AT Chemistry

Electron Configuration and Chemical Periodicity

Orbitals of Polyelectronic Atoms

Although the shapes of the orbitals for polyelectronic atoms are the same as those for hydrogen, the presence of more than one electron greatly changes the energies of the orbitals. Electron-electron repulsions, for example, cause different subshells to be at different energies. The effect of the electron repulsions can be thought of as reducing the nuclear charge. The effective nuclear charge, Z_{eff} is given by

$Z_{eff} = Z -$ S (effect of electron repulsions and much more significant the effect of **shielding by core e^-** = s).

Each electron has its own value for Z_{eff} determined experimentally. Note that as a generalization in many polyelectronic atoms, for a given value of n, the energy of an orbital increases with increasing value of l.

Recall from your previous chemistry class that we think of energy levels consisting of sublevels and sublevels made up of orbitals, with a maximum of two electrons per orbital. The first energy level consists of one sublevel (desiganted s) that in turn is made up of one spherical orbital. The second energy level is made up of two sublevels, s and p. The 2s sublevel is a larger sphere compared to the 1s while the p sublevel consists of three dumbell-shaped p orbitals aligned along the x (p_x), y (p_y) and z (p_z) axis. The p sublevel can have a maximum of six electrons. The third principle energy level consists of three sublevels (s, p and d) with a d sublevel consisting of 5 orbitals for a maximum of 10 electrons in a d sublevel. The fourth priniple energy consists of 4 sublevels (s, P, d, and f) with the f sublevel consisting of 7 orbitals for a maximum of 14 electrons.

The energy levels, sublevels, and orbitals *for hydrogen* are outlined below. Note that in the case of hydrogen (one electron only), all the orbitals in a given energy level have the same value. These orbitals are said to be generate.

H atom only:

E ↑
3s __ 3p __ __ __ 3d __ __ __ __ __
2s __ 2p __ __ __
1s __

For polyelectronic atoms, orbitals are not degenerate and some orbitals in higher principle energy levels are more likely to be found closer to the nucleus (or have lower energy) than orbitals in lower principle energy levels. This is called “orbital overlap”. The 4s orbital, for example, is found closer to the nucleus and thus lower in energy compared to any 3d orbitals.

Polyelectronic atoms:

3d __ __ __ __ __
4s __
E ↑ 3p __ __ __
3s __
2p __ __ __
2s __
1s __

Rules for Writing Electron Configurations

* electrons occupy the lowest energy orbital of the lowest energy level first

* no electron pairing takes place in p, d, or f orbitals until each orbital of the given set contains one electron (Hund's Rule)

* no orbital can contain more than two electrons

Aufbau Principal – follow the atomic number acros the periodic table in filling in orbital ectrons such that those with the lowest energies are filled first. Writing correct electron configurations should not be a problem as you simply follow atomic number going across and down the Periodic Table, which will give you the correct energy level and sublevel order of filling.

s block = Groups 1 and 2

p blocks = Groups 13 – 18

d block = transition metals; note the following exceptions:

- Cr, Mo, W, according to Aufbau, would hace d^4s^2 but its more stable to have 5 half-filed orbitals so it changes to d^5s^1
- Cu, Ag, Au, according top Aufbau, would have d^9s^2 but again, the s electron jumps to the d orbital to gain more stability and thus these elements have an outer configuration of $d^{10}s^1$

Sc: $[Ar]4s^2 3d^1$
Ti: " $3d^2$
V: " $3d^3$
Cr: " $4s^1 3d^5$
Mn: " $4s^2 3d^5$
Fe: " $3d^6$
Co: “ $3d^7$
Ni: “ $3d^8$
Cu: " $4s^1 3d^{10}$

Zn " $4s^2 3d^{10}$

f block = lanthanide series (start filling 4f)
actinide series (start filling 5f)

- When you begin and end the inner transition metals: Starting at the sixth-period element 56, barium has an electron configuration $[Xe]6s^2$, then comes lanthanum with the first d-electron $[Xe]6s^2 5d^1$. Now come the inner-transition metals. Cerium has an electron configuration $[Xe]6s^2 4f^1 5d^1$ and lutetium ends the lanthanide series with $[Xe]6s^2 4f^{14} 5d^1$. The actinides follow the same configuration as the lanthanides.

