Chemistry 2e
10: Liquids and Solids
10.1: Intermolecular Forces

1. In terms of their bulk properties, how do liquids and solids differ? How are they similar?

Solution

Liquids and solids are similar in that they are matter composed of atoms, ions, or molecules. They are incompressible and have similar densities that are both much larger than those of gases. They are different in that liquids have no fixed shape, and solids are rigid.

3. In terms of the kinetic molecular theory, in what ways are liquids similar to gases? In what ways are liquids different from gases?

Solution

They are similar in that the atoms or molecules are free to move from one position to another. They differ in that the particles of a liquid are confined to the shape of the vessel in which they are placed. In contrast, a gas will expand without limit to fill the space into which it is placed.

5. What is the evidence that all neutral atoms and molecules exert attractive forces on each other?

Solution

All atoms and molecules will condense into a liquid or solid in which the attractive forces exceed the kinetic energy of the molecules, at sufficiently low temperature.

7. Define the following and give an example of each:
(a) dispersion force
(b) dipole-dipole attraction
(c) hydrogen bond

Solution

(a) Dispersion forces occur as an atom develops a temporary dipole moment when its electrons are distributed asymmetrically about the nucleus. This structure is more prevalent in large atoms such as argon or radon. A second atom can then be distorted by the appearance of the dipole in the first atom. The electrons of the second atom are attracted toward the positive end of the first atom, which sets up a dipole in the second atom. The net result is rapidly fluctuating, temporary dipoles that attract one another (e.g., Ar).
(b) A dipole-dipole attraction is a force that results from an electrostatic attraction of the positive end of one polar molecule for the negative end of another polar molecule (e.g., ICI molecules attract one another by dipole-dipole interaction).
(c) Hydrogen bonds form whenever a hydrogen atom is bonded to one of the more electronegative atoms, such as a fluorine, oxygen, nitrogen, or chlorine atom. The electrostatic attraction between the partially positive hydrogen atom in one molecule and the partially negative atom in another molecule gives rise to a strong dipole-dipole interaction called a hydrogen bond (e.g., $HF\cdots HF$).

9. Why do the boiling points of the noble gases increase in the order He < Ne < Ar < Kr < Xe?

Solution

The London forces typically increase as the number of electrons increase.

11. Arrange each of the following sets of compounds in order of increasing boiling point temperature:
(a) HCl, H_2O, SiH_4
(b) F_2, Cl_2, Br_2
(c) CH_4, C_2H_6, C_3H_8

(d) O_2, NO, N_2

Solution

(a) $SiH_4 < HCl < H_2O$; (b) $F_2 < Cl_2 < Br_2$; (c) $CH_4 < C_2H_6 < C_3H_8$; (d) $N_2 < O_2 < NO$

13. On the basis of intermolecular attractions, explain the differences in the boiling points of *n*–butane (–1 °C) and chloroethane (12 °C), which have similar molar masses.

Solution

Only rather small dipole-dipole interactions from C-H bonds are available to hold *n*-butane in the liquid state. Chloroethane, however, has rather large dipole interactions because of the Cl-C bond; the interaction, therefore, is stronger, leading to a higher boiling point.

15. The melting point of $H_2O(s)$ is 0 °C. Would you expect the melting point of $H_2S(s)$ to be –85 °C, 0 °C, or 185 °C? Explain your answer.

Solution

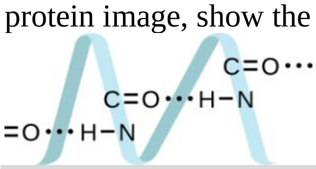
–85 °C. Water has stronger hydrogen bonds, so it melts at a higher temperature.

17. Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

Solution

The hydrogen bond between two hydrogen fluoride molecules is stronger than that between two water molecules because the electronegativity of F is greater than that of O. Consequently, the partial negative charge on F is greater than that on O. The hydrogen bond between the partially positive H and the larger partially negative F will be stronger than that formed between H and O.

19. Proteins are chains of amino acids that can form in a variety of arrangements, one of which is a helix. What kind of IMF is responsible for holding the protein strand in this shape? On the protein image, show the locations of the IMFs that hold the protein together:



Solution

H-bonding is the principle IMF holding the protein strands together. The H-bonding is between the $N-H$ and $C=O$.

