CHAPTER 2

ATOMIC STRUCTURE AND INTERATOMIC BONDING

PROBLEM SOLUTIONS

Fundamental Concepts
Electrons in Atoms

2.1 Atomic mass is the mass of an individual atom, whereas atomic weight is the average (weighted) of the atomic masses of an atom's naturally occurring isotopes.

2.2 The average atomic weight of silicon $(\overline{A}_{\text{Si}})$ is computed by adding fraction-of-occurrence/atomic weight products for the three isotopes. Thus

$$\overline{A}_{\text{Si}} = f_{^{28}\text{Si}} A_{^{28}\text{Si}} + f_{^{29}\text{Si}} A_{^{29}\text{Si}} + f_{^{30}\text{Si}} A_{^{30}\text{Si}}$$

$$= (0.9223)(27.9769) + (0.0468)(28.9765) + (0.0309)(29.9738) = 28.0854$$

2.3 (a) In order to determine the number of grams in one amu of material, appropriate manipulation of the amu/atom, g/mol, and atom/mol relationships is all that is necessary, as

$$\# \text{ g/amu} = \left(\frac{1 \text{ mol}}{6.023 \text{ x } 10^{23} \text{ atoms}}\right)\left(\frac{1 \text{ g/mol}}{1 \text{ amu/atom}}\right)$$

$$= 1.66 \text{ x } 10^{-24} \text{ g/amu}$$

(b) Since there are 453.6 g/lb$_m$,

$$1 \text{ lb-mol} = (453.6 \text{ g/lb}_m)(6.023 \text{ x } 10^{23} \text{ atoms/g-mol})$$

$$= 2.73 \text{ x } 10^{26} \text{ atoms/lb-mol}$$

2.4 (a) Two important quantum-mechanical concepts associated with the Bohr model of the atom are (1) that electrons are particles moving in discrete orbitals, and (2) electron energy is quantized into shells.

(b) Two important refinements resulting from the wave-mechanical atomic model are (1) that electron position is described in terms of a probability distribution, and (2) electron energy is quantized into both shells and subshells--each electron is characterized by four quantum numbers.

2.5 The n quantum number designates the electron shell.

The l quantum number designates the electron subshell.
The m_l quantum number designates the number of electron states in each electron subshell.

The m_s quantum number designates the spin moment on each electron.

2.6 For the *L* state, $n = 2$, and eight electron states are possible. Possible l values are 0 and 1, while possible m_l values are 0 and ±1; and possible m_s values are $\pm\frac{1}{2}$. Therefore, for the *s* states, the quantum numbers are $200(\frac{1}{2})$ and $200(-\frac{1}{2})$. For the *p* states, the quantum numbers are $210(\frac{1}{2})$, $210(-\frac{1}{2})$, $211(\frac{1}{2})$, $211(-\frac{1}{2})$, $21(-1)(\frac{1}{2})$, and $21(-1)(-\frac{1}{2})$.

For the *M* state, $n = 3$, and 18 states are possible. Possible l values are 0, 1, and 2; possible m_l values are 0, ±1, and ±2; and possible m_s values are $\pm\frac{1}{2}$. Therefore, for the *s* states, the quantum numbers are $300(\frac{1}{2})$, $300(-\frac{1}{2})$, for the *p* states they are $310(\frac{1}{2})$, $310(-\frac{1}{2})$, $311(\frac{1}{2})$, $311(-\frac{1}{2})$, $31(-1)(\frac{1}{2})$, and $31(-1)(-\frac{1}{2})$; for the *d* states they are $320(\frac{1}{2})$, $320(-\frac{1}{2})$, $321(\frac{1}{2})$, $321(-\frac{1}{2})$, $32(-1)(\frac{1}{2})$, $32(-1)(-\frac{1}{2})$, $322(\frac{1}{2})$, $322(-\frac{1}{2})$, $32(-2)(\frac{1}{2})$, and $32(-2)(-\frac{1}{2})$.