- When forming ions, the transitions metals lose their outermost s-electrons before losing any d-electrons. Thus, the electron configuration of Mn^{2+} would be $[Ar]3d^5$.

Poblem: Write electron configurations for the cobalt atom and the cobaltic ion:

Problem: Write electron configuration for Gretzkyium using the Periodic Table:

Problem: Write electron configuration and orbital diagram for arsenic; distinguish between valence electrons and core electrons.

Periodicity

In discusing periodicity we will focus on those properties that ultimately involve outermost or valence electrons. There three key ideas to consider:

Nuclear Charge –

Shielding Effect –

Electron-Electron Repulsion -

Ionization Energy (IE)

by definition: $X(g) + IE \rightarrow X^+(g) + e^-$

How does one determine ionization energy?

Photoelectron Spectroscopy

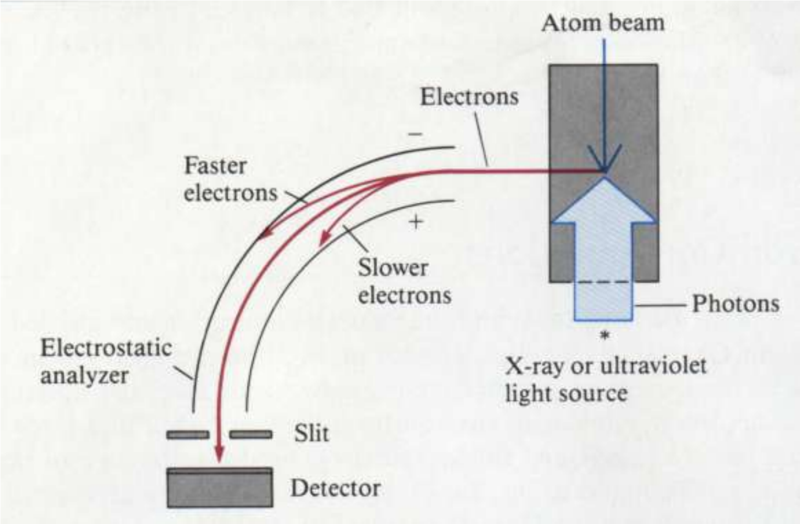
Photoelectron spectroscopy is very similar to the photoelectric effect, except that photons are used to knock electrons out of atoms in the gas phase instead of from the surface of a metal. And because electrons are usually less easily removed from the atoms of other elements than they are from the atoms of metals, very-high-energy photons such as the photons of very-short-wavelength ultraviolet radiation or even X-rays must be used. If the energy of the photon is greater than the ionization energy of the electron, the excess energy appears as kinetic energy, $1/2mv^2$, of the electron, which is ejected from the atom with a speed v. In other words, the speed of the ejected electron depends on how much excess energy it has received. So, if IE is the ionization energy of the electron and KE is the kinetic energy with which it leaves the atom we have

$$E_{photon} = h\nu = IE + KE$$

Rearranging this equation gives

$$IE = h\nu - KE$$

Hence we can find the ionization energy IE if we know the frequency or wavelength of the photon-electron. The kinetic energy of the photon is measured in the photoelectron spectrometer illustrated below:



A beam of atoms is irradiated with ultraviolet light or X-rays of a known frequency. The kinetic energies of the ejected electrons are measured by passing them into an electrostatic analyzer which consists of two curved plates, one charged positively and the other negatively. The electric field between the plates deflects each electron into a curved path, the curvature depending upon the speed and therefore the kinetic energy of the electron. Thus only electrons of one particular speed and therefore one particular kinetic energy will have a path of just the right curvature to pass right through the analyzer and through the slit to reach the detector. The detector counts the electrons as they arrive. By varying the charges on the plates, that is, the voltage between the plates, electrons of different energies can be detected.