21. Identify the intermolecular forces present in the following solids:

(a) CH_3CH_2OH

(b) $CH_3CH_2CH_3$

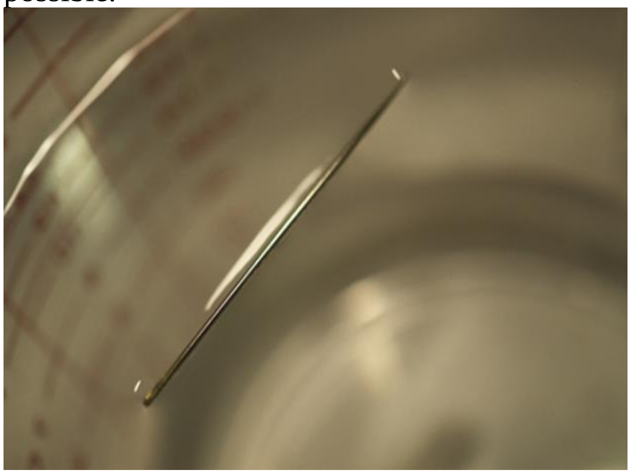
(c) CH_3CH_2Cl

Solution

(a) hydrogen bonding, dipole-dipole attraction, and dispersion forces; (b) dispersion forces; (c) dipole-dipole attraction and dispersion forces

Chemistry 2e
10: Liquids and Solids
10.2: Properties of Liquids

23. Although steel is denser than water, a steel needle or paper clip placed carefully lengthwise on the surface of still water can be made to float. Explain at a molecular level how this is possible.



(credit: Cory Zanker)

Solution

The water molecules have strong intermolecular forces of hydrogen bonding. The water molecules are thus attracted strongly to one another and exhibit a relatively large surface tension, forming a type of “skin” at its surface. This skin can support a bug or paper clip if gently placed on the water.

25. You may have heard someone use the figure of speech “slower than molasses in winter” to describe a process that occurs slowly. Explain why this is an apt idiom, using concepts of molecular size and shape, molecular interactions, and the effect of changing temperature.

Solution

Temperature has an effect on intermolecular forces: The higher the temperature, the greater the kinetic energies of the molecules and the greater the extent to which their intermolecular forces are overcome, and so the more fluid (less viscous) the liquid. The lower the temperature, the less the intermolecular forces are overcome, and so the less viscous the liquid.

27. The surface tension and viscosity of water at several different temperatures are given in this table.

Water	Surface Tension (mN/m)	Viscosity (mPa s)
0 °C	75.6	1.79
20 °C	72.8	1.00
60 °C	66.2	0.47
100 °C	58.9	0.28

(a) As temperature increases, what happens to the surface tension of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

(b) As temperature increases, what happens to the viscosity of water? Explain why this occurs, in terms of molecular interactions and the effect of changing temperature.

Solution

(a) As the water reaches higher temperatures, the increased kinetic energies of its molecules are more effective in overcoming hydrogen bonding, and so its surface tension decreases. Surface tension and intermolecular forces are directly related. (b) The same trend in viscosity is seen as in surface tension, and for the same reason.

29. Water rises in a glass capillary tube to a height of 17 cm. What is the diameter of the capillary tube?

Solution

This time we will solve for *r*, as we are given h = 17 cm = 0.17 m.

$$0.17\text{ m} = \frac{2(0.07199\text{ kg/s}^2)}{r(1000\text{ kg/m}^2)(9.8\text{ m/s}^2)}$$

$$r = 8.6 \times 10^{-5}\text{ m}$$

$$d = 2r = 1.7 \times 10^{-4}\,m$$

Chemistry 2e
10: Liquids and Solids
10.3: Phase Transitions

31. Heat is added to ice at 0 °C. Explain why the temperature of the ice does not change. What does change?

Solution

The heat is absorbed by the ice, providing the energy required to partially overcome intermolecular attractive forces in the solid and causing a phase transition to liquid water. The solution remains at 0 °C until all the ice is melted. Only the amount of water existing as ice changes until the ice disappears. Then the temperature of the water can rise.

33. Identify two common observations indicating some liquids have sufficient vapor pressures to noticeably evaporate?

Solution

We can see the amount of liquid in an open container decrease and we can smell the vapor of some liquids.

35. What is the relationship between the intermolecular forces in a liquid and its vapor pressure?

Solution

The vapor pressure of a liquid decreases as the strength of its intermolecular forces increases.

37. Why does spilled gasoline evaporate more rapidly on a hot day than on a cold day?

Solution

As the temperature increases, the average kinetic energy of the molecules of gasoline increases and so a greater fraction of molecules have sufficient energy to escape from the liquid than at lower temperatures.

39. When is the boiling point of a liquid equal to its normal boiling point?

Solution

They are equal when the pressure of gas above the liquid is exactly 1 atm.

41. Use the information in Figure 10.24 to estimate the boiling point of water in Denver when the atmospheric pressure is 83.3 kPa.

Solution

Follow an imaginary horizontal line at 83.3 kPa to the curve representing the vapor pressure of water. Then drop a vertical line to the temperature axis. The intersection is at approximately 95 °C.

43. Explain the following observations:

(a) It takes longer to cook an egg in Ft. Davis, Texas (altitude, 5000 feet above sea level) than it does in Boston (at sea level).