2.7 The electron configurations for the ions are determined using Table 2.2 (and Figure 2.6).

P^{5+}: $1s^2 2s^2 2p^6$

P^{3-}: $1s^2 2s^2 2p^6 3s^2 3p^6$

Sn^{4+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10}$

Se^{2-}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6$

I^-: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^{10} 5s^2 5p^6$

Ni^{2+}: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^8$

2.8 The K^+ ion is just a potassium atom that has lost one electron; therefore, it has an electron configuration the same as argon (Figure 2.6).

The I^- ion is a iodine atom that has acquired one extra electron; therefore, it has an electron configuration the same as xenon.

The Periodic Table

2.9 Each of the elements in Group IIA has two *s* electrons.

2.10 From the periodic table (Figure 2.6) the element having atomic number 112 would belong to group IIB. According to Figure 2.6, Ds, having an atomic number of 110 lies below Pt in the periodic table and in the right-most column of group VIII. Moving two columns to the right puts element 112 under Hg and in group IIB.

2.11 (a) The $1s^22s^22p^63s^23p^5$ electron configuration is that of a halogen because it is one electron deficient from having a filled *p* subshell.

(b) The $1s^22s^22p^63s^23p^63d^74s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(c) The $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$ electron configuration is that of an inert gas because of filled 4*s* and 4*p* subshells.

(d) The $1s^22s^22p^63s^23p^64s^1$ electron configuration is that of an alkali metal because of a single *s* electron.

(e) The $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^55s^2$ electron configuration is that of a transition metal because of an incomplete *d* subshell.

(f) The $1s^22s^22p^63s^2$ electron configuration is that of an alkaline earth metal because of two *s* electrons.

2.12 (a) The 4*f* subshell is being filled for the rare earth series of elements.

(b) The 5*f* subshell is being filled for the actinide series of elements.

Bonding Forces and Energies

2.13 The attractive force between two ions F_A is just the derivative with respect to the interatomic separation of the attractive energy expression, Equation 2.8, which is just

$$F_A = \frac{dE_A}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} = \frac{A}{r^2}$$

The constant A in this expression is defined in footnote 3. Since the valences of the Ca^{2+} and O^{2-} ions (Z_1 and Z_2) are both 2, then

$$F_A = \frac{(Z_1 e)(Z_2 e)}{4\pi\varepsilon_0 r^2}$$

$$= \frac{(2)(2)(1.6 \text{ x } 10^{-19} \text{ C})^2}{(4)(\pi)(8.85 \text{ x } 10^{-12} \text{ F/m})(1.25 \text{ x } 10^{-9} \text{ m})^2}$$

$$= 5.89 \text{ x } 10^{-10} \text{ N}$$

2.14 (a) Differentiation of Equation 2.11 yields

$$\frac{dE_N}{dr} = \frac{d\left(-\frac{A}{r}\right)}{dr} + \frac{d\left(\frac{B}{r^n}\right)}{dr}$$

$$= \frac{A}{r^{(1\,+\,1)}} - \frac{nB}{r^{(n\,+\,1)}} = 0$$

(b) Now, solving for r (= r_0)

