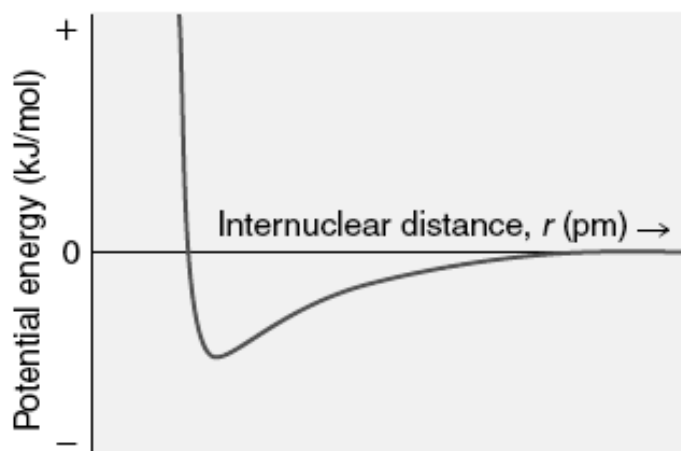


Homework #3

solution outlines

16. The charge on the Cr ion is 3+ and 2+ in CrCl_3 and CrCl_2 , respectively. Thus, the product Q_1Q_2 in Equation 8.4 is larger for CrCl_3 than it is for CrCl_2 . Further, the Cr^{3+} ion is smaller than the Cr^{2+} ion, allowing for shorter internuclear separations r_0 among the ions. Both of these indicate that U , which is proportional to Q_1Q_2/r_0 , should increase as we move from CrCl_2 to CrCl_3 .
18. The compound with the higher lattice energy will have the higher melting point because the individual ions need more kinetic energy to overcome the attractive forces in the lattice. To determine which has the larger U , note that Equation 8.4 tells us that $U \sim Q_1Q_2/r_0$. Therefore, compare the product Q_1Q_2 and the ionic radii for the given cations. The compound with the largest product Q_1Q_2 and the smallest r_0 will have the largest lattice energy. Below we quote ionic radii from Figure 7.9, but *you ought to be able to qualitatively determine which is smaller* from our work in Chapter 7. (We must do this for Fe^{3+} .)
- (a) $Q_1Q_2 = -4$ for MgO and SrO . From Figure 7.9 $r(\text{Mg}^{2+}) = 72$ pm and $r(\text{Sr}^{2+}) = 118$ pm. Thus, with Q_1Q_2 being equal in both cases, the shorter r_0 in MgO indicates that MgO should have the higher lattice energy. [Actual values are 3795 (MgO) and 3217 (SrO). Source: *CRC Handbook of Chemistry and Physics* (2004). Units are kJ/mol.]
- (b) $Q_1Q_2 = -2$ for each $\text{Cs}^+/\text{O}^{2-}$ interaction and $Q_1Q_2 = -4$ for BaO . From Figure 7.9 $r(\text{Cs}^+) = 167$ pm and $r(\text{Ba}^{2+}) = 135$ pm. Thus, the interactions in BaO are stronger and at shorter r_0 . BaO should have the higher lattice energy. [Actual values are 2131 (Cs_2O) and 3029 (BaO). Source: *CRC Handbook of Chemistry and Physics* (2004). Units are kJ/mol.]
- (c) $Q_1Q_2 = -4$ for FeO and $Q_1Q_2 = -6$ for each $\text{Fe}^{3+}/\text{O}^{2-}$ interaction. From Figure 7.9 $r(\text{Fe}^{2+}) = 78$ pm. $r(\text{Fe}^{3+})$ must be smaller than this, however, because Fe^{3+} has one less electron than Fe^{2+} and (obviously!) the same Z . Thus, the interactions in Fe_2O_3 are stronger and at shorter r_0 . Fe_2O_3 should have the higher lattice energy. [Actual values are 3795 (FeO) and 14,309 (Fe_2O_3). Source: *CRC Handbook of Chemistry and Physics* (2004). Units are kJ/mol.]

