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Chapter 2

Atomic Structure

2-6

- (a) Aluminum foil used for storing food weighs about 0.3 g per square inch. How many atoms of aluminum are contained in one square inch of foil?
- (b) Using the densities and atomic weights given in Appendix A, calculate and compare the number of atoms per cubic centimeter in (i) lead and (ii) lithium.

Solution: (a) In a one square inch sample:

$$\frac{(0.3 \text{ g}) \left(6.022 \times 10^{23} \text{ atoms/mol} \right)}{(26.981 \text{ g/mol})} = 6.7 \times 10^{21} \text{ atoms}$$

(b) (i) In lead:

$$\frac{(11.36 \text{ g/cm}^3) \left(6.022 \times 10^{23} \text{ atoms/mol} \right)}{(207.19 \text{ g/mol})} = 3.30 \times 10^{22} \text{ atoms/cm}^3$$

(ii) In lithium:

$$\frac{(0.534 \text{ g/cm}^3) \left(6.022 \times 10^{23} \text{ atoms/mol} \right)}{(6.94 \text{ g/mol})} = 4.63 \times 10^{22} \text{ atoms/cm}^3$$

Despite the different mass densities of Pb and Li, their atomic densities are approximately the same.

2-7

- (a) Using data in Appendix A, calculate the number of iron atoms in one ton (2000 pounds) of iron.
- (b) Using data in Appendix A, calculate the volume in cubic centimeters occupied by one mole of boron.

Solution: (a)

$$\frac{(2000 \text{ lb}) \left(453.59 \text{ g/lb} \right) \left(6.022 \times 10^{23} \text{ atoms/mol} \right)}{(55.847 \text{ g/mol})} = 9.8 \times 10^{27} \text{ atoms}$$

$$(b) \frac{(1 \text{ mol})(10.8 \text{ g/mol})}{2.36 \text{ g/cm}^3} = 4.6 \text{ cm}^3$$

2-8 In order to plate a steel part having a surface area of 2.00 in.^2 with a 0.002-in. -thick layer of nickel:

(a) How many atoms of nickel are required?

(b) How many moles of nickel are required?

Solution: Volume = $(2.00 \text{ in.}^2)(0.002 \text{ in.})(2.54 \text{ cm/in.})^3 = 6.555 \text{ cm}^3$

$$(a) \frac{(6.555 \text{ cm}^3)(8.902 \text{ g/cm}^3)(6.022 \times 10^{23} \text{ atoms/mol})}{(58.71 \text{ g/mol})} = 5.99 \times 10^{23} \text{ atoms}$$

$$(b) \frac{(6.555 \text{ cm}^3)(8.902 \text{ g/cm}^3)}{(58.71 \text{ g/mol})} = 0.994 \text{ mol}$$

2-9 Write the electron configuration for the element Tc.

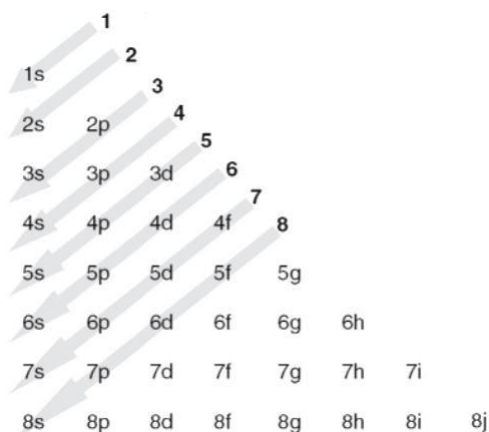
Solution: The atomic number of Tc is 43.

$[\text{Tc}] = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^5$
or rearranging from lowest to highest principal quantum number

$[\text{Tc}] = 1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^5 5s^2$

2-10 Assuming that the Aufbau Principle is followed, what is the expected electronic configuration of the element with atomic number $Z = 116$?