(b) Perspiring is a mechanism for cooling the body.

Solution

(a) At 5000 feet, the atmospheric pressure is lower than at sea level, and water will therefore boil at a lower temperature. This lower temperature will cause the physical and chemical changes involved in cooking the egg to proceed more slowly, and a longer time is required to fully cook the egg. (b) As long as the air surrounding the body contains less water vapor than the maximum that air can hold at that temperature, perspiration will evaporate, thereby cooling the body by removing the heat of vaporization required to vaporize the water.

45. Explain why the molar enthalpies of vaporization of the following substances increase in the order $CH_4 < C_2H_6 < C_3H_8$, even though all three substances experience the same dispersion forces when in the liquid state.

Solution

Dispersion forces increase with molecular mass or size. As the number of atoms composing the molecules in this homologous series increases, so does the extent of intermolecular attraction via dispersion forces and, consequently, the energy required to overcome these forces and vaporize the liquids.

47. The enthalpy of vaporization of $CO_2(l)$ is 9.8 kJ/mol. Would you expect the enthalpy of vaporization of $CS_2(l)$ to be 28 kJ/mol, 9.8 kJ/mol, or –8.4 kJ/mol? Discuss the plausibility of each of these answers.

Solution

The boiling point of CS_2 is higher than that of CO_2 partially because of the higher molecular weight of CS_2; consequently, the attractive forces are stronger in CS_2. It would be expected, therefore, that the heat of vaporization would be greater than that of 9.8 kJ/mol for CO_2. A value of 28 kJ/mol would seem reasonable. A value of –8.4 kJ/mol would indicate a release of energy upon vaporization, which is clearly implausible.

49. Ethyl chloride (boiling point, 13 °C) is used as a local anesthetic. When the liquid is sprayed on the skin, it cools the skin enough to freeze and numb it. Explain the cooling effect of liquid ethyl chloride.

Solution

The thermal energy (heat) needed to evaporate the liquid is removed from the skin.

51. How much heat is required to convert 422 g of liquid H_2O at 23.5 °C into steam at 150 °C?

Solution

$$422 \text{ g H}_2\text{O} \times \frac{1 \text{ mol}}{18.02 \text{ g H}_2\text{O}} = 23.4 \text{ mol H}_2\text{O}$$

Heat needed to bring this amount of water to the normal boiling point: $\Delta H_1 = mC_s\Delta T$ = (422 g)(4.184 J/g °C)(100.0 – 23.5) = 135,000 J

Heat needed to vaporize this amount of water: $\Delta H_2 = n\Delta H_{vap}$ = (23.4 mol)(40,650 J/mol) = 951,000 J

Heat to needed to increase the temperature of the steam: $\Delta H_3 = mC_s\Delta T$ = (422 g)(2.09 J/g °C)(150 – 100) = 44,100 J.

Adding ΔH_1, ΔH_2, and ΔH_3: 135,000 J + 951,000 J + 44,100 J = 1,130,000 J = 1130 kJ.

53. Titanium tetrachloride, $TiCl_4$, has a melting point of –23.2 °C and has a ΔH_{fusion} = 9.37 kJ/mol.

(a) How much energy is required to melt 263.1 g $TiCl_4$?

(b) For $TiCl_4$, which will likely have the larger magnitude: ΔH_{fusion} or $\Delta H_{vaporization}$? Explain your reasoning.

Solution

(a) $263.1 \text{ g TiCl}_4 \times \frac{1 \text{ mol}}{189.9 \text{ g}} = 1.385 \text{ mol TiCl}_4$. Heat required to melt this amount of $TiCl_4$ is $n\Delta H_{fusion}$ = 1.385 mol × 9.37 kJ/mol = 13.0kJ. (b) It is likely that the heat of vaporization will have a larger magnitude since in the case of vaporization the intermolecular interactions have to be completely overcome, while melting weakens or destroys only some of them.

Chemistry 2e
10: Liquids and Solids
10.4: Phase Diagrams

55. What phase changes will take place when water is subjected to varying pressure at a constant temperature of 0.005 °C? At 40 °C? At –40 °C?

Solution

At low pressures and 0.005 °C, the water is a gas. As the pressure increases to 4.6 torr, the water becomes a solid; as the pressure increases still more, it becomes a liquid. At 40 °C, water at low pressure is a vapor; at pressures higher than about 75 torr, it converts into a liquid. At –40 °C, water goes from a gas to a solid as the pressure increases above very low values.

