

## CHAPTER 2

### ATOMIC STRUCTURE AND INTERATOMIC BONDING

#### PROBLEM SOLUTIONS

2.2 Chromium has four naturally-occurring isotopes: 4.34% of  $^{50}\text{Cr}$ , with an atomic weight of 49.9460 amu, 83.79% of  $^{52}\text{Cr}$ , with an atomic weight of 51.9405 amu, 9.50% of  $^{53}\text{Cr}$ , with an atomic weight of 52.9407 amu, and 2.37% of  $^{54}\text{Cr}$ , with an atomic weight of 53.9389 amu. On the basis of these data, confirm that the average atomic weight of Cr is 51.9963 amu.

#### Solution

The average atomic weight of chromium ( $\bar{A}_{\text{Cr}}$ ) is computed by adding fraction-of-occurrence/atomic weight products for the four isotopes. Thus

$$\begin{aligned}\bar{A}_{\text{Cr}} &= f_{50_{\text{Cr}}} A_{50_{\text{Cr}}} + f_{52_{\text{Cr}}} A_{52_{\text{Cr}}} + f_{53_{\text{Cr}}} A_{53_{\text{Cr}}} + f_{54_{\text{Cr}}} A_{54_{\text{Cr}}} \\ &= (0.0434)(49.9460 \text{ amu}) + (0.8379)(51.9405 \text{ amu}) + (0.0950)(52.9407 \text{ amu}) \\ &\quad + (0.0237)(53.9389 \text{ amu}) = 51.9963 \text{ amu}\end{aligned}$$

2.5 Relative to electrons and electron states, what does each of the four quantum numbers specify?

Solution

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.

2.7 Give the electron configurations for the following ions:  $\text{Fe}^{2+}$ ,  $\text{Al}^{3+}$ ,  $\text{Cu}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Br}^-$ ,  $\text{O}^{2-}$ ,  $\text{Fe}^{3+}$  and  $\text{S}^{2-}$ .

Solution

The electron configurations for the ions are determined using Table 2.2 (and Figure 2.8).

$\text{Fe}^{2+}$ : From Table 2.2, the electron configuration for an atom of iron is  $1s^22s^22p^63s^23p^63d^64s^2$ . In order to become an ion with a plus two charge, it must lose two electrons—in this case the two  $4s$ . Thus, the electron configuration for an  $\text{Fe}^{2+}$  ion is  $1s^22s^22p^63s^23p^63d^6$ .

$\text{Al}^{3+}$ : From Table 2.2, the electron configuration for an atom of aluminum is  $1s^22s^22p^63s^23p^1$ . In order to become an ion with a plus three charge, it must lose three electrons—in this case two  $3s$  and the one  $3p$ . Thus, the electron configuration for an  $\text{Al}^{3+}$  ion is  $1s^22s^22p^6$ .

$\text{Cu}^+$ : From Table 2.2, the electron configuration for an atom of copper is  $1s^22s^22p^63s^23p^63d^{10}4s^1$ . In order to become an ion with a plus one charge, it must lose one electron—in this case the  $4s$ . Thus, the electron configuration for a  $\text{Cu}^+$  ion is  $1s^22s^22p^63s^23p^63d^{10}$ .

$\text{Ba}^{2+}$ : The atomic number for barium is 56 (Figure 2.6), and inasmuch as it is not a transition element the electron configuration for one of its atoms is  $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^66s^2$ . In order to become an ion with a plus two charge, it must lose two electrons—in this case two the  $6s$ . Thus, the electron configuration for a  $\text{Ba}^{2+}$  ion is  $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6$ .

