Chapter 10: Liquids and Solids

UNIT 57 Intermolecular Forces

Question 57-1.

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.

Question 57-2.

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

Solution

Similarities: Both are composed of atoms, ions, or molecules; there is little empty space between these particles; the motion of the particles changes with changing temperature. Differences: Particles in the solid are fixed in a regular arrangement; although they vibrate, they do not move about; particles in the liquid have no regular arrangement and are free to move past each other.

Question 57-3.

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.

Question 57-4.

Explain why liquids assume the shape of any container into which they are poured, whereas solids are rigid and retain their shape.

Solution

Molecules in a liquid are free to move past each other, whereas molecules in a solid are held in fixed positions.

Question 57-5.

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.

Question 57-6.

Open the PhET States of Matter Simulation (http://phet.colorado.edu/en/simulation/states-ofmatter) to answer the following questions:

(a) Select the Solid, Liquid, Gas tab. Explore by selecting different substances, heating and cooling the systems, and changing the state. What similarities do you notice between the four substances for each phase (solid, liquid, gas)? What differences do you notice?

(b) For each substance, select each of the states and record the given temperatures. How do the given temperatures for each state correlate with the strengths of their intermolecular attractions? Explain.

(c) Select the Interaction Potential tab, and use the default neon atoms. Move the Ne atom on the right and observe how the potential energy changes. Select the Total Force button, and move the Ne atom as before. When is the total force on each atom attractive and large enough to matter? Then select the Component Forces button, and move the Ne atom. When do the attractive (van der Waals) and repulsive (electron overlap) forces balance? How does this relate to the potential energy versus the distance between atoms graph? Explain.

Solution

(a) The common general trend is that the substances retain both volume and shape in the solid state, generally retain the volume but change shape in the liquid state (and also produce more vapor/gas phase as the systems transition from solids to liquids), and the shape is not retained in the gas phase while the substances can expand to occupy the whole available volume. The difference is that water molecules have highly directional interactions resulting in a hydrogenbonded structured network in the solid state, and the oxygen molecules have ordered packing in the solid state because of their nonsymmetric molecule shape, while argon and neon atoms show no directionality in their interactions. (b) Neon – solid at 13 K, liquid at 26 K, gas at 55 K. Argon – solid at 43 K, liquid at 86 K, gas at 189 K. Oxygen – solid at 31 K, liquid at 69 K, gas at 194 K. Water – solid at 157 K, liquid at 328 K, gas at 809 K. Water molecules have the strongest intermolecular interactions (hydrogen bonds, electrostatic forces), and so the transitions from solid to liquid and from liquid to gas occur at higher temperatures. The other three compounds experience weaker van der Waals (nonpolar) interactions only, and thus they turn to less ordered phases (liquid and gas) at lower temperatures. (c) The total forces are attractive and large enough to matter when the distance between the atoms is larger than at the equilibrium point, but still not too large so that the interactions are still not too weak. The attractive and repulsive components balance each other at the equilibrium point. At the point the interaction energy has a minimum, and so its derivative is equal to zero. Forces are derivatives of the energy multiplied by –1.

Question 57-7.

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 HF).

Question 57-8.

The types of intermolecular forces in a substance are identical whether it is a solid, a liquid, or a gas. Why then does a substance change phase from a gas to a liquid or to a solid? **Solution**

At some point, the amount of available heat decreases to a level such that the kinetic energy is just equal to or less than the attractive forces that are present in the gas, allowing it to condense into a liquid. A similar situation exists when the kinetic energy falls below the level required to exceed the attractive forces of the solid; in this case the liquid will solidify.

Question 57-9.

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.

Question 57-10.

Neon and HF have approximately the same molecular masses.

