Up Problems 8.2

Problems 8.23, 27, 31, 35, 37, 39, 82 (no paramagnetism)

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3.3 Periodic table Properties — Physical

The properties we will examine are based on three principles (in general order of importance):

1. Electrons in large orbits are farther from the nucleus and experience less attraction.
2. More protons means more attraction.
3. Electrons in the same sub-orbital repel each other.

These factors repeat periodically as one moves along the periodic table. That is why the properties of elements also repeat periodically.

Atomic size is a measure of the radius of the outer electrons in an atom.

A trend is a general relationship that can have many exceptions.

Each family (column) increases in size (larger orbital).

Across each period, the size decreases from left to right because the number of protons is increasing (more attraction to the nucleus).

There is also a notable jump in size for the start of the 4p and 5p orbitals. (Further down the table, the increase in protons has a smaller affect.)

Ionic radii is also related to orbital size and number of protons.

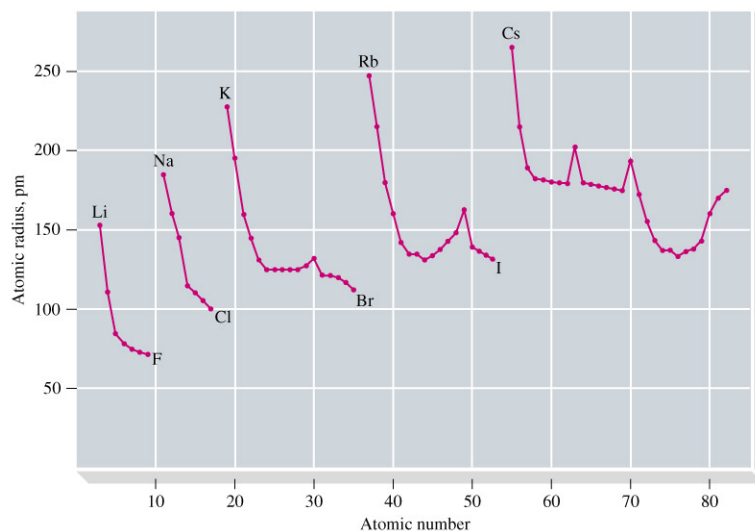
We will compare a set of ions that are isoelectric:

N^{3-} , O^{2-} , F^- , Ne , Na^+ , Mg^{2+} , Al^{3+}
These ions are all $1s^2 2s^2 3p^6$.

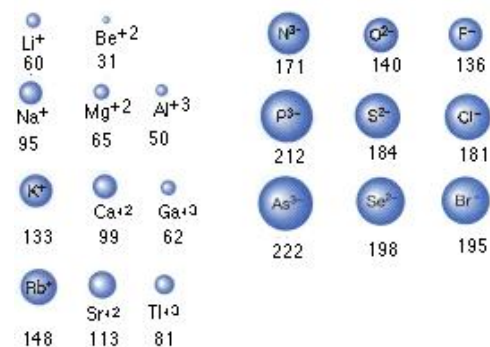
What other ions combinations are isoelectric?

The difference between these species is the number of protons. More protons means stronger attraction and a smaller radii.

These values are all given on p. 7 of your data booklet. You will be asked to explain why these trends are present, not what the trends are.