*53. The diagram is below



At distances somewhat less than r_0 , electron-electron repulsion becomes large, raising the potential energy. As this distance decreases further, the repulsion becomes stronger and, eventually, includes repulsion between the nuclei. The diagram shows the potential energy rises very quickly at short r .

58. This is analogous to the NaCl case shown in Figure 8.1. For SrO the ionic charges are twice what they are for NaCl, and r_0 is 258 pm and 283 pm for SrO and NaCl, respectively, from Figure 7.9. Thus, Equation 8.1 indicates that the combination for SrO(g) ought to be very stable, more stable than NaCl(g), and should form via an exothermic reaction. The valence-electron configurations help us to know that Sr forms a 2+ ion and that O forms a 2- ion, in accord with the octet rule. These charges were used to qualitatively analyze Equation 8.1 above.
- *59. Appendix A gives $\Delta H_f^\circ = -641.3$ kJ/mol for $\text{MgCl}_2(s)$. Table 8.2 gives $\Delta H_{\text{sub}}^\circ$ for $\text{Mg}(s)$ as 147.1 kJ/mol. [This is, of course, ΔH_f° for $\text{Mg}(g)$ from Appendix A; these are not numerically equal by coincidence.] Table 7.5 gives $I_1 + I_2 = (737.7 + 1450.7)$ kJ/mol = 2188.4 kJ/mol for the formation of $\text{Mg}^{2+}(g)$. Table 8.3 gives $(\Delta H_{\text{diss}}^\circ)D = 242.6$ for the process $\text{Cl}_2(g) \rightarrow 2\text{Cl}(g)$. Figure 7.13 gives $(\Delta H_{\text{EA}}^\circ)EA = -348.6$ kJ/mol for the electron affinity of $\text{Cl}(g)$. As in Equation 8.9 for $\text{CsF}(s)$, the lattice energy for $\text{MgCl}_2(s)$ is

$$U = \Delta H_{\text{sub}}^\circ(\text{Mg}) + I_1 + I_2 + D(\text{Cl}_2) + 2EA(\text{Cl}) - \Delta H_f^\circ(\text{MgCl}_2)$$

Thus, $U = (147.1 + 2188.4 + 242.6 - 2(348.6) + 641.3)$ kJ/mol = 2522.2 kJ/mol.

- 60.** Appendix A gives $\Delta H_f^\circ = -634.9$ kJ/mol for CaO(s). Table 8.2 gives $\Delta H_{\text{sub}}^\circ$ for Ca(s) as 177.8 kJ/mol. [This is, of course, ΔH_f° for Ca(g) from Appendix A; these are not numerically equal by coincidence.] We are given $I_1 + I_2 = (589.8 + 1145.4)$ kJ/mol = 1735.2 kJ/mol for the formation of $\text{Ca}^{2+}(\text{g})$. Table 8.3 gives ($\Delta H_{\text{diss}}^\circ =$) $D = 498.4$ kJ/mol for the process $\text{O}_2(\text{g}) \rightarrow 2\text{O}(\text{g})$. Equation 7.14 gives ($\Delta H_{\text{EA}}^\circ =$) $EA = +603$ kJ/mol for $EA_1 + EA_2$ of O(g). As in Equation 8.9 for CsF(s), the lattice energy for CaO(s) is

$$U = \Delta H_{\text{sub}}^\circ(\text{Ca}) + I_1 + I_2 + \frac{1}{2}D(\text{O}_2) + EA_1(\text{O}) + EA_2(\text{O}) - \Delta H_f^\circ(\text{CaO})$$

Thus, $U = (177.8 + 1735.2 + \frac{1}{2}(498.4) + 603 + 634.9)$ kJ/mol = 3.40×10^3 kJ/mol. Note that we had to use $\frac{1}{2}$ in front of $D(\text{O}_2)$ to keep the equations balanced, just as in both cycles of Figure 8.5.