(a) Explain why the boiling points of Neon and HF differ.
(b) Compare the change in the boiling points of Ne, Ar, Kr, and Xe with the change of the boiling points of HF, HCl, HBr, and HI, and explain the difference between the changes with increasing atomic or molecular mass. **Solution**

(a) The boiling point of Ne is –245.9 °C, whereas that of HF is –83.1 °C. As their molecular masses are similar, the higher boiling point of HF can be explained on the basis of its hydrogen bonds preventing the escape of molecules from the liquid surface. (b) In each case (HF and Ne; HCl and Ar; HBr and Kr; HI and Xe), the corresponding pairs have similar molecular or atomic masses. The much higher boiling point of HF compared with Ne is due to hydrogen bonding in HF. HCl has a much higher (about 100 °C) boiling point than Ar because of dipole-dipole interactions. In HBr and HI, where hydrogen bonding is impossible, dipole-dipole interactions make the boiling points of HBr and HI approximately 60 °C to 40 °C higher than those of the corresponding atomic species.

Question 57-11.

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) $N_2 < O_2 < NO$

Question 57-12.

The molecular mass of butanol, C_4H_9OH, is 74.14; that of ethylene glycol, $CH_2(OH)CH_2OH$, is 62.08, yet their boiling points are 117.2 °C and 174 °C, respectively. Explain the reason for the difference. **Solution**

The two hydroxyl groups in ethylene glycol provide more locations for the formation of hydrogen bonds. The existence of more hydrogen bonds considerably increases the boiling point.

Question 57-13.

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.

Question 57-14.

On the basis of dipole moments and/or hydrogen bonding, explain in a qualitative way the differences in the boiling points of acetone (56.2 °C) and 1-propanol (97.4 °C), which have similar molar masses.

Solution

Both have approximately equal London dispersion forces, but because it contains an –OH group, 1-propanol forms hydrogen bonds, which are stronger intermolecular forces than the dipoledipole attractions in acetone that result from the C = O bond.

Question 57-15.

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.

Question 57-16.

Silane (SiH_4), phosphine (PH_3), and hydrogen sulfide (H_2S) melt at –185 °C, –133 °C, and –85 °C, respectively. What does this suggest about the polar character and intermolecular attractions of the three compounds?

Solution

The molecules become more polar and the intermolecular forces increase as the melting temperatures increase from –185 °C to –85 °C.

Question 57-17.

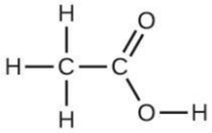
Explain why a hydrogen bond between two water molecules is weaker than a hydrogen bond between two hydrogen fluoride molecules.

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.

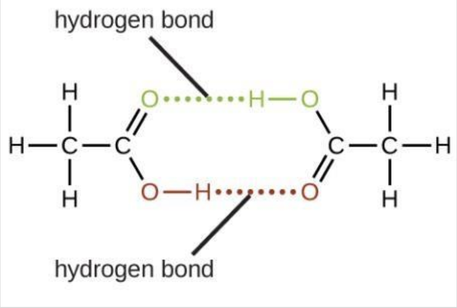
Question 57-18.

Under certain conditions, molecules of acetic acid, CH_3COOH, form “dimers,” pairs of acetic acid molecules held together by strong intermolecular attractions:



Draw a dimer of acetic acid, showing how two CH_3COOH molecules are held together, and stating the type of IMF that is responsible.

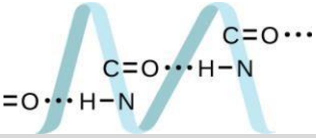
Solution



A dimer of acetic acid is displayed by showing two acetic acid molecules. The molecules combine by H-bonding between the H and O. Two H-bonds per dimer are thus established.

Question 57-19.

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.

Question 57-20.

The density of liquid NH_3 is 0.64 g/mL; the density of gaseous NH_3 at STP is 0.0007 g/mL. Explain the difference between the densities of these two phases. **Solution**

Molecules of gases are widely separated, whereas molecules in a liquid touch. Thus, a given volume of a gas contains a much smaller number of molecules and a much smaller mass than the same volume of a liquid.

Question 57-21.