$$\frac{A}{r_0^2} = \frac{nB}{r_0^{(n\,+\,1)}}$$

or

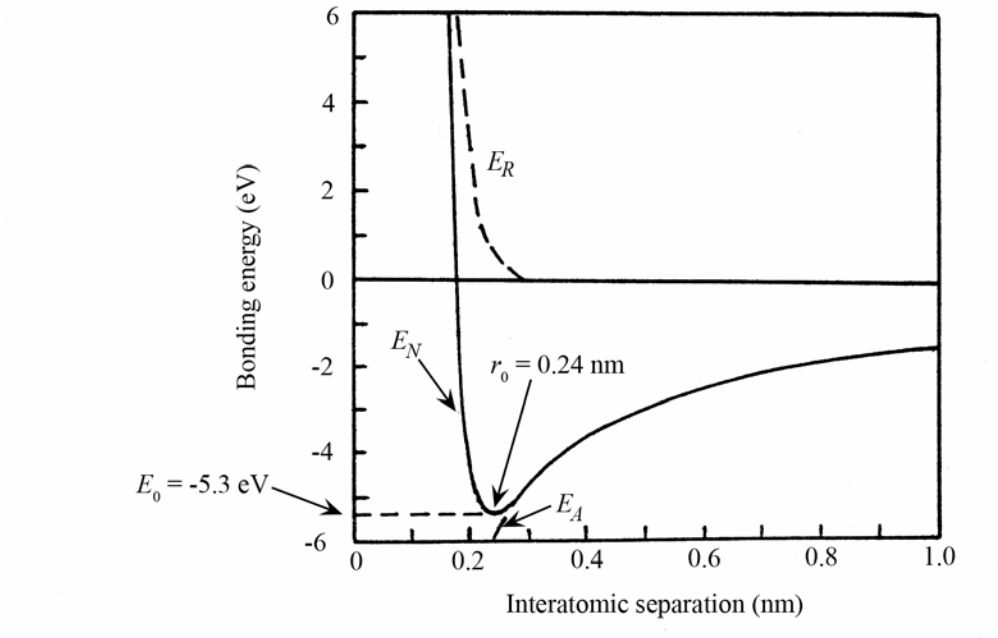
$$r_0 = \left(\frac{A}{nB}\right)^{1/(1\,-\,n)}$$

(c) Substitution for r_0 into Equation 2.11 and solving for E (= E_0)

$$E_0 = -\frac{A}{r_0} + \frac{B}{r_0^n}$$

$$= -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1\,-\,n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1\,-\,n)}}$$

2.15 (a) Curves of E_A, E_R, and E_N are shown on the plot below.



(b) From this plot

$$r_0 = 0.24 \text{ nm}$$

$$E_0 = -5.3 \text{ eV}$$

(c) From Equation 2.11 for E_N

$$A = 1.436$$

$$B = 7.32 \times 10^{-6}$$

$$n = 8$$

Thus,

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1 - n)}$$

$$\left[\frac{1.436}{(8)(7.32 \times 10^{-6})}\right]^{1/(1 - 8)} = 0.236 \text{ nm}$$

and

$$E_0 = -\frac{1.436}{\left[\dfrac{1.436}{(8)\left(7.32 \times 10^{-6}\right)}\right]^{1/(1-8)}} + \frac{7.32 \times 10^{-6}}{\left[\dfrac{1.436}{(8)\left(7.32 \times 10^{-6}\right)}\right]^{8/(1-8)}}$$

$$= -5.32 \text{ eV}$$

2.16 This problem gives us, for a hypothetical X^+-Y^- ion pair, values for r_0 (0.38 nm), E_0 (– 5.37 eV), and n (8), and asks that we determine explicit expressions for attractive and repulsive energies of Equations 2.8 and 2.9. In essence, it is necessary to compute the values of A and B in these equations. Expressions for r_0 and E_0 in terms of n, A, and B were determined in Problem 2.14, which are as follows:

$$r_0 = \left(\frac{A}{nB}\right)^{1/(1 - n)}$$

$$E_0 = -\frac{A}{\left(\frac{A}{nB}\right)^{1/(1 - n)}} + \frac{B}{\left(\frac{A}{nB}\right)^{n/(1 - n)}}$$

Thus, we have two simultaneous equations with two unknowns (viz. A and B). Upon substitution of values for r_0 and E_0 in terms of n, these equations take the forms

$$0.38 \text{ nm} = \left(\frac{A}{8B}\right)^{1/(1 - 8)} = \left(\frac{A}{8B}\right)^{-1/7}$$

and

$$-5.37 \text{ eV} = -\frac{A}{\left(\frac{A}{8B}\right)^{1/(1-8)}} + \frac{B}{\left(\frac{A}{8B}\right)^{8/(1-8)}}$$

$$= -\frac{A}{\left(\frac{A}{8B}\right)^{-1/7}} + \frac{B}{\left(\frac{A}{10B}\right)^{-8/7}}$$