- *61.** CaO has a much higher lattice energy than MgCl_2 , and a greater input of energy is required to destroy the CaO lattice than to destroy the MgCl_2 lattice. Thus, CaO should have the higher melting point. The actual melting points are 2898°C and 714°C for CaO and MgCl_2 , respectively. [Source: *CRC Handbook of Chemistry and Physics* (2004).] Our prediction was correct.
- *67.** Valence electrons are defined on page 288. For main group elements do not include closed $(n-1)d$ or $(n-2)f$ subshells as valence electrons. For transition elements do not include closed $(n-2)f$ subshells.
- (a) 11 valence electrons from $[\text{Kr}]5s^1 4d^{10}$
- (b) 8 valence electrons from $[\text{Xe}]4f^{14} 5d^8$.
- (c) 6 valence electrons due to S from $[\text{Ne}]3s^2 3p^4$
 1 valence electron due to each H from $1s^1$
 Total of 8 valence electrons
- (d) 6 valence electrons due to O from $[\text{He}]2s^2 2p^4$
 1 valence electron due to H from $1s^1$
 Total of 8 electrons in the Lewis structure from 7 valence electrons plus
 1 electron from 1- charge
- (e) 7 valence electrons due to each I from $[\text{Kr}]5s^2 4d^{10} 5p^5$

Total of 14 valence electrons

(f) 4 valence electrons due to C from $[\text{He}]2s^2 2p^2$

1 valence electron due to each H from $1s^1$

Total of 8 valence electrons

(g) 6 valence electrons due to S from $[\text{Ne}]3s^2 3p^4$

6 valence electrons due to each O from $[\text{He}]2s^2 2p^4$

Total of 32 electrons in the Lewis structure from 30 valence electrons plus

2 electrons from 2- charge

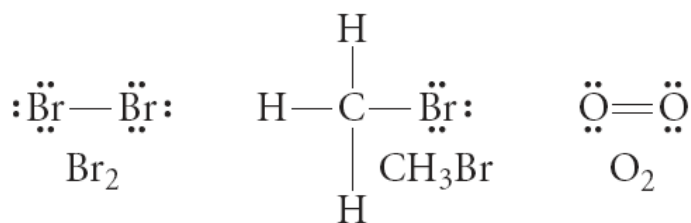
(h) 5 valence electrons due to N from $[\text{He}]2s^2 2p^3$

1 valence electron due to each H from $1s^1$

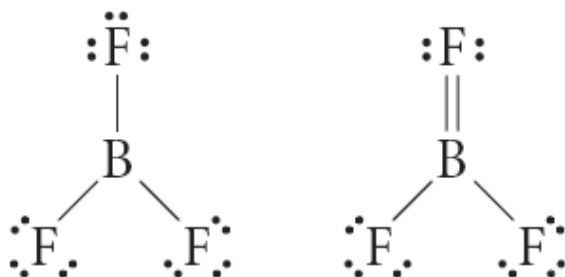
Total of 8 electrons in the Lewis structure from 9 valence electrons, where one electron has been lost

- *69. The procedure for drawing Lewis structures is given in Section 8.5. Difficult structures will be discussed below. As you draw Lewis structures, become familiar with recurring parts of them: N usually makes three bonds, O usually makes two bonds, the halogens usually make one bond, N usually has one lone pair, and so on. If your structure does not look “normal,” double-check your work or apply formal charges. Of course, there *certainly* are exceptions to “normal” Lewis structures.

Br_2 , CH_3Br , and O_2 are well-behaved Lewis structures. They should pose little trouble. The structures are:

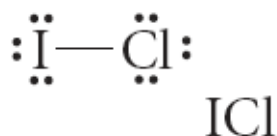


S_2^{2-} is solved in Example 8.4 (b). The very important sulfate ion SO_4^{2-} is explicitly discussed on page 364, where structure (b) in the margin is the preferred structure. Finally, BF_3 is analogous to the BCl_3 example before Example 8.8, leading to two possible structures:

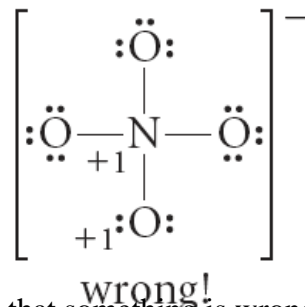


As with the BCl_3 example in the text, the structure on the right contains a halogen with a +1 formal charge and the *less* electronegative B with a -1 formal charge. Given the high electronegativity of F, this structure is probably not a significant one; the BF_3 structure on the left above is more important. “More important” means most “true” or “correct.”

