2.15   a.   The possible values are shown in the following table.

Orbital	l	m_l
$5d$	2	-2, -1, 0, +1, +2
$4f$	3	-3, -2, -1, 0, +1, +2, +3
$7g$	4	-4, -3, -2, -1, 0, +1, +2, +3, +4

   b.   For a $3d$ electron, $n = 3$, $l = 2$, m_l = -2, -1, 0, +1, +2 (any one), and m_s = -½, +½ (either one), for a total of ten unique sets of n, l, m_l, and m_s.

   c.   For an f orbital, $l = 3$, so m_l = -3, -2, -1, 0, +1, +2, +3 (any one).

   d.   Any orbital can only have two electrons. The orbital is defined by the set of values of n, l, m_l, and electrons may have either spin state, m_s = +½ or m_s = -½. (This is a bit of a trick question. If it had asked, "How many electrons can occupy a $4d$ *subshell*", the answer would be 10.)

2.22   a.   At Cr the $3d$ and $4s$ levels are nearly degenerate. Therefore, electron repulsions are minimized by having all unpaired electrons with the configuration $3d^5 4s^1$. The half-filled subshell configuration, with a spherical distribution of electron density in the $3d$ subshell, results in an energy advantage, generally referred to as "exchange energy".

   b.   At Ti ($Z = 22$) the $4s$ electrons are lower in energy than the $3d$ electrons, resulting in the configuration $3d^2 4s^2$. But in the ion Ti^{2+}, as with all transition metal ions, the $3d$ level is lower in energy. As a result, the configuration $3d^2 4s^0$ is favored over the configuration $3d^0 4s^2$.
   Remember: when forming transition element cations, always remove ns electrons before removing $(n$-1$)d$ electrons.

2.23   Learn to write these and all electronic configurations in so-called "shell order" rather than in the aufbau order. Doing this will always place the valence electrons at the end of the written configuration. The actual configuration is the same; just the order in which it is written is different. Both ways of writing are shown below.

		Shell Order	Aufbau Order
a.	V	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^3$
b.	Br	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^5$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^5$
c.	Ru^{3+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 4d^5$
d.	Hg^{2+}	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 4f^{14} 5s^2 5p^6 5d^{10}$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 4f^{14} 5d^{10}$
e.	Sb	$1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^3$	$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^3$

2.26   a.   Adding one electron to fluorine's $2s^2 2p^7$ configuration results in a fully-filled shell configuration, isoelectronic with Ne. Adding an electron beyond this would be at the $n = 3$ level, which is energetically very unfavorable.

b. The two $4s$ electrons of zinc's configuration $3d^{10}4s^2$ are lost, resulting in the configuration $3d^{10}$ for Zn^{2+}. This is a fully-filled subshell configuration with a spherical distribution of electron density, which results in a lower overall energy (exchange energy advantage).

c. This is analogous to the configuration of chromium. The half-filled $4d^5$ configuration has a spherical distribution, which results in a lower overall energy (again, exchange energy advantage).

2.28 a. Ti^{2+} is $3d^2$, and Ni^{2+} is $3d^8$. As noted above, transition elements always lose the ns electrons before any $(n–1)d$ electrons when forming cations.

b. Without a doubt, Mn^{2+} is $[Ar]3d^5$. Not only does this conform to the general rule that transition elements always lose the s electrons before any d electrons when forming cations, but it also results in a stable half-filled subshell configuration (exchange energy advantage).

2.38 Most of these can be understood on the basis of size. A smaller atom tends to have a higher ionization energy, because the electron removed in ionizations is closer to the nucleus to which it is attracted.

a. Fe > Ru   Fe is in the 4th period, and Ru is in the 5th period. Thus, Ru is bigger.

b. P > S   Although S lies to the right of P and is smaller, the stable half filled $3p^3$ configuration of phosphorous gives it slightly greatly stability, which requires more energy for ionization. This reversal of trend is similar to that observed with N and O. In this case, the energy difference is very slight: P = 1012 kJ/mol, S = 1000 kJ/mol.

c. K < Br   Br is at the end of the 4th period and therefore considerably smaller than K.

d. C < N   N is smaller than C. Also, N has a stable $2p^3$ half-filled configuration, which makes its first ionization energy even higher than O, which is somewhat smaller. O has the configuration $2p^4$, with no special stability. If an electron is lost, O^- has the $2p^3$ configuration isoelectronic with N, which is an additional energy advantage. The lower first ionization energy of O with respect N is a reversal of the usual periodic trend, whereby ionization tends to increase left-to-right in a period.

e. Cd > In   Here the stable closed configuration $4d^{10}5s^2$ of Cd makes it resistant to ionization, relative to In, which is actually somewhat smaller.
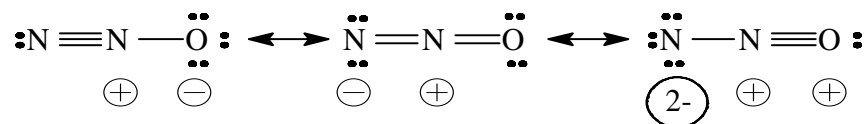
f. F > Cl   Fluorine is considerably smaller than chlorine.