Identify the intermolecular forces present in the following solids:

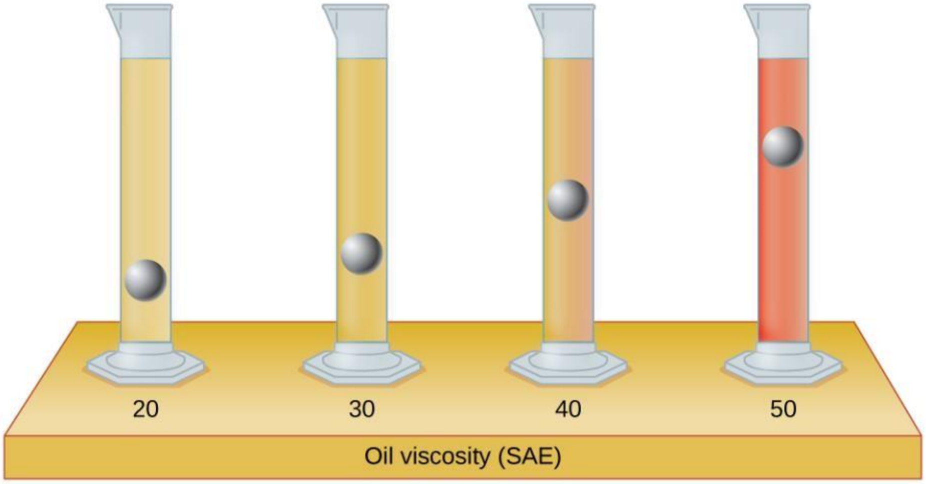
(a) CH_3CH_2OH
(b) $CH_3CH_2CH_3$
(c) CH_3CH_2Cl

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

UNIT 58 Properties of Liquids

Question 58-1.

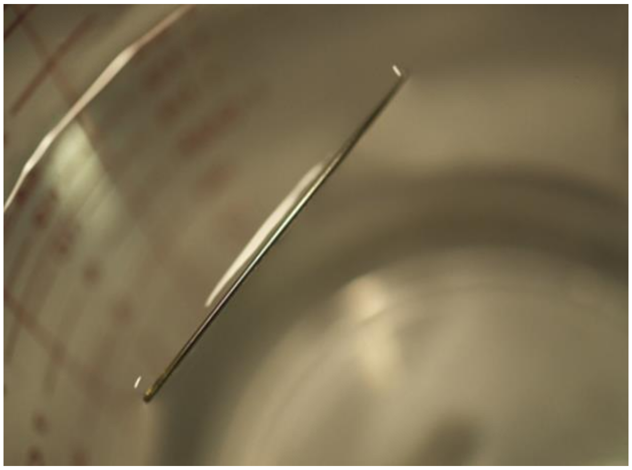
The test tubes shown here contain equal amounts of the specified motor oils. Identical metal spheres were dropped at the same time into each of the tubes, and a brief moment later, the spheres had fallen to the heights indicated in the illustration.
Rank the motor oils in order of increasing viscosity, and explain your reasoning:



Solution
The more viscous the oil, the more slowly the sphere will descend. The depth to which the metal sphere has descended at any given time is therefore inversely related to the viscosity of the oil. The relative viscosities of these oil samples is then SAE 20 < SAE 30 < SAE 40 < SAE 50.

Question 58-2.

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.



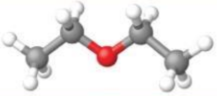
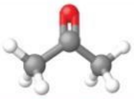
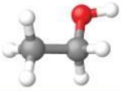
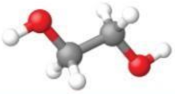
(credit: Cory Zanker)

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.

Question 58-3.

The surface tension and viscosity values for diethyl ether, acetone, ethanol, and ethylene glycol are shown here.

Compound	Molecule	Surface Tension (mN/m)	Viscosity (mPa s)
diethyl ether $C_2H_5OC_2H_5$		17	0.22
acetone CH_3COCH_3		23	0.31
ethanol C_2H_5OH		22	1.07
ethylene glycol $CH_2(OH)CH_2(OH)$		48	16.1

(a) Explain their differences in viscosity in terms of the size and shape of their molecules and their IMFs.

(b) Explain their differences in surface tension in terms of the size and shape of their molecules and their IMFs: **Solution**

(a) The higher the viscosity, the stronger the intermolecular forces are. Ethylene glycol and ethanol both exhibit hydrogen bonding, but ethylene glycol molecules contain twice as many –

OH groups as ethanol molecules, and so its viscosity is higher. Acetone has a lower viscosity than ethanol since its dipole-dipole force is weaker than hydrogen bonding. Ether has a lower viscosity than acetone, since it is less polar than acetone. (b) The higher the surface tension, the stronger the intermolecular forces are. Ethylene glycol has a higher surface tension than ethanol, since it can hydrogen bond more with its two –OH groups per molecule. Surprisingly, the surface tension of ethanol and acetone are roughly the same. The acetone molecules are planar, and so are able to orient themselves in a planar manner so as to create a tight skin at the surface to match the hydrogen bonding of ethanol. Ether is nonplanar, and it displays a weaker dipole and so its surface tension is lowest.

