

Chapter 2: Atomic Structure

2-1 What is meant by the term *composition* of a material?

Solution:

The chemical make-up of the material.

2-2 What is meant by the term *structure* of a material?

Solution:

The spatial arrangement of atoms or ions in the material.

2-3 What are the different levels of structure of a material?

Solution:

Atomic structure, short- and long-range atomic arrangements, nanostructure, microstructure, and macrostructure.

2-4 Why is it important to consider the structure of a material when designing and fabricating engineering components?

Solution:

The structure of the material at all levels will affect the physical and mechanical properties of the final product.

2-5 What is the difference between the microstructure and macrostructure of a material?

Solution:

A length scale of about 100,000 nm (100 μm) separates microstructure (less than 100,000 nm) from macrostructure (greater than 100,000 nm).

2-6 (a) Aluminum foil used for storing food weighs about 0.3 grams per square inch. How many atoms of aluminum contained in one square inch of the 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)

$$N_{atoms} = (1 \text{ in.}^2) \left(\frac{0.3 \text{ g Al}}{1 \text{ in.}^2} \right) \left(\frac{1 \text{ mol Al}}{26.982 \text{ g Al}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \right)$$

$$N_{atoms} = 6.7 \times 10^{21} \text{ Al atoms}$$

(b)

$$N_{atoms} = \left(\frac{11.36 \text{ g Pb}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ mol Pb}}{207.19 \text{ g Pb}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \right)$$

$$N_{atoms} = 33.0 \times 10^{21} \frac{\text{Pb atoms}}{\text{cm}^3}$$

$$N_{atoms} = \left(\frac{0.534 \text{ g Li}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ mol Li}}{6.94 \text{ g Li}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \right)$$

$$N_{atoms} = 46.3 \times 10^{21} \frac{\text{Li atoms}}{\text{cm}^3}$$

2-7 (a) Using data in Appendix A, calculate the number of iron atoms in one ton (2000 pounds). (b) Using data in Appendix A, calculate the volume in cubic centimeters occupied by one mole of boron.

Solution:

$$N_{atoms} = \left(\frac{2000 \text{ lb}}{1 \text{ ton}} \right) \left(\frac{454 \text{ g}}{1 \text{ lb}} \right) \left(\frac{1 \text{ mol Fe}}{55.847 \text{ g Fe}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \right)$$

$$N_{atoms} = 9.8 \times 10^{27} \frac{\text{Fe atoms}}{\text{ton}}$$

$$V = (1 \text{ mol B}) \left(\frac{10.81 \text{ g B}}{1 \text{ mol B}} \right) \left(\frac{1 \text{ cm}^3 \text{ B}}{2.36 \text{ g B}} \right)$$

$$V = 4.58 \text{ cm}^3 \text{ B}$$

2-8 In order to plate a steel part having a surface area of 200 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:

(a)

We start with the volume required:

$$V = (200 \text{ in.}^2)(0.002 \text{ in.}) \left(\frac{2.54 \text{ cm}}{1 \text{ in.}} \right)^3 = 6.55 \text{ cm}^3$$

$$N_{atoms} = (6.55 \text{ cm}^3) \left(\frac{8.902 \text{ g Ni}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ mol Ni}}{58.71 \text{ g Ni}} \right) \left(\frac{6.022 \times 10^{23} \text{ atoms}}{1 \text{ mol}} \right)$$

$$N_{atoms} = 598 \times 10^{21} \text{ atoms Ni}$$

(b)

$$N_{moles} = (6.55 \text{ cm}^3) \left(\frac{8.902 \text{ g Ni}}{1 \text{ cm}^3} \right) \left(\frac{1 \text{ mol Ni}}{58.71 \text{ g Ni}} \right)$$

$$N_{moles} = 0.99 \text{ mol Ni}$$

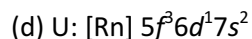
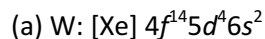
2-9 Define *electronegativity*.

Solution:

Electronegativity is the tendency of an atom to accept an electron (which has a negative charge) and become an anion.

2-10 Write the electronic configuration of the following elements (a) tungsten, (b) cobalt, (c) zirconium, (d) uranium, and (e) aluminum.

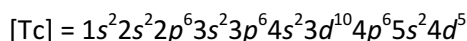
Solution:



2-11 Write the electron configuration for the element Tc.

Solution:

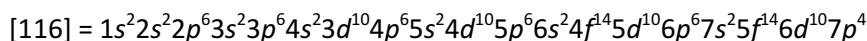
Since Technetium is element 43:



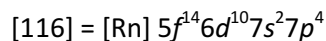
2-12 Assuming that the Aufbau Principle is followed, what is the expected electronic configuration of the element with atomic number $Z = 116$?