2.43 a. $Se^{2-} > Br^- > Rb^+ > Sr^{2+}$ For isoelectronic ions, size decreases with increasing nuclear charge.

b. $Y^{3+} > Zr^{4+} > Nb^{5+}$ For isoelectronic ions, size decreases with increasing nuclear charge.

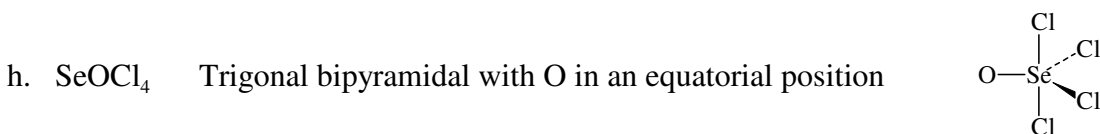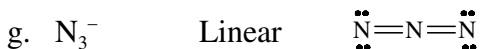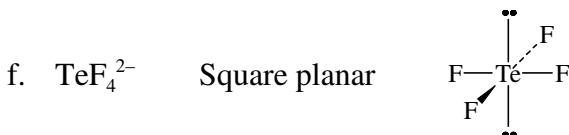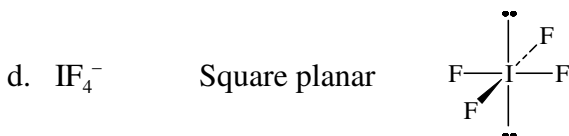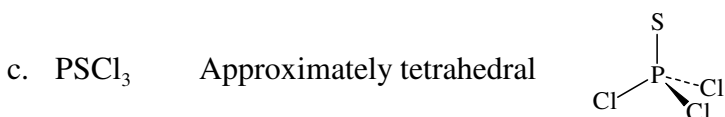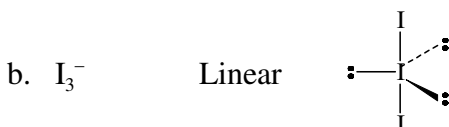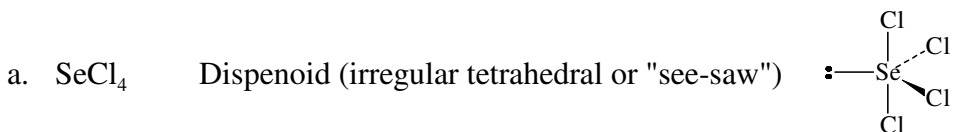c. $Co > Co^{2+} > Co^{3+} > Co^{4+}$ For the same nuclear charge, size decreases with positive charge.
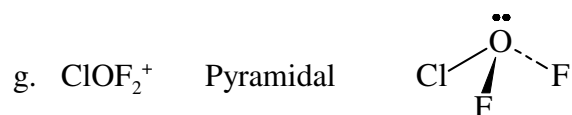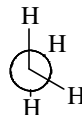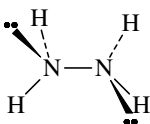
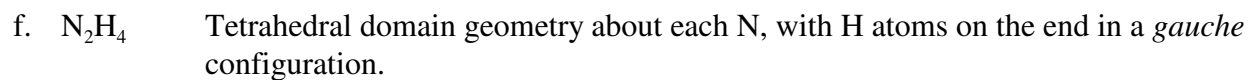3.5   The three principal forms are the following:

$$:N\equiv N-\overset{..}{\underset{..}{O}}: \longleftrightarrow \overset{..}{N}=N=\overset{..}{\underset{..}{O}} \longleftrightarrow :\overset{..}{N}-N\equiv O:$$

$$\quad\quad\quad \oplus \ \ominus \quad\quad\quad \ominus \ \ \oplus \quad\quad\quad 2\text{-} \ \oplus \ \ \oplus$$

The first form, which places the negative formal charge on the more electronegative oxygen, is the best, followed by the second form, which places the negative formal charge on the slightly less electronegative nitrogen. The third form, which has adjacent positive charges and a high doubly negative charge on the nitrogen, is clearly the least favored.