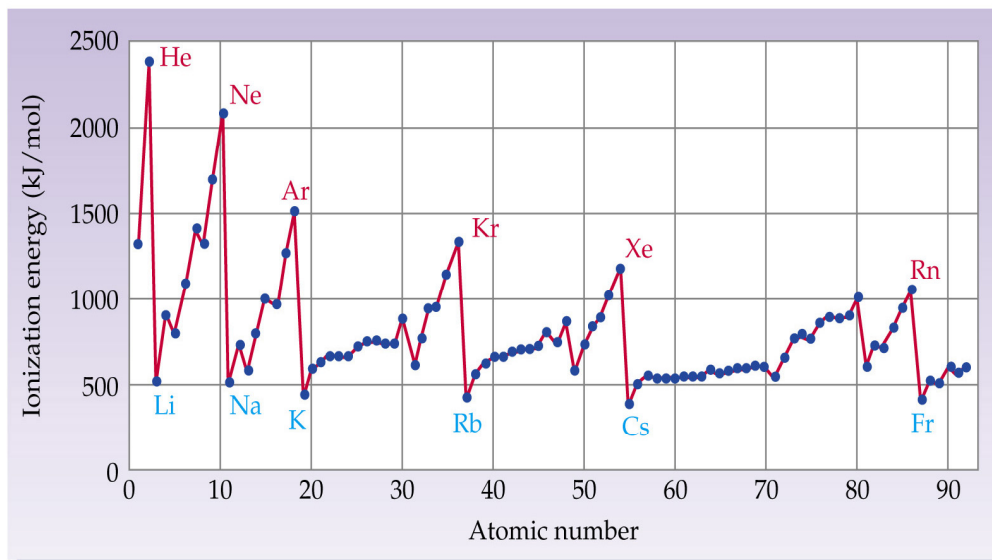
Ionic Radii of Selected Elements (picometers)



Ionization energy is the energy needed to remove an electron from an atom.

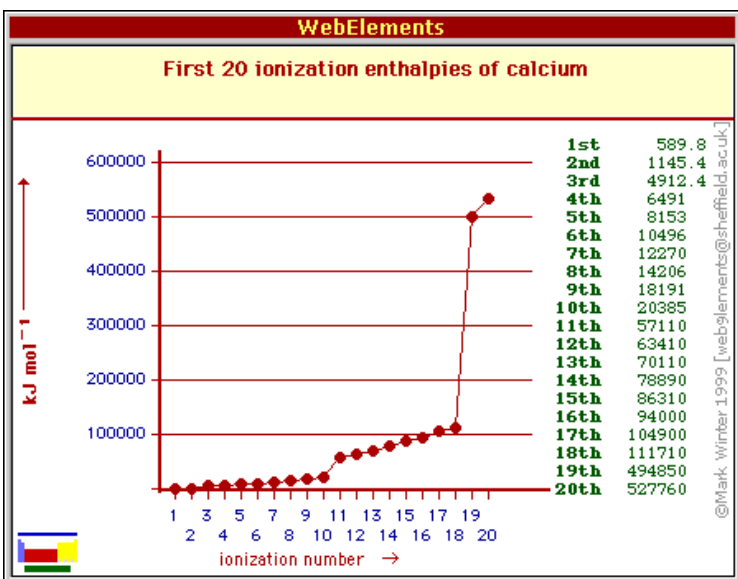
First ionization energy is the energy required to remove the first electron from an atom.

This property is directly related to the attraction of the electrons to the nucleus. The trend should follow the same trend as the atomic size.



What accounts for the variations in the trend between Li and Ne and between Na and Ar?

Successive ionization energies (to remove more than one electron) also show evidence of periodic changes in electron configuration. The energy to remove another electron is always higher than the previous, but the increase in energy is not uniform. Explain the “jumps” after 2, 10, and 18 electrons.