We now want to solve these two equations simultaneously for values of A and B. From the first of these two equations, solving for $A/8B$ leads to

$$\frac{A}{8B} = (0.38 \text{ nm})^{-7}$$

Furthermore, from the above equation the A is equal to

$$A = 8B(0.38 \text{ nm})^{-7}$$

When the above two expressions for $A/8B$ and A are substituted into the above expression for E_0 (- 5.37 eV), the following results

$$-5.37 \text{ eV} \;=\; = \; -\frac{A}{\left(\dfrac{A}{8B}\right)^{-1/7}} + \frac{B}{\left(\dfrac{A}{10B}\right)^{-8/7}}$$

$$= \; -\frac{8B(0.38 \text{ nm})^{-7}}{\left[(0.38 \text{ nm})^{-7}\right]^{-1/7}} + \frac{B}{\left[(0.38 \text{ nm})^{-7}\right]^{-8/7}}$$

$$= \; -\frac{8B(0.38 \text{ nm})^{-7}}{0.38 \text{ nm}} + \frac{B}{(0.38 \text{ nm})^{8}}$$

Or

$$-5.37 \text{ eV} \;=\; = \; -\frac{8B}{(0.38 \text{ nm})^{8}} + \frac{B}{(0.38 \text{ nm})^{8}} \;=\; -\frac{7B}{(0.38 \text{ nm})^{8}}$$

Solving for B from this equation yields

$$B \;=\; 3.34 \times 10^{-4} \text{ eV - nm}^{8}$$

Furthermore, the value of A is determined from one of the previous equations, as follows:

$$A \;=\; 8B(0.38 \text{ nm})^{-7} \;=\; (8)\left(3.34 \times 10^{-4} \text{ eV - nm}^{8}\right)(0.38 \text{ nm})^{-7}$$

$$= \; 2.34 \text{ eV - nm}$$

Thus, Equations 2.8 and 2.9 become

$$E_A \;=\; -\frac{2.34}{r}$$

$$E_R \;=\; \frac{3.34 \text{ x } 10^{-4}}{r^{8}}$$

Of course these expressions are valid for r and E in units of nanometers and electron volts, respectively.

2.17 (a) Differentiating Equation 2.12 with respect to r yields

$$\frac{dE}{dr} = \frac{d\left(-\frac{C}{r}\right)}{dr} - \frac{d\left[D\exp\left(-\frac{r}{\rho}\right)\right]}{dr}$$

$$= \frac{C}{r^2} - \frac{De^{-r/\rho}}{\rho}$$

At $r = r_0$, $dE/dr = 0$, and

$$\frac{C}{r_0^2} = \frac{De^{-(r_0/\rho)}}{\rho} \qquad (2.12b)$$

Solving for C and substitution into Equation 2.12 yields an expression for E_0 as

$$E_0 = De^{-(r_0/\rho)}\left(1 - \frac{r_0}{\rho}\right)$$

(b) Now solving for D from Equation 2.12b above yields

$$D = \frac{C\rho\, e^{(r_0/\rho)}}{r_0^2}$$

Substitution of this expression for D into Equation 2.12 yields an expression for E_0 as

$$E_0 = \frac{C}{r_0}\left(\frac{\rho}{r_0} - 1\right)$$

Primary Interatomic Bonds

2.18 (a) The main differences between the various forms of primary bonding are:

Ionic--there is electrostatic attraction between oppositely charged ions.

Covalent--there is electron sharing between two adjacent atoms such that each atom assumes a stable electron configuration.

Metallic--the positively charged ion cores are shielded from one another, and also "glued" together by the sea of valence electrons.

(b) The Pauli exclusion principle states that each electron state can hold no more than two electrons, which must have opposite spins.

2.19 The percent ionic character is a function of the electron negativities of the ions X_A and X_B according to Equation 2.10. The electronegativities of the elements are found in Figure 2.7.

