CHAPTER 2

ATOMIC STRUCTURE AND INTERATOMIC BONDING

PROBLEM SOLUTIONS

Fundamental Concepts

Electrons in Atoms

2.1 *Cite the difference between* atomic mass *and* atomic weight.

Solution

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 *Zinc has five naturally occurring isotopes: 48.63% of* ^{64}*Zn with an atomic weight of 63.929 amu; 27.90% of* ^{66}*Zn with an atomic weight of 65.926 amu; 4.10% of* ^{67}*Zn with an atomic weight of 66.927 amu; 18.75% of* ^{68}*Zn with an atomic weight of 67.925 amu; and 0.62% of* ^{70}*Zn with an atomic weight of 69.925 amu. Calculate the average atomic weight of Zn.*

Solution

The average atomic weight of zinc $\bar{A}_{\mathrm{Zn}}$ is computed by adding fraction-of-occurrence—atomic weight products for the five isotopes—i.e., using Equation 2.2. (Remember: fraction of occurrence is equal to the percent of occurrence divided by 100.) Thus

$$\bar{A}_{\mathrm{Zn}} = f_{^{64}\mathrm{Zn}} A_{^{64}\mathrm{Zn}} + f_{^{66}\mathrm{Zn}} A_{^{66}\mathrm{Zn}} + f_{^{67}\mathrm{Zn}} A_{^{67}\mathrm{Zn}} + f_{^{68}\mathrm{Zn}} A_{^{68}\mathrm{Zn}} + f_{^{70}\mathrm{Zn}} A_{^{70}\mathrm{Zn}}$$

Including data provided in the problem statement we solve for $\bar{A}_{\mathrm{Zn}}$ as

$$\bar{A}_{\mathrm{Zn}} = (0.4863)(63.929\text{ amu}) + (0.2790)(65.926\text{ amu})$$

$$+ (0.0410)(66.927\text{ amu}) + (0.1875)(67.925\text{ amu}) + (0.0062)(69.925)$$

$$= 65.400\text{ amu}$$

2.3 *Indium has two naturally occurring isotopes: ^{113}In with an atomic weight of 112.904 amu, and ^{115}In with an atomic weight of 114.904 amu. If the average atomic weight for In is 114.818 amu, calculate the fraction-of-occurrences of these two isotopes.*

Solution

The average atomic weight of indium $(\bar{A}_{\text{In}})$ is computed by adding fraction-of-occurrence—atomic weight products for the two isotopes—i.e., using Equation 2.2, or

$$\bar{A}_{\text{In}} = f_{^{113}\text{In}} A_{^{113}\text{In}} + f_{^{115}\text{In}} A_{^{115}\text{In}}$$

Because there are just two isotopes, the sum of the fracture-of-occurrences will be 1.000; or

$$f_{^{113}\text{In}} + f_{^{115}\text{In}} = 1.000$$

which means that

$$f_{^{113}\text{In}} = 1.000 - f_{^{115}\text{In}}$$

Substituting into this expression the one noted above for $f_{^{113}\text{In}}$, and incorporating the atomic weight values provided in the problem statement yields the following expressions:

$$114.818 \text{ amu} = f_{^{113}\text{In}} A_{^{113}\text{In}} + f_{^{115}\text{In}} A_{^{115}\text{In}}$$

$$114.818 \text{ amu} = (1.000 - f_{^{113}\text{In}}) A_{^{113}\text{In}} + f_{^{115}\text{In}} A_{^{115}\text{In}}$$

$$114.818 \text{ amu} = (1.000 - f_{^{115}\text{In}})(112.904 \text{ amu}) + f_{^{115}\text{In}}(114.904 \text{ amu})$$

$$114.818 \text{ amu} = 112.904 \text{ amu} - f_{^{115}\text{In}}(112.904 \text{ amu}) + f_{^{115}\text{In}}(114.904 \text{ amu})$$

Solving this expression for $f_{^{115}\text{In}}$ yields $f_{^{115}\text{In}} = 0.957$. Furthermore, because

$$f_{^{113}\text{In}} = 1.000 - f_{^{115}\text{In}}$$

then

$$f_{^{113}\mathrm{In}} = 1.000 - 0.957 = 0.043$$

2.4 *(a) Cite two important quantum-mechanical concepts associated with the Bohr model of the atom.*

(b) Cite two important additional refinements that resulted from the wave-mechanical atomic model.