Solution:

Using the Aufbau diagram produces:



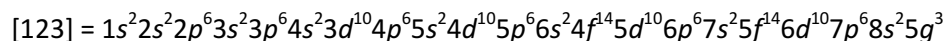
Or in shorthand:



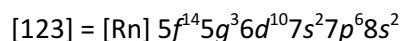
- 2-13** Using the Aufbau Principle, what is the expected electronic configuration of the hypothetical element with atomic number $Z = 123$?

Solution:

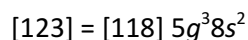
Using the Aufbau diagram produces:



Or in shorthand:



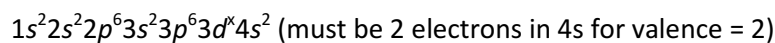
Or assuming that [118] is another inert gas:



- 2-14** 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 3*d* energy level?

Solution:

We can let x be the number of electrons in the 3*d* energy level. Then:



Since $27 - (2 + 2 + 6 + 2 + 6 + 2) = 7 = x$ there must be 7 electrons in the 3*d* level.

- 2-16** 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.

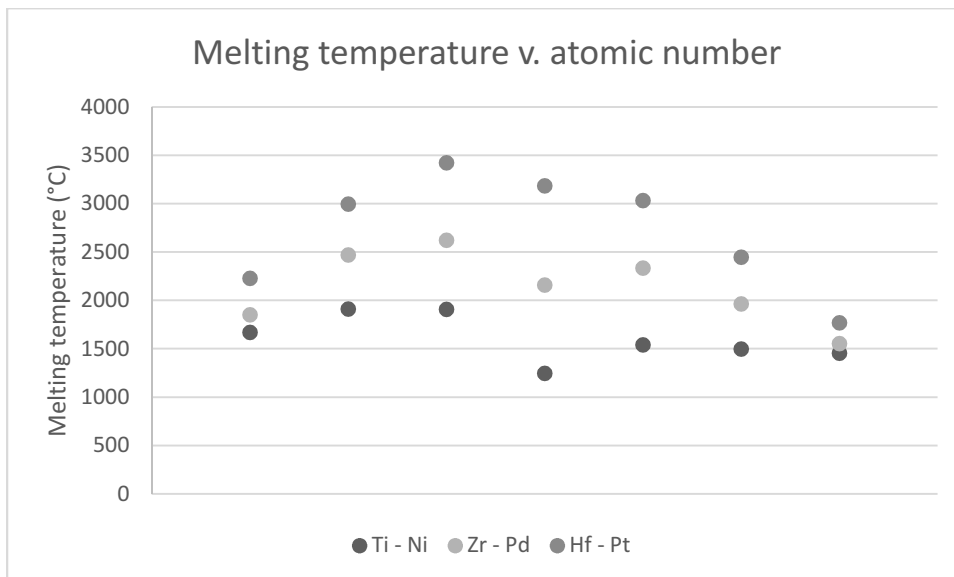
Solution:

The electronegativity of Al is 1.5, while that of Ni is 1.9. 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.

- 2-17** 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:

The melting temperatures are taken from Figure 2-9 and are plotted below:

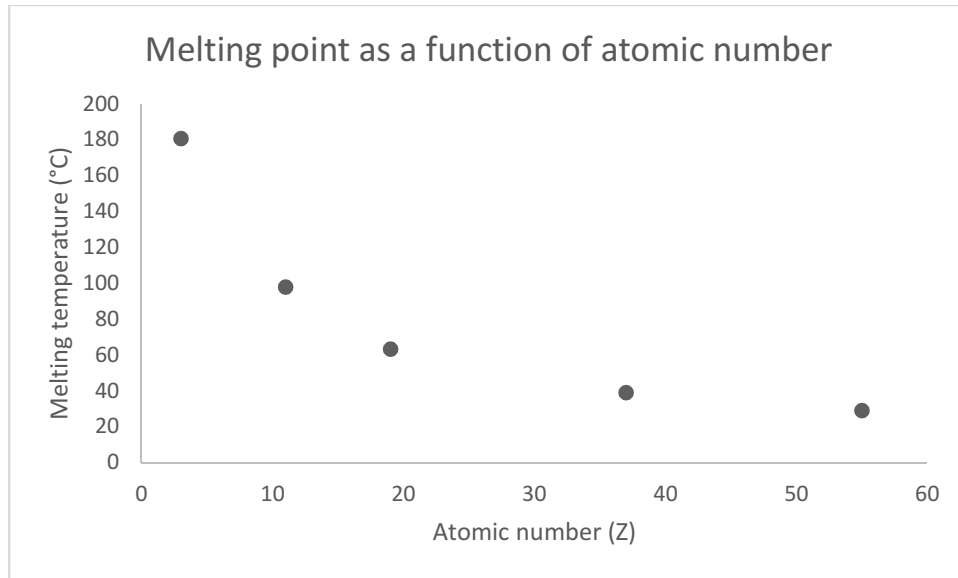


For each row, the melting temperature is highest when the outer “*d*” energy level is partly full. In Cr, there are 5 electrons in the 3*d* shell; in Mo, there are 5 electrons in the 4*d* shell; in W there are 4 electrons in the 5*d* shell. In each column, the melting temperature increases as the atomic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

- 2-18** 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:

Using data from Figure 2-9:



As the atomic number increases, the melting temperature decreases, in contrast to the trend found in Problem 2-17.