57. From the phase diagram for carbon dioxide in Figure 10.34, determine the state of CO_2 at:
(a) 20 °C and 1000 kPa
(b) 10 °C and 2000 kPa
(c) 10 °C and 100 kPa
(d) –40 °C and 500 kPa
(e) –80 °C and 1500 kPa
(f) –80 °C and 10 kPa

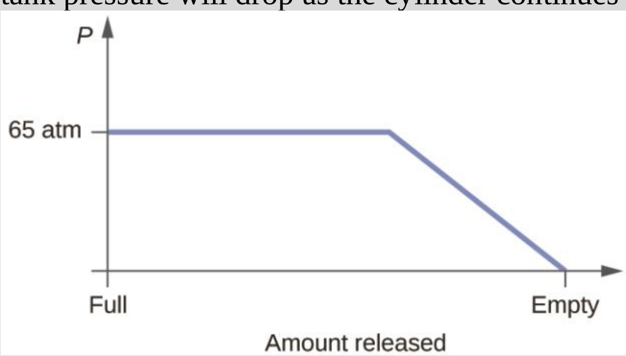
Solution

(a) gas; (b) gas; (c) gas; (d) gas; (e) solid; (f) gas

59. Consider a cylinder containing a mixture of liquid carbon dioxide in equilibrium with gaseous carbon dioxide at an initial pressure of 65 atm and a temperature of 20 °C. Sketch a plot depicting the change in the cylinder pressure with time as gaseous carbon dioxide is released at constant temperature.

Solution

The carbon dioxide pressure will remain roughly constant at 65 atm (the equilibrium vapor pressure of CO_2 at 20 °C) as long as liquid CO_2 remains in the cylinder. The gas released from the cylinder will be replaced by vaporization of the liquid. When all the liquid has vaporized, the tank pressure will drop as the cylinder continues to release gas:

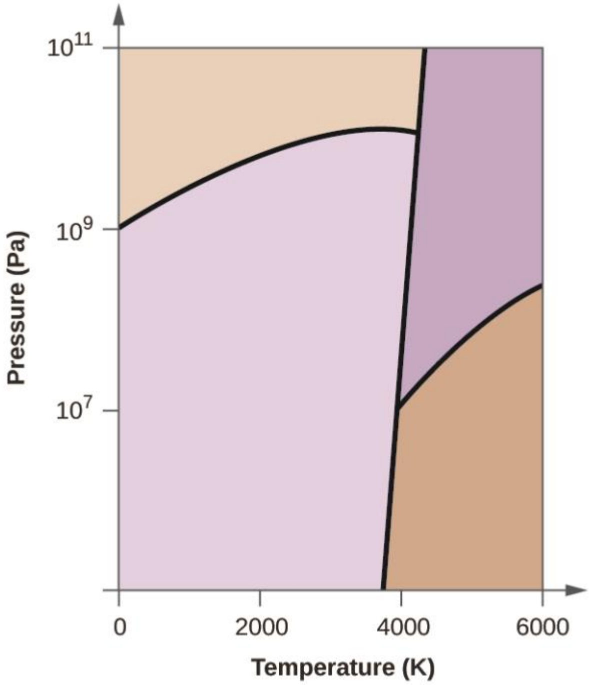


61. If a severe storm results in the loss of electricity, it may be necessary to use a clothesline to dry laundry. In many parts of the country in the dead of winter, the clothes will quickly freeze when they are hung on the line. If it does not snow, will they dry anyway? Explain your answer.

Solution

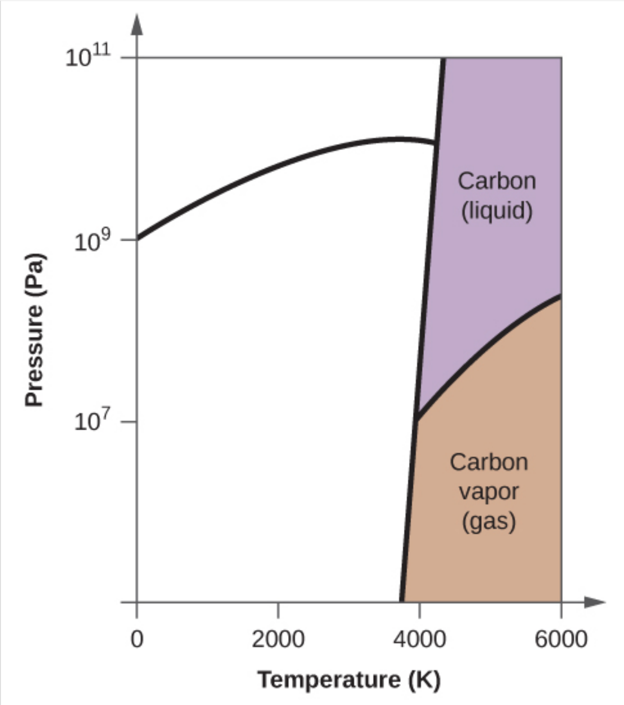
Yes, ice will sublime, although it may take it several days. Ice has a small vapor pressure, and some ice molecules form gas and escape from the ice crystals. As time passes, more and more solid converts to gas until eventually the clothes are dry.