74. The Lewis dot symbols for F, Cl, Br, and I are the same. The Lewis dot symbol for F is in Table 8.5. Each has seven valence electrons, indicating that each should form one bond. Thus, compounds between the halogens, ICl and others, should form. The Lewis structure is

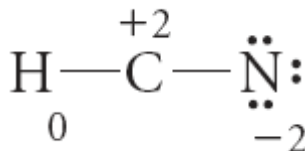


The Lewis dot symbol for N indicates that it should form three bonds, and it usually does. Of course, we also know that NH_4^+ is a stable ion and that N can form four bonds. Thus, we need to look a little further. With 30 electrons steps 1 through 5 of Section 8.5 lead to the following unreasonable structure:

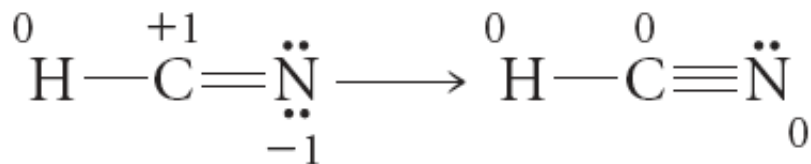


The formal charges indicate that something is wrong. The proposed NO_4^- has a negative one charge. The sum of the formal charges, however, is +2. This can't be. No reasonable Lewis structure can be drawn, and we predict that such a structure will not be stable.

80. There are $1+4+5=10$ electrons in this compound. H must be terminal, and $\chi(\text{C}) < \chi(\text{N})$ (step 1), thus we place C at the center. Steps 1 through 5 give use the following structure, shown with formal charges:



This should immediately be seen as not good! C does not have an octet, and the formal charges are high. We can successively move in lone pairs via step 6 and examine the octet situation and the formal charges at each stage. We find:



The final structure is the best in every way. C and N have an octet, H makes one bond, and the formal charges are all zero. There are no plausible resonance structures.

Additional questions:

1. How many of the following electron configurations are allowed?

- | | |
|--------------------------------|--|
| (a) $1s^2 2s^2 2p^7$ | NO [No p^7 occupation] |
| (b) $1s^2 2s^2 2p^6 2d^1$ | NO [No 2d orbitals] |
| (c) $[\text{Ne}] 4s^2 4p^4$ | NO [3s and 3p orbital filling would precede 4s, 3d would precede 4p] |
| (d) $[\text{Ar}] 4s^2 3d^6$ | YES |
| (e) $1s^2 2s^2 2p^8 3s^2 3p^4$ | NO [No $2p^8$ configuration] |

There are two conventions for writing electron configurations (see text p. 88): list subshells (1) in order of increasing energy or (2) following the arrangement of elements in the periodic table. The text favors the latter; some periodic tables favor the former. Prof. Sadoway is with the authors of the text but will accept both answers.