For MgO, X_{Mg} = 1.2 and X_O = 3.5, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(3.5-1.2)^2}\right] \times 100 = 73.4\%$$

For GaP, X_{Ga} = 1.6 and X_P = 2.1, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(2.1-1.6)^2}\right] \times 100 = 6.1\%$$

For CsF, X_{Cs} = 0.7 and X_F = 4.0, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(4.0-0.7)^2}\right] \times 100 = 93.4\%$$

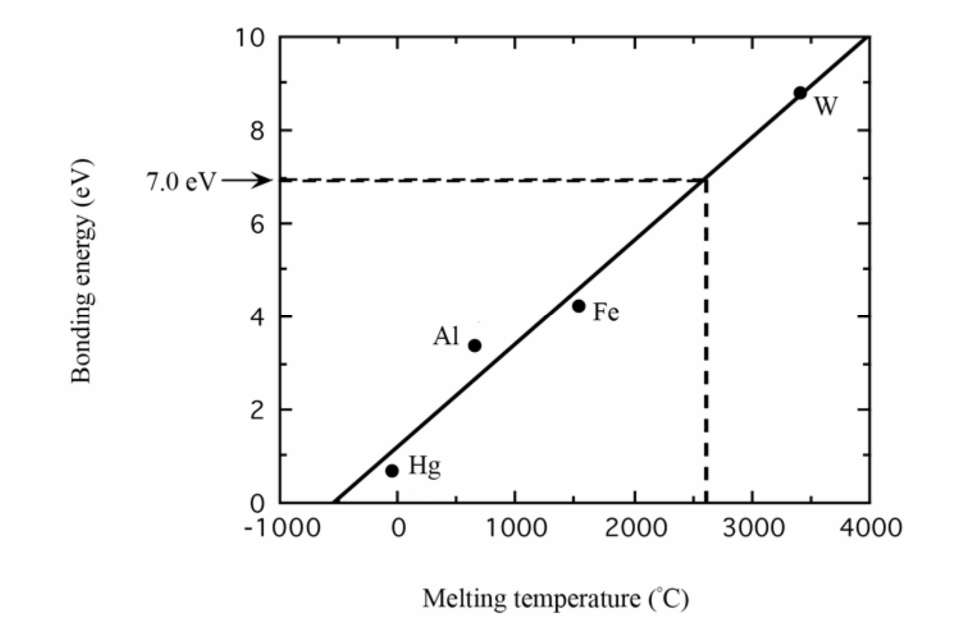
For CdS, X_{Cd} = 1.7 and X_S = 2.5, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(2.5-1.7)^2}\right] \times 100 = 14.8\%$$

For FeO, X_{Fe} = 1.8 and X_O = 3.5, and therefore,

$$\%IC = \left[1 - e^{(-0.25)(3.5-1.8)^2}\right] \times 100 = 51.4\%$$

2.20 Below is plotted the bonding energy versus melting temperature for these four metals. From this plot, the bonding energy for molybdenum (melting temperature of 2617°C) should be approximately 7.0 eV. The experimental value is 6.8 eV.



2.21 For silicon, having the valence electron structure $3s^2 3p^2$, N' = 4; thus, there are 8 – N' = 4 covalent bonds per atom.

For bromine, having the valence electron structure $4s^2 4p^5$, N' = 7; thus, there is 8 – N' = 1 covalent bond per atom.

For nitrogen, having the valence electron structure $2s^2 2p^3$, N' = 5; thus, there are 8 – N' = 3 covalent bonds per atom.

For sulfur, having the valence electron structure $3s^2 3p^4$, N' = 6; thus, there are 8 – N' = 2 covalent bonds per atom.

For neon, having the valence electron structure $2s^2 2p^6$, N' = 8; thus, there are 8 – N' = 0 covalent bonds per atom, which is what we would expect since neon is an inert gas.

2.22 For solid xenon, the bonding is van der Waals since xenon is an inert gas.

For CaF_2, the bonding is predominantly ionic (but with some slight covalent character) on the basis of the relative positions of Ca and F in the periodic table.

For bronze, the bonding is metallic since it is a metal alloy (composed of copper and tin).

For CdTe, the bonding is predominantly covalent (with some slight ionic character) on the basis of the relative positions of Cd and Te in the periodic table.

For rubber, the bonding is covalent with some van der Waals. (Rubber is composed primarily of carbon and hydrogen atoms.)

For tungsten, the bonding is metallic since it is a metallic element from the periodic table.

Secondary Bonding or van der Waals Bonding

2.23 The intermolecular bonding for HF is hydrogen, whereas for HCl, the intermolecular bonding is van der Waals. Since the hydrogen bond is stronger than van der Waals, HF will have a higher melting temperature.