63. Elemental carbon has one gas phase, one liquid phase, and three different solid phases, as shown in the phase diagram:

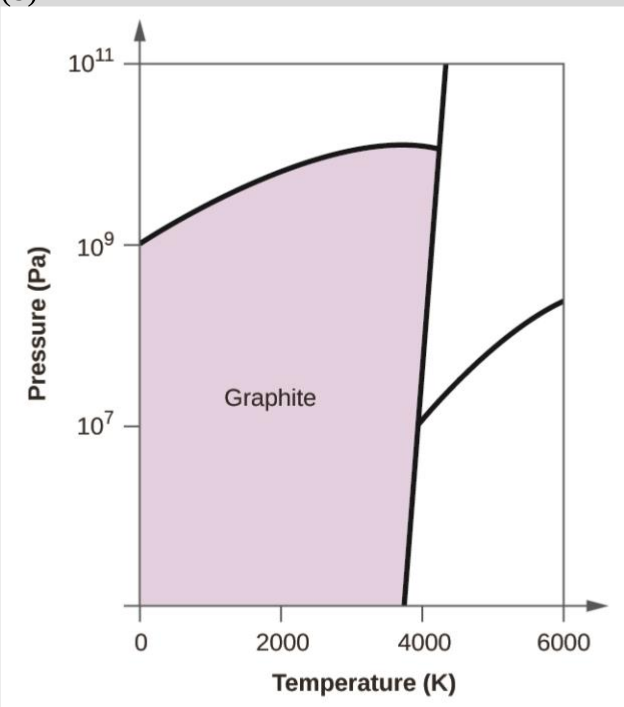


(a) On the phase diagram, label the gas and liquid regions.
(b) Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
(c) If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.
(d) Circle each triple point on the phase diagram.
(e) In what phase does carbon exist at 5000 K and 10^8 Pa?
(f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^6 Pa, which phase transition occurs, if any?

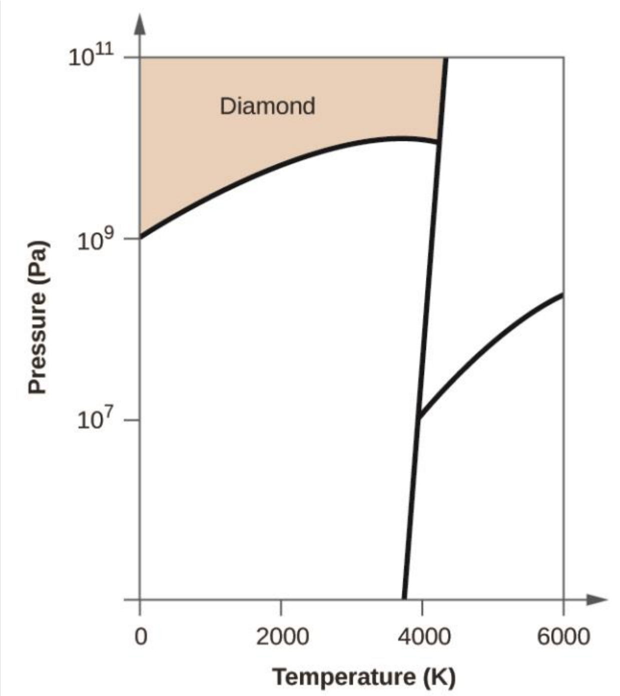
Solution
(a)


10^11
10^9
10^7
Pressure (Pa)
Carbon
(liquid)
Carbon
vapor
(gas)
0
2000
4000
6000
Temperature (K)

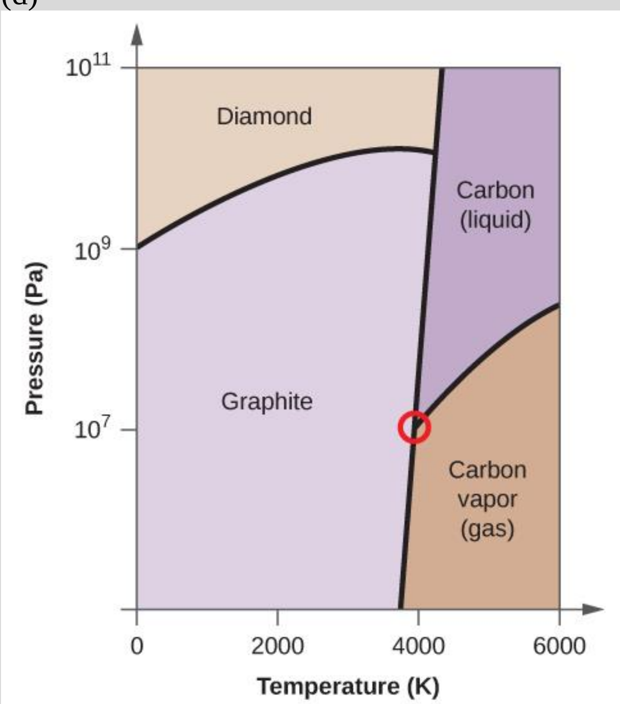
(b)


10^11
10^9
10^7
Pressure (Pa)
Graphite
0
2000
4000
6000
Temperature (K)

(c)



(d)



(e) Carbon exists in the liquid phase under these conditions. (f) The phase transition would be one of sublimation. Carbon would convert from graphite to vapor.