3.8   Only the shapes are shown here.

a. $SeCl_4$ Dispenoid (irregular tetrahedral or "see-saw")

b. I_3^- Linear

c. $PSCl_3$ Approximately tetrahedral

d. IF_4^- Square planar

e. PH_2^- Bent

f. TeF_4^{2-} Square planar

g. N_3^- Linear

h. $SeOCl_4$ Trigonal bipyramidal with O in an equatorial position

i. PH_4^+ Tetrahedral

3.10   Only the shapes and structurally important lone pairs are shown here.

a. SOF_6 Octahedral around S

b. POF_3 Approximately tetrahedral

c. ClO_2 Free radical (odd number of electrons) with a bent shape based on four domains. Observed bond angle is 117.5°.

d. NO_2 Free radical (odd number of electrons) with a bent structure based on three domains. Observed bond angle is 134.25°.

e. $S_2O_4^{2-}$ Tetrahedral domain geometry about each S atom.

f. N_2H_4 Tetrahedral domain geometry about each N, with H atoms on the end in a *gauche* configuration.

g. $ClOF_2^+$ Pyramidal

h. CS_2 Linear, like CO_2 S=C=S

i. $XeOF_5^-$ Distorted octahedral, owing to the lone pair on Xe
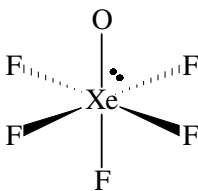
3.12   a. $AsH_3 < PH_3 < NH_3$ The ligand close packing (LCP) radii of the hydrogen ligands are very similar in all three compounds, so the size of the central atom is the determining factor. Arsenic, being the largest of the three central atoms, allows the three hydrogen ligands to approach each other with approximately the same separation as in PH_3 and NH_3, but with a smaller H–A–H angle (A = N, P, As).

   b. $SOF_2 < SOCl_2$ The LCP radius of fluorine attached to sulfur is smaller than for chlorine. This allows the two fluorine atoms to approach more closely, resulting in a smaller bond angle.

   c. NO_2^- (115°) $< O_3$ (116.8°) The LCP radii of the pendant oxygen atoms are very similar in both cases, but the central oxygen atom in ozone is slightly smaller. With a larger central atom in NO_2^-, the same O···O distance can be achieved with a smaller angle. (This is similar to the case in a.)

   d. $BrO_3^- < ClO_3^-$ Assuming similar oxygen LCP radii in both cases, the angle will be smaller about the larger bromine central atom.

3.17   a. Hypervalence is limited to compounds with central atoms in the third or higher periods, because elements in the second period are too small to accommodate more than four ligands. This is true even when stereochemically active lone pairs are assumed on the central atom, because they act as pseudo-lands.

   b. Sulfur compounds can be hypervalent, but oxygen compounds cannot. SF_4 is an AX_4E case, and SF_6 is an AX_6 case. As noted above, only central atoms from the third and higher periods are big enough to accommodate five and six ligands. SF_4 is a CN5 case consisting of four genuine ligands and a lone pair acting as a pseudo-ligand. SF_6 is a straightforward CN6 case.

3.36   For a given ligand (here F) attached to a given central atom (here C) the ligand radius remains fairly constant. Assuming close packing around the central atom, this results in a constant inter-ligand distance, regardless of changes in other bonds. The C–F bond lengths do change as a result of changes in coordination number (CN) and bond lengths of the other ligands ($=O$, $=CF_2$), but the $F\cdots F$ distance varies little, as shown in the following data.

Molecule	CN	C–F (pm)	$\angle$F–C–F ($^\circ$)	$F\cdots F$ (pm)
$F_2C{=}CF_2$	3	133.6	109.2	218
F_2CO	3	131.9	107.6	216
CF_4	4	131.9	109.5	216
F_3CO^-	4	139.2	101.3	215

3.37   Consider the following model:
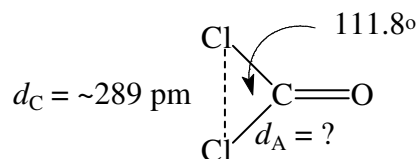
Based on CCl_4 and LCP considerations, the $Cl\cdots Cl$ distance is approximately 289 pm. Because the two C–Cl distances are the same, the CCl_2 moiety forms an isosceles triangle, for which (from the Law of Cosines) we can write

$$d_C = 2d_A \sin(\gamma/2)$$

This rearranges to give

$$d_A = \frac{d_C/2}{\sin(\gamma/2)} = \frac{144.5\,\text{pm}}{\sin(55.9^\circ)} = \frac{144.5\,\text{pm}}{0.82806} = 174.5\ \text{pm}$$

This is close to the C–Cl distance in CCl_4 (171.1 pm), so it is a reasonable prediction for the C–Cl distance in Cl_2CO.