Solution

(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 *Give the electron configurations for the following ions:* P^{5+}, P^{3-}, Sn^{4+}, Se^{2-}, I^{-}, *and* Ni^{2+}.

Solution

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

P^{5+}: From Table 2.2, the electron configuration for an atom of phosphorus is $1s^22s^22p^63s^23p^3$. In order to become an ion with a plus five charge, it must lose five electrons—in this case the three $3p$ and the two $3s$. Thus, the electron configuration for a P^{5+} ion is $1s^22s^22p^6$.

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

Sn^{4+}: From the periodic table, Figure 2.8, the atomic number for tin is 50, which means that it has fifty electrons and an electron configuration of $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^2$. In order to become an ion with a plus four charge, it must lose four electrons—in this case the two $4s$ and two $5p$. Thus, the electron configuration for an Sn^{4+} ion is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}$.

Se^{2-}: From Table 2.2, the electron configuration for an atom of selenium is $1s^22s^22p^63s^23p^63d^{10}4s^24p^4$. In order to become an ion with a minus two charge, it must acquire two electrons—in this case another two $4p$. Thus, the electron configuration for an Se^{2-} ion is $1s^22s^22p^63s^23p^63d^{10}4s^24p^6$.

I^{-}: From the periodic table, Figure 2.8, the atomic number for iodine is 53, which means that it has fifty three electrons and an electron configuration of $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^5$. In order to become an ion with a minus one charge, it must acquire one electron—in this case another $5p$. Thus, the electron configuration for an I^{-} ion is $1s^22s^22p^63s^23p^63d^{10}4s^24p^64d^{10}5s^25p^6$.

Ni^{2+}: From Table 2.2, the electron configuration for an atom of nickel is $1s^22s^22p^63s^23p^63d^84s^2$. 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 a Ni^{2+} ion is $1s^22s^22p^63s^23p^63d^8$.

Electrons in Atoms

2.6 *To what group in the periodic table would an element with atomic number 112 belong?*

Solution

From the periodic table (Figure 2.8) the element having atomic number 112 would belong to group IIB. According to Figure 2.8, 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.

This element has been artificially created and given the name Copernicium with the symbol Cn. It was named after Nicolaus Copernicus, the Polish scientist who proposed that the earth moves around the sun (and not vice versa).

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

(a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^7 4s^2$

(b) $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

(c) $1s^2 2s^2 2p^6 3s^2$

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

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

Bonding Forces and Energies

2.8 *The atomic radii of* Mg^{2+} *and* F^- *ions are 0.072 and 0.133 nm, respectively.*

(a) Calculate the force of attraction between these two ions at their equilibrium interionic separation (i.e., when the ions just touch one another).

(b) What is the force of repulsion at this same separation distance.

Solution

This problem is solved in the same manner as Example Problem 2.2.

(a) The force of attraction F_A is calculated using Equation 2.14 taking the interionic separation r to be r_0 the equilibrium separation distance. This value of r_0 is the sum of the atomic radii of the Mg^{2+} and F^- ions (per Equation 2.15)—that is

$$r_0 = r_{\mathrm{Mg}^{2+}} + r_{\mathrm{F}^-}$$

$$= 0.072 \text{ nm} + 0.133 \text{ nm} = 0.205 \text{ nm} = 0.205 \times 10^{-9} \text{ m}$$

We may now compute F_A using Equation 2.14. If was assume that ion 1 is Mg^{2+} and ion 2 is F^- then the respective charges on these ions are $Z_1 = Z_{\mathrm{Mg}^{2+}} = +2$, whereas $Z_2 = Z_{\mathrm{F}^-} = -1$. Therefore, we determine F_A as follows:

$$F_A = \frac{(2.31 \times 10^{-28} \text{ N-m}^2)\left(|Z_1|\right)\left(|Z_2|\right)}{r_0^2}$$

$$= \frac{(2.31 \times 10^{-28} \text{ N-m}^2)\left(|+2|\right)\left(|-1|\right)}{(0.205 \times 10^{-9} \text{ m})^2}$$

$$= 1.10 \times 10^{-8} \text{ N}$$

(b) At the equilibrium separation distance the sum of attractive and repulsive forces is zero according to Equation 2.4. Therefore

$$F_R = -F_A$$

$$= -(1.10 \times 10^{-8} \text{ N}) = -1.10 \times 10^{-8} \text{ N}$$

2.9 *The force of attraction between a divalent cation and a divalent anion is 1.67 × 10^{-8} N. If the ionic radius of the cation is 0.080 nm, what is the anion radius?*

Solution

To begin, let us rewrite Equation 2.15 to read as follows:

$$r_0 = r_\mathrm{C} + r_\mathrm{A}$$

in which r_C and r_A represent, respectively, the radii of the cation and anion. Thus, this problem calls for us to determine the value of r_A. However, before this is possible, it is necessary to compute the value of r_0 using Equation 2.14, and replacing the parameter *r* with r_0. Solving this expression for r_0 leads to the following:

$$r_0 = \sqrt{\frac{(2.31 \times 10^{-28}\ \text{N-m}^2)\left(|Z_\mathrm{C}|\right)\left(|Z_\mathrm{A}|\right)}{F_A}}$$

Here Z_C and Z_A represent charges on the cation and anion, respectively. Furthermore, inasmuch as both ions are divalent means that $Z_\mathrm{C} = +2$ and $Z_\mathrm{A} = -2$. The value of r_0 is determined as follows:

$$r_0 = \sqrt{\frac{(2.31 \times 10^{-28}\ \text{N-m}^2)\left(|+2|\right)\left(|-2|\right)}{1.67 \times 10^{-8}\ \text{N}}}$$

$$= 0.235 \times 10^{-9}\ \text{m} = 0.235\ \text{nm}$$

Using the version of Equation 2.15 given above, and incorporating this value of r_0 and also the value of r_C given in the problem statement (0.080 nm) it is possible to solve for r_A:

$$r_\mathrm{A} = r_0 - r_\mathrm{C}$$

$$= 0.235\ \text{nm} - 0.080\ \text{nm} = 0.155\ \text{nm}$$

2.10 *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,*

$$E_N = -\frac{A}{r} + \frac{B}{r^n} \tag{2.17}$$

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, because 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

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

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

(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 2.17 and solving for E (= E_0) yields

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

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

2.11 *For a* Na^+*–*Cl^- *ion pair, attractive and repulsive energies* E_A *and* E_R*, respectively, depend on the distance between the ions r, according to*

$$E_A = -\frac{1.436}{r}$$

$$E_R = \frac{7.32 \times 10^{-6}}{r^8}$$

For these expressions, energies are expressed in electron volts per Na^+*–*Cl^- *pair, and r is the distance in nanometers. The net energy* E_N *is just the sum of the preceding two expressions.*

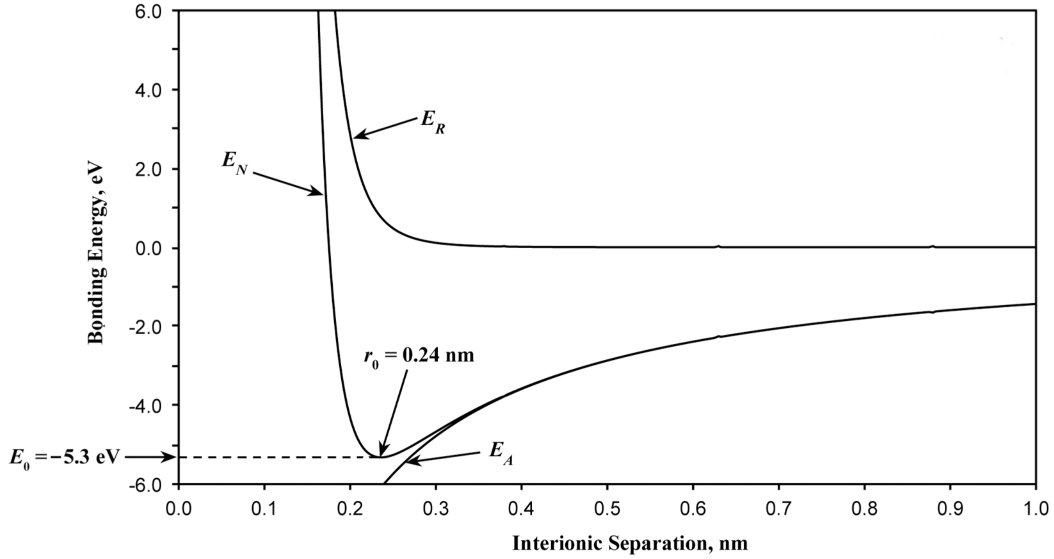
(a) Superimpose on a single plot E_N*,* E_R*, and* E_A *versus r up to 1.0 nm.*

(b) On the basis of this plot, determine (i) the equilibrium spacing r_0 *between the* Na^+ *and* Cl^- *ions, and (ii) the magnitude of the bonding energy* E_0 *between the two ions.*

(c) Mathematically determine the r_0 *and* E_0 *values using the solutions to Problem 2.10, and compare these with the graphical results from part (b).*

Solution

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



(b) From this plot:

r_0 = 0.24 nm

E_0 = –5.3 eV

(c) From Equation 2.17 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

$$E_0 = -\frac{1.436}{\left[\dfrac{1.436}{(8)(7.32\times10^{-6})}\right]^{1/(1-8)}} + \frac{7.32\times10^{-6}}{\left[\dfrac{1.436}{(8)(7.32\times10^{-6})}\right]^{8/(1-8)}}$$

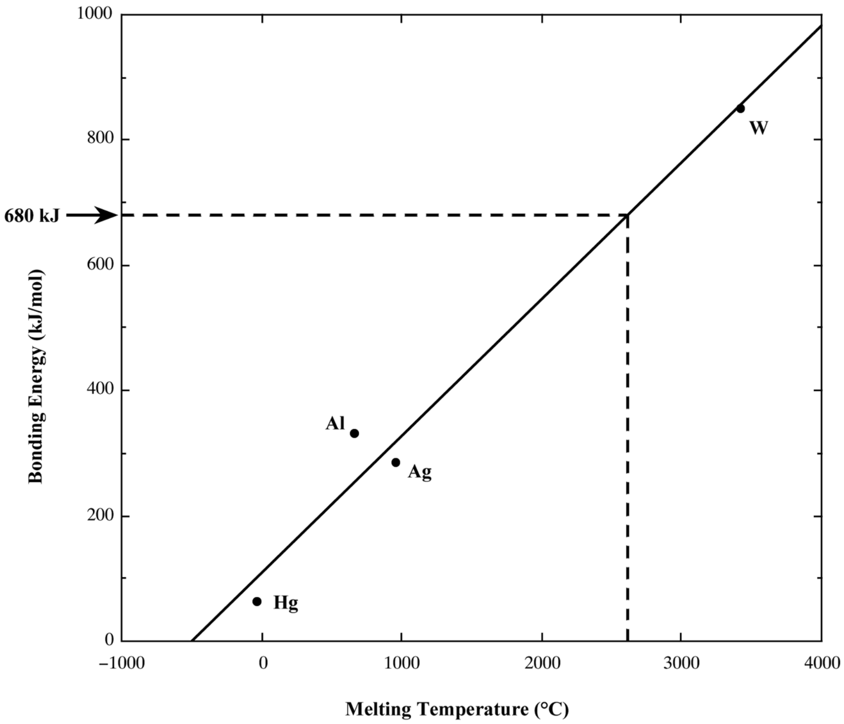
$$= -5.32 \text{ eV}$$

Primary Interatomic Bonds

2.12 *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 molybdenum, which has a melting temperature of 2617°C.*

Solution

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 680 kJ/mol. The experimental value is 660 kJ/mol.



Secondary Bonding or van der Waals Bonding

2.13 *Explain why hydrogen fluoride (HF) has a higher boiling temperature than hydrogen chloride (HCl) (19.4 vs. –85°C), even though HF has a lower molecular weight.*

Solution

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.

Mixed Bonding

2.14 *(a) Calculate %IC of the interatomic bonds for the intermetallic compound* Al_6Mn. *(b) On the basis of this result what type of interatomic bonding would you expect to be found in* Al_6Mn*?*

Solution

(a) The percent ionic character is a function of the electron negativities of the ions X_A and X_B according to Equation 2.16. The electronegativities for Al and Mn (Figure 2.9) are 1.5 and 1.6, respectively. Therefore, the percent ionic character is determined using Equation 2.16 as follows:

$$\%\text{IC} = \left[1 - \exp(-0.25)(1.6-1.5)^2\right] \times 100 = 0.25\%$$

(b) Because the percent ionic character is exceedingly small (0.25%) and this intermetallic compound is composed of two metals, the bonding is completely metallic.

Bonding Type-Material Classification Correlations

2.15 *What type(s) of bonding would be expected for each of the following materials: solid xenon, calcium fluoride* (CaF_2)*, bronze, cadmium telluride (CdTe), rubber, and tungsten?*

Solution

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.