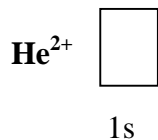
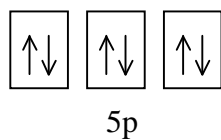
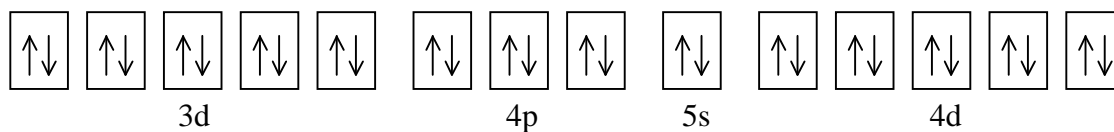
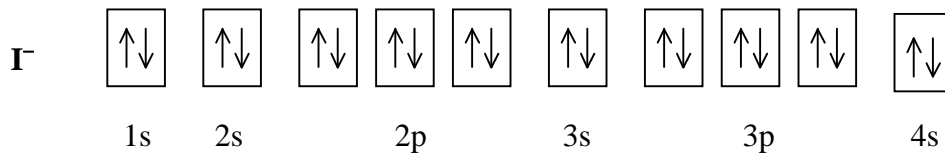
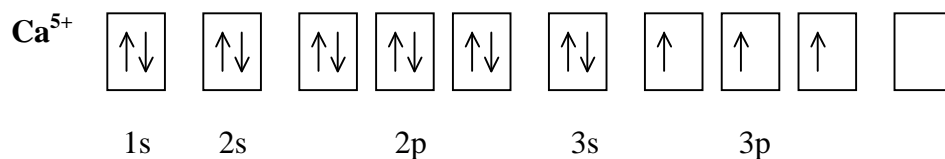
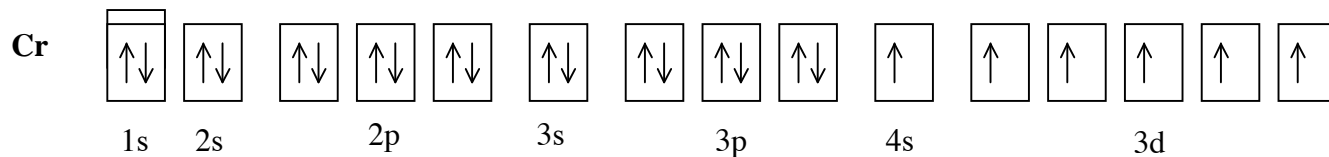
2. Determine which of the following five electronic states are forbidden:

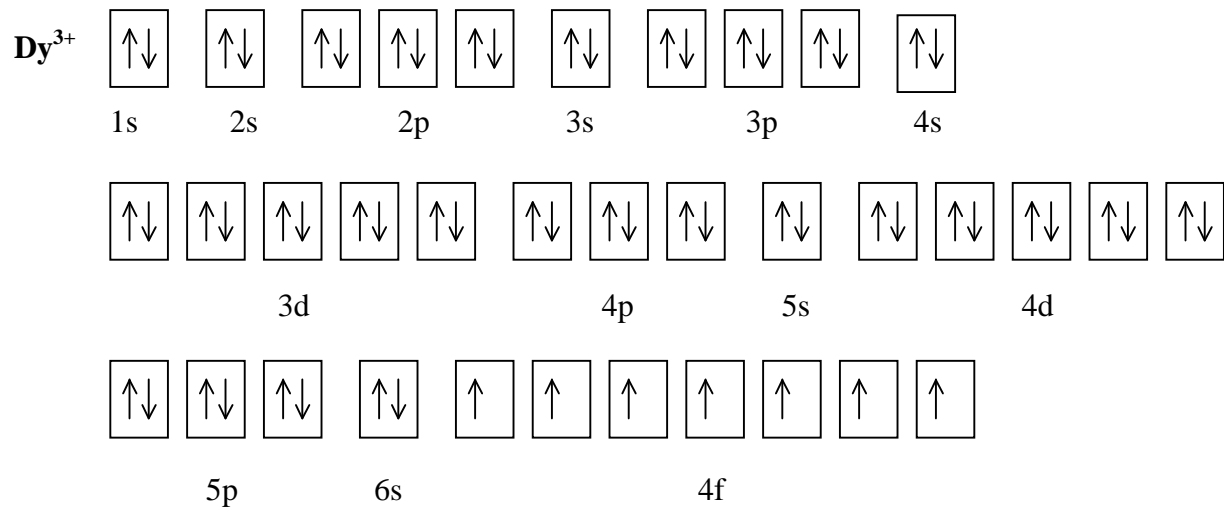
	n	ℓ	m
(1)	2	2	1
(2)	1	0	1
(3)	3	2	0
(4)	4	1	2
(5)	3	2	2

Forbidden states are:

- 1, because $l = n$
- 2, because $m > l$
- 4, because $m > l$

3. (a) In box notation, give the complete ground-state electron configuration for each of the following chemical entities: Cr, Ca^{5+} , Γ , He^{2+} , Dy^{3+} .





(b) Give the values of n , l , and m for each orbital in the 5d subshell.

n	l	M
5	2	2
5	2	1
5	2	0
5	2	-1
5	2	-2