Chemistry 2e
10: Liquids and Solids
10.5: The Solid State of Matter

65. At very low temperatures oxygen, O_2, freezes and forms a crystalline solid. Which best describes these crystals?
(a) ionic
(b) covalent network
(c) metallic
(d) amorphous
(e) molecular crystals

Solution
(e) molecular crystals

67. Explain why ice, which is a crystalline solid, has a melting temperature of 0 °C, whereas butter, which is an amorphous solid, softens over a range of temperatures.

Solution
Ice has a crystalline structure stabilized by hydrogen bonding. These intermolecular forces are of comparable strength and thus require the same amount of energy to overcome. As a result, ice melts at a single temperature and not over a range of temperatures. The various, very large molecules that compose butter experience varied van der Waals attractions of various strengths that are overcome at various temperatures, and so the melting process occurs over a wide temperature range.

69. Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances:
(a) $CaCl_2$
(b) SiC
(c) N_2
(d) Fe
(e) C (graphite)
(f) $CH_3CH_2CH_2CH_3$
(g) HCl
(h) NH_4NO_3
(i) K_3PO_4

Solution
(a) $CaCl_2$, ionic; (b) SiC, covalent network; (c) N_2, molecular; (d) Fe, metallic; (e) C (graphite), covalent network; (f) $CH_3CH_2CH_2CH_3$, molecular; (g) HCl, molecular; (h) NH_4NO_3, ionic; (i) K_3PO_4, ionic

71. Classify each substance in the table as either a metallic, ionic, molecular, or covalent network solid:

Substance	Appearance	Melting Point	Electrical Conductivity	Solubility in Water
X	brittle, white	800 °C	only if melted/dissolved	soluble
Y	shiny, malleable	1100 °C	high	insoluble
Z	hard, colorless	3550 °C	none	insoluble

Solution
X = ionic; Y = metallic; Z = covalent network

73. Substance A is shiny, conducts electricity well, and melts at 975 °C. Substance A is likely a(n):
(a) ionic solid
(b) metallic solid
(c) molecular solid
(d) covalent network solid

Solution
(b) metallic solid

Chemistry 2e
10: Liquids and Solids
10.6: Lattice Structures in Crystalline Solids

75. Describe the crystal structure of iron, which crystallizes with two equivalent metal atoms in a cubic unit cell.

Solution

The structure of this low-temperature form of iron (below 910 °C) is body-centered cubic. There is one-eighth atom at each of the eight corners of the cube and one atom in the center of the cube.

77. What is the coordination number of a chromium atom in the body-centered cubic structure of chromium?

Solution

Coordination number refers to the number of nearest neighbors. A chromium atom lies at the center of a body-centered cube and has eight nearest neighbors (at the corners of the cube): four in one plane above and four in one plane below. The coordination number is therefore eight.

79. Cobalt metal crystallizes in a hexagonal closest packed structure. What is the coordination number of a cobalt atom?

Solution

Hexagonal closest packing occurs in such a way that each atom touches 12 nearest neighbors: six in its own layer and three in each adjacent layer. The coordination number, therefore, is 12.

81. Tungsten crystallizes in a body-centered cubic unit cell with an edge length of 3.165 Å.
(a) What is the atomic radius of tungsten in this structure?
(b) Calculate the density of tungsten.

Solution

(a) In a body-centered cubic unit cell, the metal atoms are in contact along the interior diagonal of the cube. The interior diagonal forms a right triangle with the unit cell edge and the diagonal of the face. Use the Pythagorean theorem to determine the length of the diagonal, d, on the face of the cube in terms of the edge, *e*. See the figure in Example 10.14:

$d^2 = e^2 + e^2 = 2e^2$

$d = \sqrt{2}\,e$

The interior diagonal of the cube is the length of four atomic radii and can be calculated again by using the Pythagorean theorem and the face diagonal and edge.