Solution: Use the Aufbau diagram to find the electronic configuration of the element:



$$[116] = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^2 4d^{10} 5p^6 6s^2 4f^{14} 5d^{10} 6p^6 7s^2 5f^{14} 6d^{10} 7p^4$$

$$[116] = [\text{Rn}]5f^{14} 6d^{10} 7s^2 7p^4$$

2–11 Suppose an element has a valence of 2 and an atomic number of 27. Based only on the quantum numbers, how many electrons must be present in the $3d$ energy level?

Solution: We can let x be the number of electrons in the $3d$ energy level. Then:
 $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^x$ (must be 2 electrons in $4s$ for valence = 2)
Since $27 - (2+2+6+2+6+2) = 7 = x$ there must be 7 electrons in the $3d$ level.

2–12 Indium, which has an atomic number of 49, contains no electrons in its $4f$ energy levels. Based only on this information, what must be the valence of indium?

Solution: We can let x be the number of electrons in the outer sp energy level.

Then:

$$[49] = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^6 5s^x 4d^{10} 5p^y$$

$$49 - (2+2+6+2+6+2+10+6+10) = 3$$

Therefore the outer $5sp$ level must be

$$5s^2 5p^1 \text{ or valence} = 3.$$

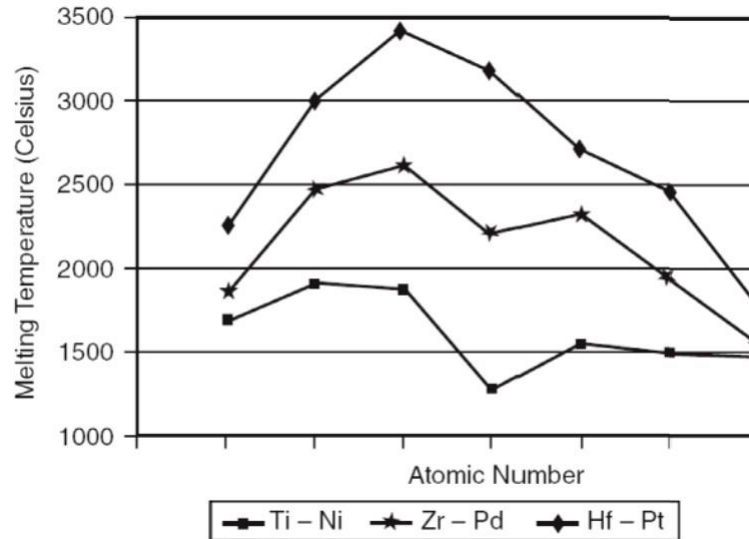
2–14 Bonding in the intermetallic compound Ni_3Al is predominantly metallic. Explain why there will be little, if any, ionic bonding component. The electronegativity of nickel is about 1.8.

Solution: The electronegativity of Al is 1.5, while that of Ni is 1.8 – 1.9. These values are relatively close, so we wouldn't expect much ionic bonding. Also, both are metals and prefer to give up their electrons rather than share or donate them.

2–15 Plot the melting temperatures of elements in the 4A to 8–10 columns of the periodic table versus atomic number (i.e., plot melting temperatures of Ti through Ni, Zr through Pd, and Hf through Pt). Discuss these relationships, based on atomic bonding and binding energies: (a) as the atomic number increases in each row of the periodic table and (b) as the atomic number increases in each column of the periodic table.

Solution:

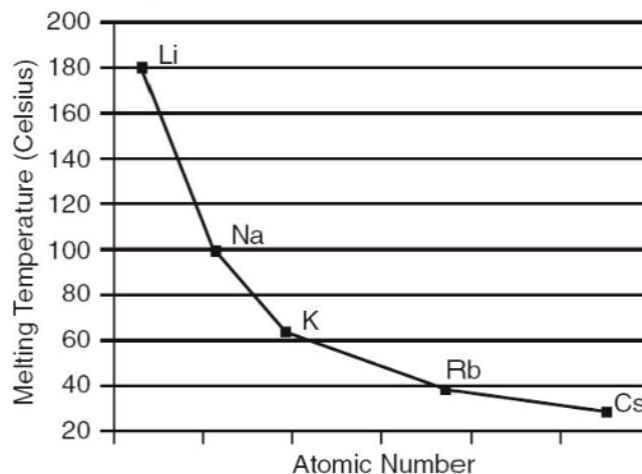
Ti – 1668	Zr – 1852	Hf – 2227
V – 1910	Nb – 2468	Ta – 2996
Cr – 1907	Mo – 2623	W – 3422
Mn – 1244	Tc – 2157	Re – 3186
Fe – 1538	Ru – 2334	Os – 3033
Co – 1495	Rh – 1963	Ir – 2447
Ni – 1453	Pd – 1552	Pt – 1769