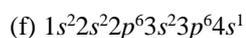
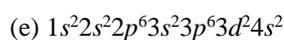
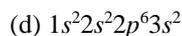
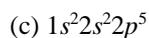
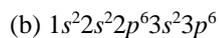
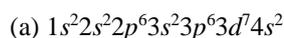
$\text{Br}^-$ : From Table 2.2, the electron configuration for an atom of bromine is  $1s^22s^22p^63s^23p^63d^{10}4s^24p^5$ . In order to become an ion with a minus one charge, it must acquire one electron—in this case another  $4p$ . Thus, the electron configuration for a  $\text{Br}^-$  ion is  $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$ .

$\text{O}^{2-}$ : From Table 2.2, the electron configuration for an atom of oxygen is  $1s^22s^22p^4$ . In order to become an ion with a minus two charge, it must acquire two electrons—in this case another two  $2p$ . Thus, the electron configuration for an  $\text{O}^{2-}$  ion is  $1s^22s^22p^6$ .

$\text{Fe}^{3+}$ : From Table 2.2, the electron configuration for an atom of iron is  $1s^22s^22p^63s^23p^63d^64s^2$ . In order to become an ion with a plus three charge, it must lose three electrons—in this case the two  $4s$  and one  $3d$ . Thus, the electron configuration for an  $\text{Fe}^{3+}$  ion is  $1s^22s^22p^63s^23p^63d^5$ .

$\text{S}^{2-}$ : From Table 2.2, the electron configuration for an atom of sulphur is  $1s^22s^22p^63s^23p^4$ . In order to become an ion with a minus two charge, it must acquire two electrons—in this case another two  $3p$ . Thus, the electron configuration for an  $\text{S}^{2-}$  ion is  $1s^22s^22p^63s^23p^6$ .

2.11 Without consulting Figure 2.8 or Table 2.2, determine whether each of the electron configurations given below is an inert gas, a halogen, an alkali metal, an alkaline earth metal, or a transition metal. Justify your choices.



Solution

(a) The  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$  electron configuration is that of a transition metal because of an incomplete  $d$  subshell.

(b) The  $1s^2 2s^2 2p^6 3s^2 3p^6$  electron configuration is that of an inert gas because of filled  $3s$  and  $3p$  subshells.

(c) The  $1s^2 2s^2 2p^5$  electron configuration is that of a halogen because it is one electron deficient from having a filled  $L$  shell.

(d) The  $1s^2 2s^2 2p^6 3s^2$  electron configuration is that of an alkaline earth metal because of two  $s$  electrons.

(e) The  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^2 4s^2$  electron configuration is that of a transition metal because of an incomplete  $d$  subshell.

(f) The  $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$  electron configuration is that of an alkali metal because of a single  $s$  electron.

2.13 Calculate the force of attraction between a  $K^+$  and an  $O^{2-}$  ion the centers of which are separated by a distance of 1.6 nm.

Solution

The attractive force between two ions  $F_A$  is just the derivative with respect to the interatomic separation of the attractive energy expression, Equation 2.9, which is just

$$F_A = \frac{dE_A}{dr} = \frac{d}{dr} \left( \frac{A}{r^2} \right) = \frac{A}{r^3}$$

The constant  $A$  in this expression is defined in Equation 2.10. Since the valences of the  $K^+$  and  $O^{2-}$  ions ( $Z_1$  and  $Z_2$ ) are +1 and -2, respectively,  $Z_1 = 1$  and  $Z_2 = 2$ , then

$$\begin{aligned} F_A &= \frac{(Z_1 e)(Z_2 e)}{4\pi\epsilon_0 r^2} \\ &= \frac{(1)(2)(1.602 \times 10^{-19} \text{ C})^2}{(4)(\pi)(8.85 \times 10^{-12} \text{ F/m})(1.6 \times 10^{-9} \text{ m})^2} \\ &= 1.8 \times 10^{-10} \text{ N} \end{aligned}$$

2.14 The net potential energy between two adjacent ions,  $E_N$ , may be represented by the sum of Equations 2.9 and 2.11; that is,

$$E_N = -\frac{A}{r} + \frac{B}{r^n}$$

Calculate the bonding energy  $E_0$  in terms of the parameters  $A$ ,  $B$ , and  $n$  using the following procedure:

1. Differentiate  $E_N$  with respect to  $r$ , and then set the resulting expression equal to zero, since the curve of  $E_N$  versus  $r$  is a minimum at  $E_0$ .
2. Solve for  $r$  in terms of  $A$ ,  $B$ , and  $n$ , which yields  $r_0$ , the equilibrium interionic spacing.
3. Determine the expression for  $E_0$  by substitution of  $r_0$  into Equation 2.17.