$(\text{diagonal})^2 = d^2 + e^2$

$= (\sqrt{2}\,e) + e^2$

$= 2e^2 + e^2$

$= 3e^2$

$\text{diagonal} = \sqrt{3}\,e = 4r$

$$\text{radius of tungsten} = \frac{\text{diagonal}}{4} = \frac{\sqrt{3}e}{4} = \frac{\sqrt{3}}{4}(3.165\ \text{Å}) = 1.370\ \text{Å};$$

(b) Given the body-centered cubic structure, each unit cell contains two atoms. Use the unit cell edge length to calculate the unit cell volume and the volume occupied by each atom. Multiply to obtain the molar volume and divide the atomic mass by this value to obtain density (e = edge length):

$V(\text{cell}) = e^3 = (3.165 \times 10^{-8}\ \text{cm})^3 = 3.170 \times 10^{-23}\ \text{cm}^3$

$$V(\text{atom}) = \frac{3.170 \times 10^{-23}\ \text{cm}^3}{2\ \text{atoms}} = 1.585 \times 10^{-23}\ \text{cm}^3\ \text{atom}^{-1}$$

V(mol) = 1.585 × 10^{-23} cm^3/atom × 6.022 × 10^{23} atoms/mol
= 9.546 cm^3/mol

$$\text{density} = \frac{183.85\ \text{g mol}^{-1}}{9.546\ \text{cm}^3\ \text{mol}^{-1}}$$

= 19.26 g/cm

83. Barium crystallizes in a body-centered cubic unit cell with an edge length of 5.025 Å
(a) What is the atomic radius of barium in this structure?
(b) Calculate the density of barium.

Solution
(a) In a body-centered cubic unit cell, the metal atoms are in contact along the diagonal of the cube. The diagonal of the cube forms a right triangle with the unit cell edge and the diagonal of a face. Use the Pythagorean theorem to determine the length of the diagonal, d, on the face of the cube in terms of e.

$d^2 = e^2 + e^2 = 2e^2$

$d = \sqrt{2}\,e$

The diagonal of the cube is the length of four atomic radii and can be calculated by again using the Pythagorean theorem:

$(\text{diagonal})^2 = (4r)^2 = (2e)^2 + e^2 = 16r^2 = 3e^2$

$\text{diagonal} = 4r = \sqrt{3e}$

$$r = \frac{\sqrt{3}}{4}e = \frac{\sqrt{3}}{4}(5.025\ \text{Å}) = 2.176\ \text{Å};$$

(b) Given a body-centered cubic structure, each unit cell contains two atoms. Use the unit cell edge length to calculate the unit cell volume and the volume occupied by each atom. Multiply to obtain the molar volume and divide the gram atomic weight by this value to obtain density (e = edge length):

$V\,(\text{cell}) = e^3 = (5.025 \times 10^{-8}\ \text{cm})^3 = 1.26884 \times 10^{-22}\ \text{cm}^3$

$$V\,(\text{atom}) = 1.26884 \times \frac{10^{-22}\ \text{cm}^3\ \text{atom}^{-1}}{2\ \text{atoms}} = 6.3442 \times 10^{-23}\ \text{cm}^3$$

$V\,(\text{mole}) = 6.3442 \times 10^{-23}\ \text{cm}^3 \times 6.022 \times 10^{23}\ \text{atoms/mol} = 38.205\ \text{cm}^3$

$$d(\text{Ba}) = \frac{137.33\ \text{g}}{38.204\ \text{cm}^3} = 3.595\ \text{g/cm}^3$$

85. The density of aluminum is 2.7 g/cm^3; that of silicon is 2.3 g/cm^3. Explain why Si has the lower density even though it has heavier atoms.

Solution
The crystal structure of Si shows that it is less tightly packed (coordination number 4) in the solid than Al (coordination number 12).

87. Cadmium sulfide, sometimes used as a yellow pigment by artists, crystallizes with cadmium, occupying one-half of the tetrahedral holes in a closest packed array of sulfide ions. What is the formula of cadmium sulfide? Explain your answer.

Solution
In a closest-packed array, two tetrahedral holes exist for each anion. If only half the tetrahedral holes are occupied, the numbers of anions and cations are equal. The formula for cadmium sulfide is CdS.

89. What is the formula of the magnetic oxide of cobalt, used in recording tapes, that crystallizes with cobalt atoms occupying one-eighth of the tetrahedral holes and one-half of the octahedral holes in a closely packed array of oxide ions?

Solution

In a closest-packed array of oxide ions, one octahedral hole and two tetrahedral holes exist for each oxide ion. If one-half of the octahedral holes are filled, there is one Co ion for every two oxide ions. If one-eighth of the tetrahedral holes are filled, there is one Co ion for each four oxide ions. For every four oxide ions, there are two Co ions in octahedral holes and one Co in a tetrahedral hole; thus the formula is Co_3O_4.

91. A compound of thallium and iodine crystallizes in a simple cubic array of iodide ions with thallium ions in all of the cubic holes. What is the formula of this iodide? Explain your answer.