For each row, the melting temperature is highest when the outer “*d*” energy level is partly full. In Cr, there are 5 electrons in the 3*d* shell; in Mo, there are 5 electrons in the 4*d* shell; in W there are 4 electrons in the 5*d* shell. In each column, the melting temperature increases as the atomic number increases—the atom cores contain a larger number of tightly held electrons, making the metals more stable.

- 2–16** Plot the melting temperature of the elements in the 1A column of the periodic table versus atomic number (i.e., plot melting temperatures of Li through Cs). Discuss this relationship, based on atomic bonding and binding energy.

Solution: $T(^{\circ}\text{C})$
 Li – 180.7
 Na – 97.8
 K – 63.2
 Rb – 38.9



As the atomic number increases, the melting temperature decreases, in contrast to the trend found in Problem 2–15.

2–17 Compare and contrast metallic and covalent primary bonds in terms of

- (a) the nature of the bond;
- (b) the valence of the atoms involved; and
- (c) the ductility of the materials bonded in these ways.

Solution:

- (a) Metallic bonds are formed between the one or two free electrons of each atom. The free electrons form a gaseous cloud of electrons that move between atoms. Covalent bonds involve the sharing of electrons between atoms.
- (b) In metallic bonding, the metal atoms typically have one or two valence electrons that are given up to the electron “sea.” Covalent bonds form between atoms of the same element or atoms with similar electronegativities.
- (c) Metallic bonds are non-directional. The non-directionality of the bonds and the shielding of the ions by the electron cloud lead to high ductilities. Covalent bonds are highly directional – this limits the ductility of covalently bonded materials by making it more difficult for the atoms to slip past one another.

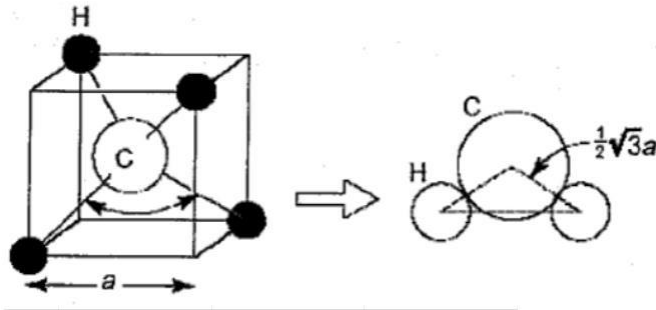
2–18 What type of bonding does KCl have? Fully explain your reasoning by referring to the electronic structure and electronic properties of each element.

Solution: KCl has ionic bonding. The electronic structure of [K] = $1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 = [\text{Ar}] 4s^1$. The electronic structure of [Cl] = $1s^2 2s^2 2p^6 3s^2 3p^5 = [\text{Ne}] 3s^2 3p^5$. Therefore, K wants to give up its $4s^1$ electron in order to achieve a stable $s^2 p^6$ configuration, and Cl wants to gain an electron in order to gain the stable $s^2 p^6$ configuration. Thus an electron is transferred from K to Cl, and the bonding is ionic.

2–19 Methane (CH_4) has a tetrahedral structure similar to that of SiO_2 , with a carbon atom of radius 0.77×10^{-8} cm at the center and hydrogen atoms of radius 0.46×10^{-8} cm at four of the eight corners. Calculate the size of the tetrahedral cube for methane.