### Solution

(a) Differentiation of Equation 2.17 yields

$$\begin{aligned} \frac{dE_N}{dr} &= \frac{d}{dr} \left( -\frac{A}{r} \right) + \frac{d}{dr} \left( \frac{B}{r^n} \right) \\ &= \frac{A}{r^2} - \frac{nB}{r^{n+1}} = 0 \end{aligned}$$

(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 2.17 and solving for  $E (= E_0)$

$$\begin{aligned} E_0 &= -\frac{A}{r_0} + \frac{B}{r_0^n} \\ &= -\frac{A}{\left( \frac{A}{nB} \right)^{1/(1-n)}} + \frac{B}{\left( \frac{A}{nB} \right)^{n/(1-n)}} \end{aligned}$$

2.16 Consider a hypothetical  $X^+Y^-$  ion pair for which the equilibrium interionic spacing and bonding energy values are 0.38 nm and  $-6.13$  eV, respectively. If it is known that  $n$  in Equation 2.17 has a value of 10, using the results of Problem 2.14, determine explicit expressions for attractive and repulsive energies  $E_A$  and  $E_R$  of Equations 2.9 and 2.11.

Solution

This problem gives us, for a hypothetical  $X^+Y^-$  ion pair, values for  $r_0$  (0.38 nm),  $E_0$  ( $-6.13$  eV), and  $n$  (10), and asks that we determine explicit expressions for attractive and repulsive energies of Equations 2.9 and 2.11. 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:

$$r_0 = \left( \frac{A}{10B} \right)^{1/(1-n)}$$

$$E_0 = - \frac{A}{\left( \frac{A}{10B} \right)^{1/(1-n)}} + \frac{B}{\left( \frac{A}{10B} \right)^{n/(1-n)}}$$

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

$$0.38 \text{ nm} = \left( \frac{A}{10B} \right)^{1/(1-10)} = \left( \frac{A}{10B} \right)^{-1/9}$$

and

$$\begin{aligned} -6.13 \text{ eV} &= - \frac{A}{\left( \frac{A}{10B} \right)^{1/(1-10)}} + \frac{B}{\left( \frac{A}{10B} \right)^{10/(1-10)}} \\ &= - \frac{A}{\left( \frac{A}{10B} \right)^{-1/9}} + \frac{B}{\left( \frac{A}{10B} \right)^{-10/9}} \end{aligned}$$

We now want to solve these two equations simultaneously for values of  $A$  and  $B$ . From the first of these two equations, solving for  $A/10B$  leads to

$$\frac{A}{10B} = (0.38 \text{ nm})^{-9}$$

Furthermore, from the above equation the  $A$  is equal to

$$A = 10B(0.38 \text{ nm})^{-9}$$

When the above two expressions for  $A/10B$  and  $A$  are substituted into the above expression for  $E_0$  ( $-6.13 \text{ eV}$ ), the following results

$$\begin{aligned} -6.13 \text{ eV} &= -\frac{A}{10B} + \frac{B}{A} \\ &= -\frac{10B(0.38 \text{ nm})^{-9}}{10B} + \frac{B}{10B(0.38 \text{ nm})^{-9}} \\ &= -\frac{10B(0.38 \text{ nm})^{-9}}{10B} + \frac{B}{(0.38 \text{ nm})^{10}} \end{aligned}$$

or

$$-6.13 \text{ eV} = -\frac{10B}{(0.38 \text{ nm})^{10}} + \frac{B}{(0.38 \text{ nm})^{10}} = -\frac{9B}{(0.38 \text{ nm})^{10}}$$