Solution

In a simple cubic array, only one cubic hole can be occupied be a cation for each anion in the array. The ratio of thallium to iodide must be 1:1; therefore, the formula for thallium is TlI.

93. What is the percent by mass of titanium in rutile, a mineral that contains titanium and oxygen, if structure can be described as a closest packed array of oxide ions with titanium ions in one-half of the octahedral holes? What is the oxidation number of titanium?

Solution

The ration of octahedral holes to oxygen anions is 1:1 in a closest-packed array. Only one-half of the octahedral holes are occupied. Thus, the titanium to oxygen ratio is 1:2 and the formula is TiO_2. The percentage by mass of Ti in the structure is:

$$\text{percent Ti} = \frac{47.90}{47.90 + 2(15.9994)} \times 100\% = 59.95\%$$

The oxidation number of titanium is +4 because there are two O^{2-} ions for each Ti ion.

95. As minerals were formed from the molten magma, different ions occupied the same cites in the crystals. Lithium often occurs along with magnesium in minerals despite the difference in the charge on their ions. Suggest an explanation.

Solution

Both ions are close in size: Mg, 0.65; Li, 0.60. This similarity allows the two to interchange rather easily. The difference in charge is generally compensated by the switch of Si^{4+} for Al^{3+}.

97. One of the various manganese oxides crystallizes with a cubic unit cell that contains manganese ions at the corners and in the center. Oxide ions are located at the center of each edge of the unit cell. What is the formula of the compound?

Solution

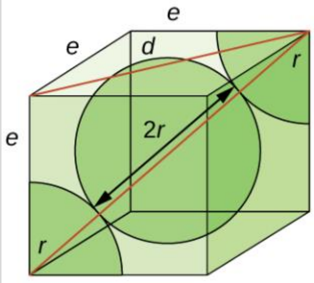
The total number of Mn ions is determined by adding the contributions from the corners and center. Mn (corners): $8 \times \frac{1}{8}$; Mn (center) = 1. Total Mn contribution to the unit cell = 2.

For O, there are a total of 12 edges in the cube and each ion in the edge contributes one-fourth to the unit cell. Consequently, there are $12 \times \frac{1}{4} = 3$ O atoms. The ratio is Mn:O = 2:3, and the formula is Mn_2O_3.

99. Thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Calculate the ionic radius of TI^+. (The ionic radius of I^- is 2.16 Å.)

Solution

A body-centered cube contains two atoms of radius r in the unit cell. The length of the face diagonal of the cube is calculated using the Pythagorean theorem:



The diagonal of the cube is $4r$.

$(4r)^2 = d^2 + e^2$

but $d^2 = e^2 + e^2$

$d^2 = e^2 + e^2 = 2e^2 = 2(4.20\ \text{Å})^2 = 35.28\ \text{Å}^2$

The diagonal of the cube is:

$d^2 + e^2 = 35.28 + (4.20)^2$

$= 35.28 + 17.64 = 52.92$

$\sqrt{d^2 + e^2} = 7.27\ \text{Å}$

$= 2r^+ + 2r^-$

Since $r^- = 2.16\ \text{Å}$,

$$r^+ = \frac{7.27\ \text{Å} - 2(2.16)\text{Å}}{2} = 1.48\ \text{Å}$$

101. What is the spacing between crystal planes that diffract X-rays with a wavelength of 1.541 nm at an angle θ of 15.55° (first order reflection)?

Solution

The Bragg equation is:

$n\lambda = 2d \sin\theta$

where d is the spacing between planes.

$$d = \frac{n\lambda}{2\sin\theta} = \frac{1\ (1.541\text{Å})}{2\sin 15.55°} = \frac{1.541\text{Å}}{2(0.2681)}$$

$= 2.874\ \text{Å}$

103. A metal with spacing between planes equal to 0.4164 nm diffracts X-rays with a wavelength of 0.2879 nm. What is the diffraction angle for the first order diffraction peak?

Solution

$$\sin\theta = \frac{n\lambda}{2d} = \frac{(1)(0.2879\ \text{nm})}{(2)(0.4164)} = 0.3457\text{, so } \theta = \sin^{-1}(0.3457) = 20.2°$$

105. When an electron in an excited molybdenum atom falls from the L to the K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by planes with a separation of 2.64 Å. What is the difference in energy between the K shell and the L shell in molybdenum assuming a first-order diffraction?

Solution

Use the Bragg equation, where $n = 1$,

$\lambda = 2d\ \sin\theta = 2(2.64\ \text{Å})\sin 7.75 = 0.712\ \text{Å}$

Then

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34}\ \text{J s})(2.998 \times 10^{8}\ \text{m s}^{-1})}{0.712 \times 10^{-10}\ \text{m}}$$
$$= 2.79 \times 10^{-15}\ \text{J} = 1.74 \times 10^{4}\ \text{eV}$$