Solution: Let a be the length of the sides of the tetrahedral cube and r be the radius of the two types of atoms.

$$\frac{1}{2} a\sqrt{3} = r_{\text{C}} + r_{\text{H}}$$
$$a = \frac{2r_{\text{C}} + 2r_{\text{H}}}{\sqrt{3}} = \frac{2(0.77 \times 10^{-8} \text{ cm} + 0.46 \times 10^{-8} \text{ cm})}{\sqrt{3}} = 1.42 \times 10^{-8} \text{ cm}$$



2-20 The compound aluminum phosphide (AlP) is a compound semiconductor having mixed ionic and covalent bonding. Calculate the fraction of the bonding that is ionic.

Solution: $E_{Al} = 1.5$ $E_P = 2.1$

$$f_{\text{covalent}} = \exp[(-0.25)(1.5 - 2.1)^2] = \exp(-0.09) = 0.914$$

$$f_{\text{ionic}} = 1 - 0.914 = 0.086 \therefore \text{bonding is mostly covalent}$$

2-21 Calculate the fraction of bonding in MgO that is ionic.

Solution: $E_{Mg} = 1.2$ $E_O = 3.5$

$$f_{\text{covalent}} = \exp[(-0.25)(3.5 - 1.2)^2] = \exp(-1.3225) =$$

$$0.27 \quad f_{\text{ionic}} = 1 - 0.27 = 0.73 \therefore \text{bonding is mostly ionic}$$

2-25 Calculate the fractions of ionic bonds in silicon carbide (SiC) and in silicon nitride (Si₃N₄).

Solution: Fraction covalent = $\exp[-0.25(E)^2]$

For silicon carbide: Fraction covalent = $\exp[-0.25(1.8 - 2.5)^2] = 0.88$; Fraction ionic = $1 - 0.88 = 0.12$ or 12%.

For silicon nitride: Fraction covalent = $\exp[-0.25(1.8 - 3.0)^2] = 0.70$; Fraction ionic = $1 - 0.70 = 0.30$ or 30%.

2-26 One particular form of boron nitride (BN) known as cubic boron nitride is a very hard material and is used in grinding applications. Calculate the fraction of the bonding that is covalent in this material.

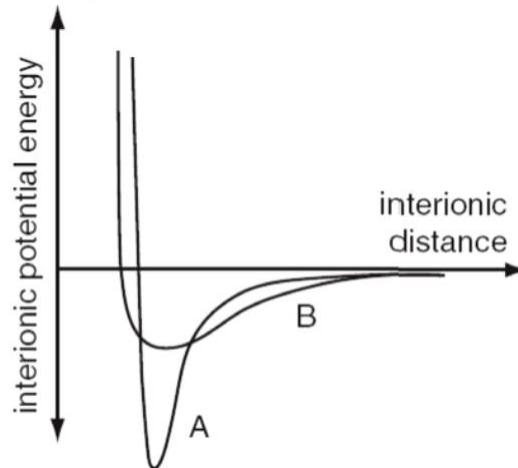
Solution: For boron nitride fraction covalent = $\exp[-0.25(2.0 - 3.0)^2] = 0.78$ or 78%.

2–27 Another form of boron nitride (BN) known as hexagonal boron nitride is used as a solid lubricant. Explain how this may be possible by comparing this situation with that encountered in two forms of carbon, namely diamond and graphite.

Solution: Hexagonal boron nitride has a graphite-like structure in which layers of atoms are bonded by van der Waals bonds. The bonds between layers are weak allowing the layers to be sheared relative to one another relatively easily. Cubic boron nitride, on the other hand, has the covalently-bonded diamond cubic structure. It is hard similar to diamond and is used in cutting tools.

2–28 Titanium is stiffer than aluminum, has a lower thermal expansion coefficient than aluminum, and has a higher melting temperature than aluminum. On the same graph, carefully and schematically draw the potential well curves for both metals. Be explicit in showing how the physical properties are manifest in these curves.