Example: Na consider 1s electron vs 3s electron

Z_{eff} for 1s electron =

Z_{eff} for 3s electron =

Shielding (Screening) Effect decreases Z_{eff}.

The shielding is not totally effective because the 3s electron has a small but significant probability of being close to the nucleus. This is referred to as the **penetration effect**, which deceases the effectiveness of shielding and thus increases the value of Z_{eff}. The pentration effect for orbitals within an energy level can be summarized below:

ns > np > nd > nf

Key Idea: electrons sharing an orbital (electron-electron repulsion) do not shield each other as well as core electrons shield outer electrons.

Periodic Trends in Atomic Properties

Ionization Energy - the energy neded to remove the outermost electron

Electronegativity - a measure of a nucleus's attraction for electrons when forming a bond

Ionization Energy (IE) and Electronegativity (EN) - the first IE and EN increases across a period and decreases down a group. Why?

Across a period there are some discontinuities:

Be → B

Explain:

N → O

Explain:

Question: Why do successive ionization energies always increase?

Problem: What is the formula of the chloride of element X given its first five ionization energies (in kJ/mole) below. Explain.

$IE_1 = 400$ kJ
$IE_2 = 850$ kJ
$IE_3 = 2700$ kJ
$IE_4 = 3200$ kJ
$IE_5 = 4100$ kJ

Electron Affinity - the energy change associated with the addition of an electron to a gaseous atom:

$$X(g) + e^- \rightarrow X^-(g)$$

note: don't let the terminology confuse the issue. Electron affinities can be positive (i.e. endothermic – unfavorable) or negative (exothermic – favorable) The more negative the energy, the greater the quantity of energy released when an electron is added.

Electron affinities generally become more negative in going across a period (makes sense because we become increasingly nonmetallic – and nonmetals trend to gain electrons) and more positive going down a group (down a group the metallic properties increase and and metals tend to loe electrons – its harder to put one on). The changes within a group are small.

I like to think of it this way: Since nonmetals tend to gain electrons to become more stable the EA for nonmetals will tend to be exothermic. Since metals tend to lose electrons, adding an electron to a metal will require an energy input; EA for metals will tend to be endothermic.

Atomic Radius = half the distance between the nuclei in a molecule consisting of identical atoms. Atomic radius decreases across a period and increases down a group. Explain:

Note: As you go down a group the spacings between energy levels decreases. Why?

Ionic Radii

A metal atom's radius is larger than its ionic radius. Why?

A nonmetal atoms radius is smaller compared to its ionic radius. Why?

The Alkali Metals

1 valence electron

ns^1 valence configuration

form +1 ions

reactivity increases as you go down the group

size increases as you go down the group

IE decreases as you go down the group

all good reducing agents

reaction with water:

$2\ M(s) + 2H_2O(l) \rightarrow H_2(g) + 2M^+(aq) + 2OH^-(aq) + \text{energy}$

For reactions between solid alkali metals and nonmetals the trend in reducing ability is

$Cs > Rb > K > Na > Li$

Physical and Chemical Properties of Sodium and Potassium (Demo)

1. List several physical properties of both of these alkali metals you observed:

2. Why is hydrogen not included in the alkali meal family?

3. List several chemical properties of the alkali metals:

4. Describe how ionization energy, electronegativity, size, and density change as you go down this group:

5. Write the general equation for the reaction of an alkali metal with water. Identify the oxidizing agent, reducing agent, substance oxidized and substance reduced.

6. Explain the flame that sometimes ignites when sodium reacts with water (and almost always occurs hen potassium reacts with water):

7. How are the alkali metals prepared into their elemental forms?

8. Describe the colors of lithium, sodium, and potassium from flame tests (i.e. dominant emission lines in the visible):

9. If 0.50 g of sodium reacts with 750.0 mL of water at 20^{o}C and 1.00 atm pressure, calculate

   a) the mass and volume of hydrogen gas produced:

   b) the resulting concentration of hydroxide ions in the solution:

   c) the mass of sodium hydroxide that will be left over if all the water evaporates: