1. Electronic Configurations

e.g. What is the electronic configuration for gold (Au, element number 79)

we expect: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^{10}\ 4p^6\ 5s^2\ 4d^{10}\ 5p^6\ 6s^2\ 4f^{14}\ 5d^9$ or, $[Xe]\ 6s^2\ 4f^{14}\ 5d^9$

in fact, it is slightly different, since half filled and filled orbitals (subshells) are unusually stable. This is analogous to Hund's rule, which says that orbitals are first half-filled with spin-up electrons, before any are filled with a spin-down electron. Thus, in the case of Au, an electron is "moved" from the 6s orbital to the 5d orbital. This makes the 6s orbital half-filled, and the 5d filled: $[Xe]\ 6s^1\ 4f^{14}\ 5d^{10}$

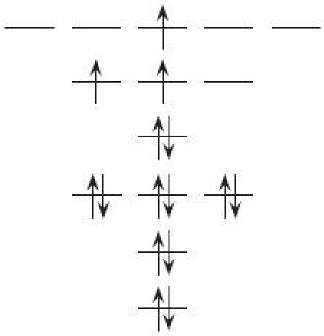
e.g. We expect Mo to be $[Kr]\ 5s^2\ 4d^4$, but it is actually $[Kr]\ 5s^1\ 4d^5$, since this configuration has two half-filled subshells, instead of a full and a 40% full orbital.

e.g. We expect Gd to be $[Xe]\ 6s^2\ 4f^8$, but it is actually $[Xe]\ 6s^2\ 4f^7\ 5d^1$, since this configuration has a half-filled f-subshell and a half-filled d-orbital, instead of a full s- and an 8/14ths full f-subshell.

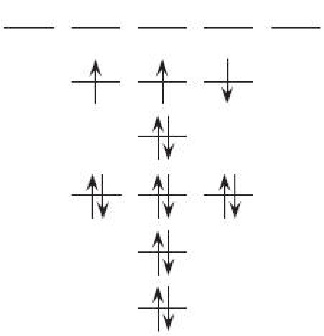
Problem 5.75 from the text:

5.75 The figure below shows four proposed electron energy diagrams for a phosphorus atom. Which are forbidden by the Pauli principle, which are excited states, and which is the ground-state configuration?

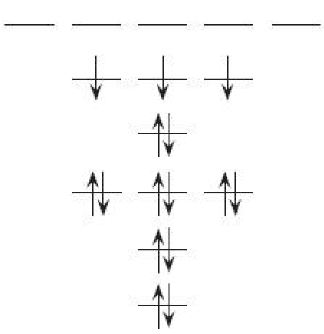
(a)



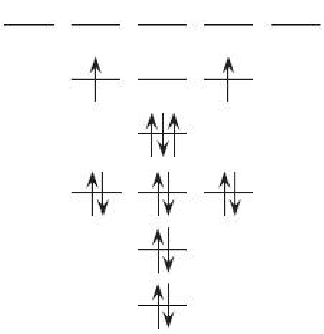
(b)



(c)



(d)



(c) is the ground state - all electrons are in the lowest possible energy states, Hund's rule is obeyed, Pauli's principle is obeyed

(b) is forbidden by Hund's rule

(d) is forbidden by Pauli's principle

(a) is an "excited state". One of the 3p electrons has been promoted into a 3d orbital, but Hund's and Pauli's principles are still being obeyed.

2. Periodic Properties

Atomic radius increases going down a group, and going R to L across a period.

e.g. arrange Mg, Si and S in increasing order of atomic radius:

We note that these are all in the same period, so the radius should simply decrease with increasing atomic number (since the nuclear charge increases). Thus, S < Si < Mg.

e.g. arrange As, N and P in increasing order of atomic radius:

We note that these elements are in the same group, so the radius should increase going down the group (adding electrons to larger shells), so the radius increases: N < P < As.

e.g. arrange As, Se, Sb in increasing order of atomic radius:

As and Se are both in the 4th period. Z(As) = 33, Z(Se) = 34. Thus, the radii increase Se < As. Sb is in the 5th period, and is expected to be larger than anything in the fourth period. Thus, Se < As < Sb.

Ionic radius: If the electronic configurations of two ions are the same (i.e. they are "isoelectronic"), a greater nuclear charge will cause the ion to be smaller.

e.g. arrange S^{-2}, K^{+}, Ca^{+2} and Mg^{+2} in increasing order of ionic radius:

S^{-2}, K^{+} and Ca^{+2} are isoelectronic (with Ar); (all are $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6$). Thus, $Ca^{+2} < K^{+} < S^{-2}$, according to the nuclear charge argument. Mg^{+2} has the same charge as Ca^{+2}, but its outer shell has n=3, whereas that of Ca^{+2} has n=4. Thus, $Mg^{+2} < Ca^{+2}$. Thus, overall, $Mg^{+2} < Ca^{+2} < K^{+} < S^{-2}$.