- 2-19** 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.

- 2-20** Differentiate the three principle bonding mechanisms in solids. What is Van der Waal’s bonding? What are the relative binding energies of the different mechanisms?

Solution:

The principle bonding mechanisms are covalent, ionic and metallic. Van der Waals bonding is a weak secondary bonding mechanism that allows some gaseous or small molecules to condense. The relative binding energies of the primary bonds are reflected

in the strength of the material. Covalent and ionic bonds produce the strongest bonds while metallic bonds have lower bonding energies than covalent or ionic materials.

- 2-21** 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.

- 2-22** The compound aluminum phosphide (AlP) is a compound semiconductor having mixed ionic and covalent bonding. Calculate the fraction of bonding that is ionic.

Solution:

Starting with Equation 2-1, we determine the fraction of ionic bonding with this equation:

$$f_{ionic} = 1 - e^{(-0.25\Delta E^2)}$$

The exponential term is the covalent fraction. Since there can be only ionic or covalent bonds, the two fractions must add to 1. In an equation form:

$$f_{ionic} + f_{covalent} = 1$$

Or:

$$f_{ionic} + e^{(-0.25\Delta E^2)} = 1$$

Anyway, the electronegativities for Al and P are 1.5 and 2.1 respectively. The difference is 0.6:

$$f_{ionic} = 1 - e^{(-0.25[0.6]^2)}$$

Doing the math:

$$\boxed{f_{ionic} = 0.086}$$

So less than one tenth of the bonding is ionic. This should not be surprising when their positions in the periodic table are compared.

- 2-23** Calculate the fraction of bonding in MgO that is ionic.

Solution:

Starting with Equation 2-1, we determine the fraction of ionic bonding with this equation:

$$f_{ionic} = 1 - e^{(-0.25\Delta E^2)}$$

The electronegativities of magnesium and oxygen are 1.2 and 3.5, so their difference is 2.3. Inserting:

$$f_{ionic} = 1 - e^{(-0.25[2.3]^2)}$$

Math time!

$$\boxed{f_{ionic} = 0.734}$$

The compound is held together mostly by ionic bonding.

2-24 Calculate the fraction of bonding that is covalent for silica (SiO₂).

Solution:

Using Equation 2-1, we determine the fraction of covalent bonding:

$$f_{covalent} = e^{(-0.25\Delta E^2)}$$

The electronegativities of silicon and oxygen are 1.8 and 3.5, so their difference is 1.7. Inserting:

$$f_{covalent} = e^{(-0.25[1.7]^2)}$$

$$\boxed{f_{covalent} = 0.486}$$

2-25 Calculate the fraction of bonding that is ionic in nature for zirconia (ZrO₂)?

Solution:

$$f_{ionic} = 1 - e^{(-0.25\Delta E^2)}$$

The electronegativities of zircon and oxygen are 1.4 and 3.5, so their difference is 2.1. Inserting:

$$f_{ionic} = 1 - e^{(-0.25[2.1]^2)}$$

$$\boxed{f_{ionic} = 0.668}$$

2-26 What is the type of bonding in diamond? Are the properties of diamond commensurate with the nature of the bonding?

Solution:

In diamond, the carbon atoms are covalently bonded. Diamond is electrically insulating, which makes sense: each carbon is bonded to four other carbon atoms thus leaving no free valence electrons available to conduct electricity.

2-27 What are the bonding mechanisms in thermoplastics?

Solution:

The primary bond in thermoplastics are the covalent bonds that hold the individual carbon atoms together along the polymer chains while van der Waals secondary bonds hold the polymer chains close together.

2-28 Why are covalently bonded materials generally less dense than those that are bonded ionically or metallically?

Solution:

Covalently bonded materials are typically less dense than metallically or ionically bonded materials due to the nature of their bonding. The bonding in covalent materials is directional in nature which doesn't allow the atoms to pack together in a dense manner like the ionic or metallic bonded materials. This results in a lower mass and lower density for covalently bonded materials.

2-31 Calculate the fractions of ionic bonds in silicon carbide (SiC) and silicon nitride (Si₃N₄).