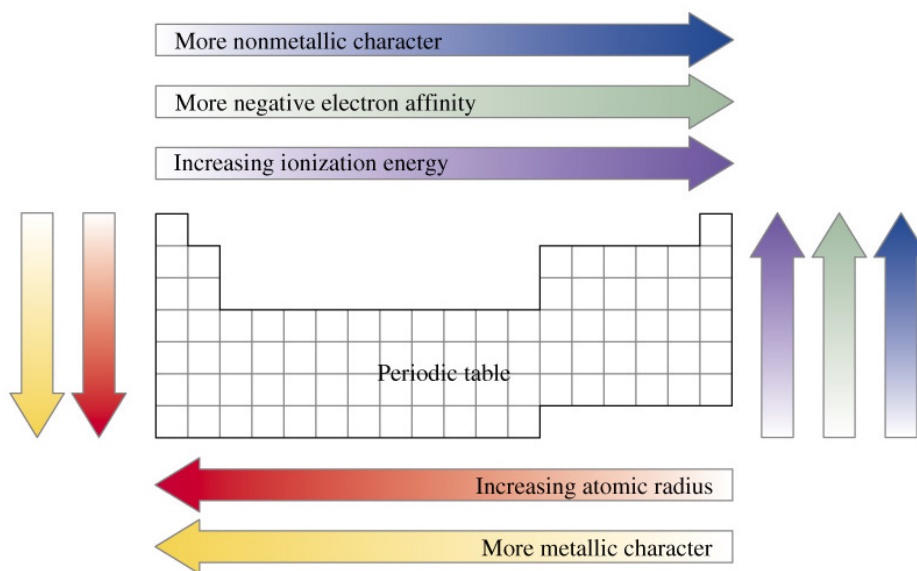
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Electronegativity is a measure of the attraction an atom has for a shared electron.

This value will have the same trend as ionization energy.

		1A	2A												3A	4A	5A	6A	7A
1		H 2.1													B 2.0	C 2.5	N 3.0	O 3.5	F 4.0
2		Li 1.0	Be 1.5																
3		Na 0.9	Mg 1.2		3B	4B	5B	6B	7B	8B			1B	2B	Al 1.5	Si 1.8	P 2.1	S 2.5	Cl 3.0
4		K 0.8	Ca 1.0	Sc 1.3	Ti 1.5	V 1.6	Cr 1.6	Mn 1.5	Fe 1.8	Co 1.8	Ni 1.8	Cu 1.9	Zn 1.7	Ga 1.6	Ge 1.8	As 2.0	Se 2.4	Br 2.8	
5		Rb 0.8	Sr 1.0	Y 1.2	Zr 1.4	Nb 1.6	Mo 1.8	Tc 1.9	Ru 2.2	Rh 2.2	Pd 2.2	Ag 1.9	Cd 1.7	In 1.7	Sn 1.8	Sb 1.9	Te 2.1	I 2.5	
6		Cs 0.7	Ba 0.9	La* 1.1	Hf 1.3	Ta 1.5	W 1.7	Re 1.9	Os 2.2	Ir 2.2	Pt 2.2	Au 2.4	Hg 1.9	Tl 1.8	Pb 1.8	Bi 1.9	Po 2.0	At 2.2	
7		Fr 0.7	Ra 0.9	Ac† 1.1	*Lanthanides: 1.1–1.3 †Actinides: 1.3–1.5														

Electronegativity helps identify metals and non-metals. Metals generally form positive ions, and non-metals form negative ions. Semi-metals can form positive and negative ions. Metallic character is not a binary choice, it is a continuum. Metallic character is highest on the bottom left of the periodic table, and weakest (most non-metallic) on the top right of the table.



Follow Up Problems 8.3, 4, 5, 8
 Problems 8.46, 48, 53, 55, 57, 59, 86
 9.52, 57, 59

3.4 Periodic table Properties — Chemical

Chemical properties provided the original clues to the periodic nature of the modern Periodic Table.

Reactions involve the breaking and forming of bonds; this involves the electronic configuration of the valence (outer) electrons.

Atoms that have similar electronic configurations (vertical families) will have similar chemical properties.

The primary driver of many of the properties of elements is stability due to low potential energy.

Atoms form ions to lower their energy (by filling, or partially filling, an outer shell of electrons).

Atoms form ionic and covalent bonds to lower their potential energy.

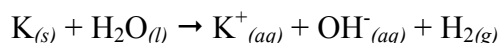
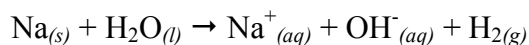
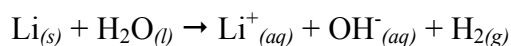
Group 1 alkali metals (family)

These atoms all have one electron in the “s” orbital.

To achieve a full outer shell, the atoms need to lose 1 electron (become a $+1$ ion).

All the atoms in this family react similarly because they all will give one electron to become more stable.

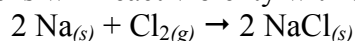
Alkali metals will react with water to give away an electron:



This reaction will become more exothermic moving down the periodic table; less attraction for electrons means the electron will be given away easier.

Halogens (F_2 , Cl_2 , Br_2 , I_2 , generically X_2) need one electron to fill their outer shell.

Halogens will react violently with the alkali ions, for example:

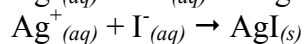
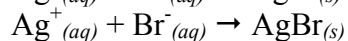
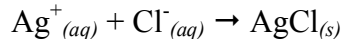


Which combination of alkali metal and halogen should react most violently? Why?

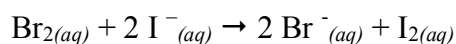
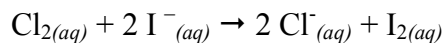
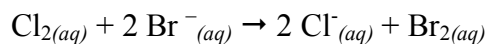
1A	2A												3A	4A	5A	6A	7A	8A	
H	Li Be												B	C	N	O	F	Ne	
Na	Mg	3B	4B	5B	6B	7B	8B					1B	2B	Al	Si	P	S	Cl	Ar
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr		
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe		
Cs	Ba	La*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn		
Fr	Ra	Ac†	Rf	Db	Sg	Bh	Hs	Mt	**	**	**								
*Lanthanide series		Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu				
†Actinide series		Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr				

** Not yet named

Halogens can be recognized by the precipitate they form with silver ions:



Halogens can also remove electrons from each other. Why do the following occur?



Across a period of the table (Na to Ar) there is a general trend from metallic elements to nonmetallic elements.

This can be seen in the bonding of compounds across the table. A metal and a nonmetal form an ionic bond. Two nonmetals form a covalent bond.

However, just as metallic nature is a continuum, ionic and covalent bonding does not have a clear separation.

To determine ionic or covalent nature, compare the electronegativity of the elements in the bond. An arbitrary dividing line is a difference of 1.7 (less than 1.7 is considered polar-covalent)

Examining oxides and chlorides of the third period, describe the ionic or covalent nature of the bonds.

Are these trends supported by the properties?

Ionic compounds conduct electricity in molten form (mobile ions)

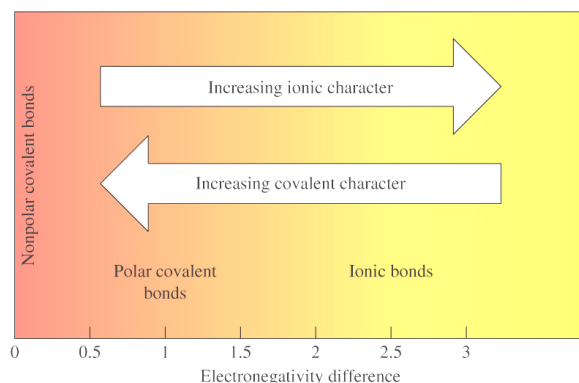
Ionic compounds usually have a higher melting point than covalent compounds.

For the reactions of these oxides and chlorides:

- Ionic oxides form basic solutions, covalent oxides for acidic solutions (revisited in later units)
- Ionic chlorides are very soluble in water
- Covalent chlorides react slightly with water.

Now, you need to be able to explain these trend. Later you will be expected to remember these reactions.

Problems 14.7, 11, 17, 29, 48, 52, 54, 113



3.5 Transition Metals

The transition metals are the groups of elements that are filling the “d” orbital.

We will examine the elements filling the “3d” orbital.

These elements have unique properties because of their “d” orbital. Scandium (Sc) and Zinc (Zn) are atypical of this group because Sc has only 1 electron in the “d” orbital, and Zn has a full “d” orbital.

Ex 1:

Write the electronic configuration for each element in the 3d transition element period.

Atoms form ions because the ion’s electronic configuration is more stable (lower energy) than the atom’s.