Solution:

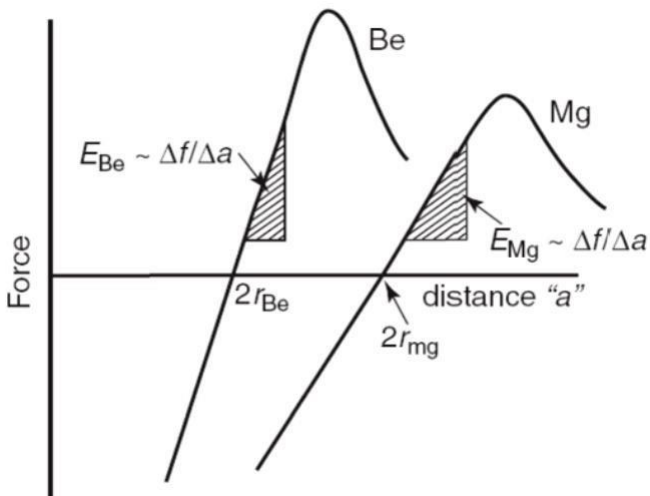


The well of titanium, represented by A, is deeper (higher melting point), has a larger radius of curvature (stiffer), and is more symmetric (smaller thermal expansion coefficient) than the well of aluminum, represented by B.

2–29 Beryllium and magnesium, both in the 2A column of the periodic table, are lightweight metals. Which would you expect to have the higher modulus of elasticity? Explain, considering binding energy and atomic radii and using appropriate sketches of force versus interatomic spacing.

Solution:

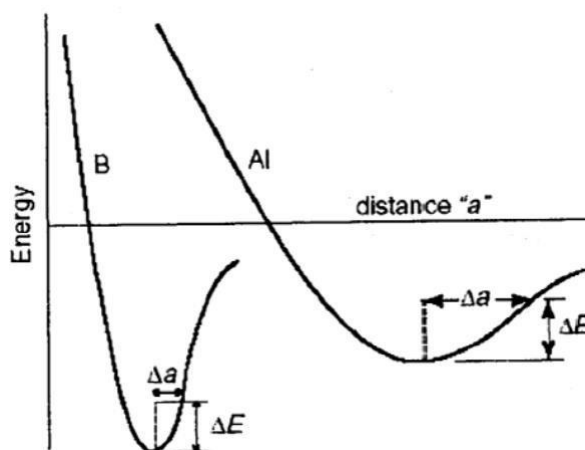
4 Be	$1s^2 2s^2$	$E = 42 \times 10^3$ kJ	$r_{\text{Be}} = 1.143$ Å
12 Mg	$1s^2 2s^2 2p^6 3s^2$	$E = 6.5 \times 10^3$ kJ	$r_{\text{Mg}} = 1.604$ Å



The smaller Be electrons are held closer to the core, held more tightly, giving a higher binding energy.

- 2-30 Boron has a much lower coefficient of thermal expansion than aluminum, even though both are in the 3B column of the periodic table. Explain, based on binding energy, atomic size, and the energy well, why this difference is expected.

Solution:



Electrons in Al are not as tightly bonded as those in B due to the smaller size of the boron atom and the lower binding energy associated with its size.

- 2-31 Would you expect MgO or magnesium to have the higher modulus of elasticity? Explain.

Solution: MgO has ionic bonds. A higher force will be required to cause the same separation between the ions in MgO compared to the atoms in Mg. Therefore, MgO should have the higher modulus of elasticity. In Mg, $E \approx 6.5 \times 10^6$ psi; in MgO, $E = 30 \times 10^6$ psi.

2–32 Would you expect Al₂O₃ or aluminum to have the higher coefficient of thermal expansion? Explain.

Solution: Al₂O₃ with ionic bonds has stronger bonds than the metallic bonds of Al; therefore, Al₂O₃ should have a lower thermal expansion coefficient than Al. In Al, $\alpha = 25 \times 10^{-6} \text{ C}^{-1}$; in Al₂O₃, $\alpha = 6.7 \times 10^{-6} \text{ C}^{-1}$.

2–33 Aluminum and silicon are side-by-side in the periodic table. Which would you expect to have the higher modulus of elasticity (E)? Explain.

Solution: Silicon has covalent bonds; aluminum has metallic bonds. Therefore, Si should have a higher modulus of elasticity.

2–34 Explain why the modulus of elasticity of simple thermoplastic polymers, such as polyethylene and polystyrene, is expected to be very low compared to that of metals and ceramics.

Solution: The chains in polymers are held to other chains by van der Waals bonds, which are much less stiff and weaker than metallic, ionic, and covalent bonds. For this reason, much less force is required to shear these weak bonds and to unkink and straighten the chains.

2–35 Steel is coated with a thin layer of ceramic to help protect against corrosion. What do you expect to happen to the coating when the temperature of the steel is increased significantly? Explain.

Solution: Ceramics are expected to have a low coefficient of thermal expansion due to strong ionic/covalent bonds; steel has a high thermal expansion coefficient. When the structure heats, steel expands more than the coating. Thus the coating may crack and expose the underlying steel to corrosion.

2–37 An aluminum-alloy bar of length 2 meters at room temperature (300 K) is exposed to a temperature of 100 °C ($\alpha = 23 \times 10^{-6} \text{ K}^{-1}$). What will be the length of this bar at 100°C?

Solution: 100 °C is 373 K.

$$\alpha = \frac{1}{L} \frac{dL}{dT}$$
$$\left(23 \times 10^{-6} \text{ K}^{-1} \right) = \frac{1}{(2 \text{ m})} \frac{dL}{(73 \text{ K})}$$

$$dL = \left(23 \times 10^{-6} \text{ K}^{-1} \right) (2 \text{ m}) (73 \text{ K}) = 0.0034 \text{ cm}$$

2–40 You want to design a material for making a mirror for a telescope that will be launched in space. Given that the temperatures in space can change considerably, what material will you consider using? Remember that this material should not expand or contract at all, if possible. It also should be as strong and have as low a density as possible, and one should be able to coat it so that it can serve as a mirror.

Solution: The temperatures encountered in space vary considerably; thus, a major consideration for selecting materials for telescope mirrors is a low coefficient of thermal expansion. Schott Glass Corporation has developed a material called Zerodur (see Chapter 15) that has essentially a zero thermal expansion coefficient. The material can be coated on one side to provide a mirror surface. It also has a low density ($\sim 2.5 \text{ g/cm}^3$).

2–41 You want to use a material that can be used for making a catalytic converter substrate. The job of this material is to be a carrier for the nanoparticles of metals (such as platinum and palladium), which are the actual catalysts. The main considerations are that this catalyst-support material must be able to withstand the constant, cyclic heating and cooling to which it will be exposed. (*Note:* The gases from automobile exhaust reach temperatures up to $500 \text{ }^\circ\text{C}$, and the material will get heated up to high temperatures and then cool down when the car is not being used.) What kinds of materials can be used for this application?

Solution: A major consideration in selecting a material for this application would be whether there is sufficient thermal shock resistance. Thermal shock resistance is the ability of a material to withstand the thermal stresses induced by thermal expansion and contraction. Secondly, the material should be inert in that it should not react with the nanoparticles of Pt/Pd/Rh that function as catalysts. Inertness also means that the catalytic substrate itself should be able to withstand the reducing and oxidizing chemical environments to which it will be exposed. Thus, most metallic materials can be ruled out on the basis of chemical inertness. Most polymers will not be able to withstand the high temperatures. Also the thermal coefficient of most polymers is relatively large. Thus, the choice is between ceramic materials. Regular inorganic glasses will not work because the thermal expansion coefficient is too high and repeated heating and cooling will cause them to fracture. Thus, ceramics such as alumina, zirconia etc. may work. A key would also be that there should be no phase transformation or change in crystal structure that causes an abrupt volume change over the temperature range of interest. A candidate is a ceramic material known as cordierite ($\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$). This is a magnesium aluminosilicate. It has a small thermal expansion coefficient ($\sim 4 \times 10^{-7}/^\circ\text{C}$), it is relatively stable, and it is not too expensive.