Solving for  $B$  from this equation yields

$$B = 4.28 \times 10^{-5} \text{ eV}\cdot\text{nm}^{10}$$

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

$$\begin{aligned} A &= 10B(0.38 \text{ nm})^{-9} = (10)(4.28 \times 10^{-5} \text{ eV}\cdot\text{nm}^{10})(0.38 \text{ nm})^{-9} \\ &= 2.59 \text{ eV}\cdot\text{nm} \end{aligned}$$

Thus, Equations 2.9 and 2.11 become

$$\begin{aligned} E_A &= -\frac{2.59}{r} \\ E_R &= \frac{4.28 \times 10^{-5}}{r^{10}} \end{aligned}$$

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

- 2.18 (a) Briefly cite the main differences between ionic, covalent, and metallic bonding.  
(b) State the Pauli exclusion principle.

Solution

- (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.

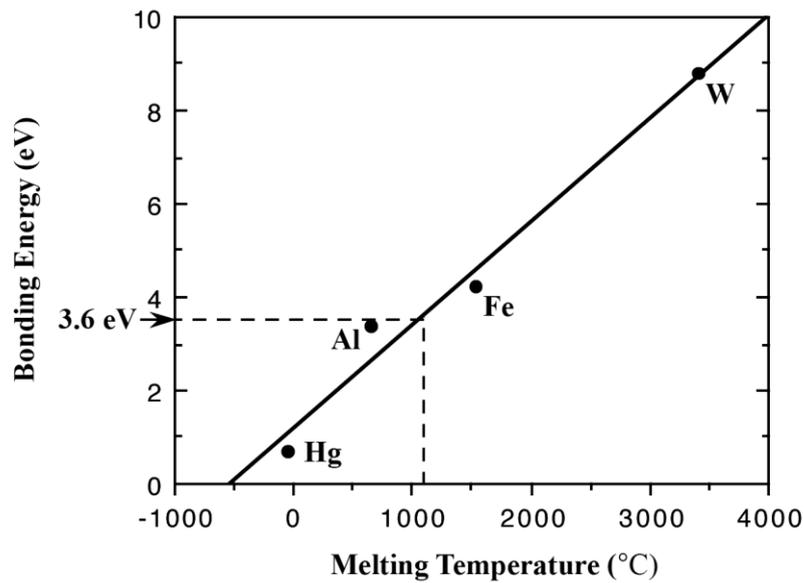
*Metallic*—the positively charged ion cores are shielded from one another, and also "glued" together by the sea of valence electrons.

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

- 2.19 Make a plot of bonding energy versus melting temperature for the metals listed in Table 2.3. Using this plot, approximate the bonding energy for copper, which has a melting temperature of 1084°C.

Solution

Below is plotted the bonding energy versus melting temperature for these four metals. From this plot, the bonding energy for copper (melting temperature of 1084°C) should be approximately 3.6 eV. The experimental value is 3.5 eV.



2.20 Using Table 2.2, determine the number of covalent bonds that are possible for atoms of the following elements: germanium, phosphorus, selenium, and chlorine.

Solution

For germanium, having the valence electron structure  $4s^24p^2$ ,  $N' = 4$ ; thus, there are  $8 - N' = 4$  covalent bonds per atom.

For phosphorus, having the valence electron structure  $3s^23p^3$ ,  $N' = 5$ ; thus, there is  $8 - N' = 3$  covalent bonds per atom.

For selenium, having the valence electron structure  $4s^24p^4$ ,  $N' = 6$ ; thus, there are  $8 - N' = 2$  covalent bonds per atom.

For chlorine, having the valence electron structure  $3s^23p^5$ ,  $N' = 7$ ; thus, there are  $8 - N' = 1$  covalent bond per atom.