Ionization potential (I_1) is the energy required to remove an electron from an isolated atom, i.e. for the process $X \rightarrow X^{+} + e^{-}$. I_1 generally decreases going down a group (the outer electrons are further from the nucleus) and increases going L to R across a group (due to higher nuclear charge).

e.g. arrange Ir, Pt, Au, Hg and Tl in increasing order of I_1.

These elements are all in period 6. As expected, I_1 increases as Ir < Pt < Au < Hg.

Ir: [Xe] $6s^2\ 4f^{14}\ 5d^7$

Pt: [Xe] $6s^2\ 4f^{14}\ 5d^8$

Au: [Xe] $6s^2\ 4f^{14}\ 5d^9$

Hg: [Xe] $6s^2\ 4f^{14}\ 5d^{10}$

Going to the next element (Tl) requires placing an electron in the 6p orbital:

Tl: [Xe] $6s^2\ 4f^{14}\ 5d^{10}6p^1$

which is at a higher energy, and thus easier to remove. Thus, I_1 for Tl is very low, and the order is Tl < Ir < Pt < Au < Hg.

Electron Affinity is the energy required (or gained) when an atom picks up an electron, i.e. for the process $X + e^- \rightarrow X^-$. EA becomes more negative (i.e. more energy is released) going from L to R across the periodic table. However, EA for the noble gases (group 8) are essentially zero, since they have full shells and do not "wish" to pick up another electron. Read section 5.4 in the text!

3. The Born-Haber Cycle

Suppose we want to know whether energy is released (i.e. the reaction is favorable) or required (i.e. the reaction is not expected to proceed). For example, calculate the standard enthalpy of formation of $CaF_{2(s)}$, given the following information:

Enthalpy of vapourization of Ca metal:	178.3 kJ/mol
I_1(Ca)	589.8
I_2(Ca)	1145
BDE(F_2)	158
EA(F)	-328
U($CaF_{2(s)}$)	2630

To solve this, we need to write out the steps and find the total:

$Ca_{(s)} \rightarrow Ca_{(g)}$	+178.3 kJ/mol
$Ca_{(g)} \rightarrow Ca^+_{(g)} + e^-$	+589.8
$Ca^+_{(g)} \rightarrow Ca^{2+}_{(g)} + e^-$	+1145

$F_{2(g)} \rightarrow 2\ F_{(g)}$	+158
$2\ F_{(g)} + 2\ e^- \rightarrow 2\ F^-_{(g)}$	2(-328)
$Ca^{2+}_{(g)} + 2\ F^-_{(g)} \rightarrow CaF_{2(s)}$	-(2630)
$Ca_{(s)} + F_{2(g)} \rightarrow CaF_{2(s)}$	Sum = -1215 kJ/mol

Suppose we want to calculate the electron affinity of fluorine. This may be difficult to measure in the lab, so we make up a series of hypothetical steps which add up to an overall reaction whose energy is known. If we know the energies required for the overall reaction and for each of the other steps, we can calculate the energy that would be required for the missing step.

For example, we know that the standard enthalpy of formation of LiF is -617 kJ/mol. Beginning with the elements, we make the steps add up to this formation reaction and find the electron affinity of fluorine by difference:

$Li_{(s)} \rightarrow Li_{(g)}$ (+161 kJ/mol, the enthalpy of vaporization of lithium)

$Li_{(g)} \rightarrow Li^+_{(g)} + e^-$ (+520 kJ/mol, the ionization potential of lithium)

$\frac{1}{2}\ F_{2(g)} \rightarrow F_{(g)}$ (½ (154) = +77 kJ/mol, the enthalpy of dissociation of fluorine gas per mol of F atoms)

$F_{(g)} + e^- \rightarrow F^-_{(g)}$ (?? kJ/mol, but we expect it to be negative)

$Li^+_{(g)} + F^-_{(g)} \rightarrow LiF_{(s)}$ (-1047 kJ/mol, which is the negative of the lattice energy, the energy need to blast apart one mole of LiF into its ions)

overall: $Li_{(s)} + \frac{1}{2}\ F_{2(g)} \rightarrow LiF_{(s)}$ (sum of above = -617 kJ/mol)

By difference, the electron affinity of F is -617 - (161+520+77-1047) = -328 kJ/mol.