All these elements can form a +2 ions by losing both of the $4s^2$ electrons.

What other ions could these elements be expected to form? (Refer to electron diagrams above.)

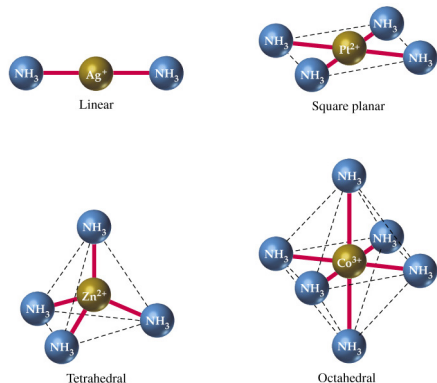
A half full “d” orbital is also stable.

Because transition metals can have various and variable charges, they are often good catalysts.

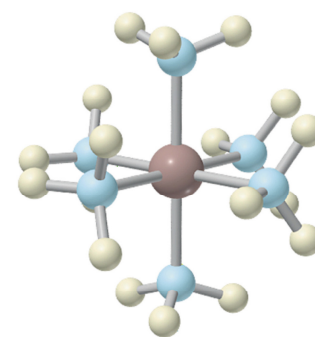
- Iron in the Haber process
- Vanadium(V) oxide in the production of sulfuric acid (contact process)
- Nickel in the hydrogenation process
- Manganese(IV)oxide in the decomposition of hydrogen peroxide.

Transition metals also form colourful complex ions.

A complex ion is formed with ligands. A ligand is a compound with a pair of electrons that forms a weak covalent bond with the small transition metal ion. Both electrons in the bond come from one atom. It is called a coordinate covalent bond.



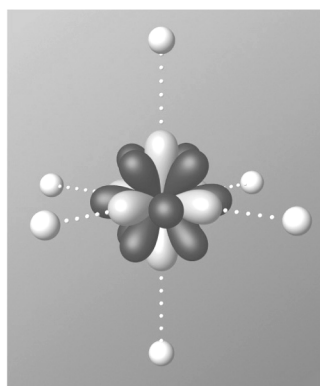
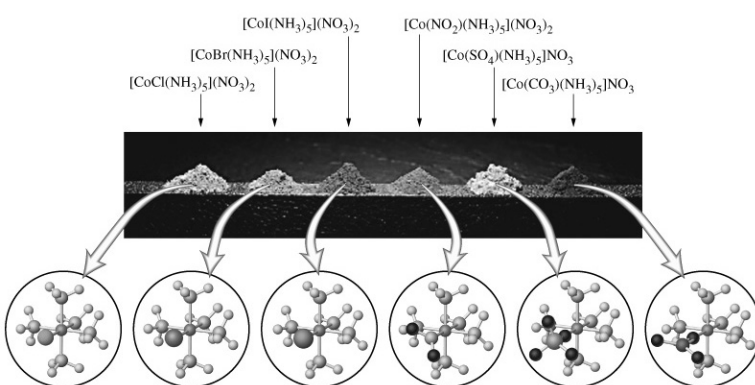
The ligands can be arranged in many different ways depending on the size and number of the ligands. Different ligands and different arrangements produce different properties.



This shows a complex ion with 6 ligands.

These complexes are often very colourful. They are colourful because there are electron orbitals that are in the energy range that absorbs visible light.

Some of the ligands are close to a “d” orbital. That orbital gains energy. The “d” orbitals are no longer degenerate. The new energy level change often corresponds to the energy of visible light.



<i>d</i> -orbital energies in “free” metal atom or ion	Average energy of <i>d</i> orbitals in the presence of ligands	(a) <i>d</i> orbitals in tetrahedral complex	(b) <i>d</i> orbitals in octahedral complex	(c) <i>d</i> orbitals in square planar complex

Follow Up Problems 23.1, 5

Problems 23.4, 14, 16, 18

Be able to explain why colours form for complex transition metal ions.