Solution:

We use Equation 2.1 and take the electronegativities from Figure 2-9:

$$f_{ionic} = 1 - e^{(-0.25\Delta E^2)}$$

The electronegativities of silicon and carbon are 1.8 and 2.5, so their difference is 0.7. Inserting:

$$f_{ionic} = 1 - e^{(-0.25[0.7]^2)}$$

Math time!

$$f_{ionic} = 0.115$$

Repeating this for silicon nitride:

$$f_{ionic} = 1 - e^{(-0.25\Delta E^2)}$$

The electronegativities of silicon and nitrogen are 1.8 and 3.0, so their difference is 1.2. Inserting:

$$f_{ionic} = 1 - e^{(-0.25[1.2]^2)}$$

$$f_{ionic} = 0.302$$

- 2-32** 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 bonding that is covalent in this material.

Solution:

Using Equation 2-1, we determine the fraction of covalent bonding:

$$f_{covalent} = e^{(-0.25\Delta E^2)}$$

The electronegativities of boron and nitrogen are 2.0 and 3.0, so their difference is 1.0. Inserting:

$$f_{covalent} = e^{(-0.25[1.0]^2)}$$

$$f_{covalent} = 0.779$$

- 2-34** Is there a trend in the number of electrons in the outermost energy shell of atoms or ions that have formed bonds?

Solution:

Yes. They try to fill their valence shells.

- 2-35** In order to increase the operating temperature of an engine, it is suggested that some of the aluminum components be coated with a ceramic. What kinds of problems could this pose? How could you overcome these problems?

Solution:

Creating a mechanical bond between the ceramic and the metallic component could pose a problem since the ceramic is ionic in nature and the component is metallically bonded. This can be overcome by creating a slightly roughened surface and choosing a ceramic that has a limited degree of chemical reactivity with the metal which would enhance bonding.

Another problem that we face is likely to spallation or debonding of the coating due to the differences in the coefficients of thermal expansion. To overcome this problem, it would be possible to select a ceramic that could have a compatible coefficients of thermal expansion with the aluminum for the given operating temperature range.

- 2-36** Aluminum and silicon are side by side on the periodic table. Compare the melting temperatures of the two elements and explain the difference in terms of atomic bonding.

Solution:

The melting temperature of silicon is 1410°C while aluminum is 660°C. The differences in melting temperatures can be explained by the types of bonds that bind the elements together. It is expected that since aluminum is a metal that it would have metallic bonding. Silicon on the other hand is a metalloid (between metal and non-metal) and has covalent bonding. Since covalent bonding has higher binding energy than metallic bonding, we can conclude that the silicon has the higher melting temperature due to the higher strength of the silicon bonds when compared to aluminum.

- 2-37** 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.

- 2-38** Would you expect iron or silicon nitride (SiN) to have a higher modulus of elasticity? Why?

Solution:

It is expected that SiN would have the higher modulus of elasticity due to its bonding nature (covalent) compared to iron (metallic). Covalent bonds result in higher binding energies thus having a direct result for a higher modulus of elasticity.

- 2-39** 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:

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

$$4 \text{ Be } 1s^2 2s^2 \quad E = 42 \times 10^6 \text{ psi } r_{\text{Be}} = 1.143 \text{ \AA}$$

$$12 \text{ Mg } 1s^2 2s^2 2p^6 3s^2 \quad E = 6 \times 10^6 \text{ psi } r_{\text{Mg}} = 1.604 \text{ \AA}$$

- 2-41** 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, $E \approx 6 \times 10^6$ psi; in MgO, $E \approx 30 \times 10^6$ psi.

- 2-43** Aluminum and silicon are side-by-side in the periodic table. Which would you expect to have the higher modulus of elasticity? Explain.

Solution:

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

- 2-45** 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, which may crack and expose the underlying steel to corrosion.

- 2-48** Name at least four allotropes of carbon. Why is graphite electrically conductive while diamond is not if both are pure forms of carbon?

Solution:

The four allotropes of carbon are diamond, graphite, nanotubes and buckminsterfullerene. In diamond, the carbon atoms are covalently bonded to four other carbon atoms thus leaving no free valence electrons available to conduct electricity. In graphite, the carbon is arranged in layers where the carbon atoms form 3 strong bonds with other carbon atoms, but have a fourth bond between layers which is a weak van der Waals bond. This results in the fourth electron for each of the carbon atom to be available to conduct electricity.

- 2-49** Bond hybridization in carbon leads to numerous crystalline forms. With only six electrons, how is this possible? Explain.

Solution:

Carbon in graphite form has the electron configuration of $1s^2 2s^2 2p^2$ which only allows for 3 bonds. Additions of pressure and heat, hybridization occurs to the point that the electron moves from the 2s to the 2p orbital ($1s^2 2s^1 2p^3$) allowing access for 4 bonds to occur.