Question 58-4.

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.

Question 58-5.

It is often recommended that you let your car engine run idle to warm up before driving, especially on cold winter days. While the benefit of prolonged idling is dubious, it is certainly true that a warm engine is more fuel efficient than a cold one. Explain the reason for this.

Solution

A warm engine's oil is less viscous, and so it flows more freely and thus more effectively lubricates the engines internal parts (primarily its pistons). This permits the engine to run with less friction and, subsequently, more fuel efficiently.

Question 58-6.

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.

Question 58-7.

At 25 °C, how high will water rise in a glass capillary tube with an inner diameter of 0.63 mm? Refer to Example 10.4 for the required information.

Solution

The liquid will rise to a height h given by: $h = \frac{2T\cos\square}{r\square g}$.

$$h = \frac{2(0.07199\ \text{kg/s}^2)}{(0.000315\ \text{m})(1000\ \text{kg/m})(9.8\ \text{m/s})} = 0.047\ \text{m} = 4.7\ \text{cm}$$

Question 58-8.

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.

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

$r = 8.6 \square 10^{-5}\ \text{m}\ d = \ =2r\ 1.7$
$10\square\ ^{-4}m$

UNIT 59 Phase Transitions

Question 59-1.

Heat is added to boiling water. Explain why the temperature of the boiling water does not change. What does change?

Solution

The heat increases the kinetic energy of a limited number of molecules in the liquid water so that they have enough energy to escape into the gas phase. The escape of these molecules requires the additional energy be used to overcome intermolecular attractive forces in the liquid, and so the temperature of the remaining liquid does not increase. The amount of liquid water changes (decreases) as the additional heat causes some to change to a gas.

Question 59-2.

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.

Question 59-3.

What feature characterizes the dynamic equilibrium between a liquid and its vapor in a closed container? **Solution**

Molecules are continually exchanged between the liquid and the vapor. This exchange of position and energy maintains a constant vapor pressure and a constant temperature.

Question 59-4.

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.

Question 59-5.

Identify two common observations indicating some solids, such as dry ice and mothballs, have vapor pressures sufficient to sublime?

Solution

We can see solid ice disappear outside even when the temperature is below freezing and no liquid water is formed. The other substances disappear without forming the respective liquids, and an aroma can be detected for mothballs, attesting to the sublimation of the substance.

Question 59-6.

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.

Question 59-7.

What is the relationship between the intermolecular forces in a solid and its melting temperature?

Solution

The melting point of a substance increases as the strength of its intermolecular increases.

Question 59-8.

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.

Question 59-9.

Carbon tetrachloride, CCl_4, was once used as a dry cleaning solvent, but is no longer used because it is carcinogenic. At 57.8 °C, the vapor pressure of CCl_4 is 54.0 kPa, and its enthalpy of vaporization is 33.05 kJ/mol. Use this information to estimate the normal boiling point for CCl_4.

Solution

Normal boiling point corresponds to pressure of 1 atm. Using Clausius Clapeyron equation,

$$\ln\left(\frac{P_1}{P_2}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

54 kPa = 0.53 atm

$$\ln\left(\frac{0.53 \text{ atm}}{1 \text{ atm}}\right) = \left(\frac{33050 \text{ J/mol}}{8.31 \text{ J/mol K}}\right)\left(\frac{1}{T_2} - \frac{1}{331.0 \text{ K}}\right)$$

Solving for $\frac{1}{T_2} = 0.00286$ and so, $T_2 = 349$ K or, 76 °C

Question 59-10.

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.

Question 59-11.

How does the boiling of a liquid differ from its evaporation?

Solution
At the boiling point, the vapor pressure of the liquid is the same as the atmospheric pressure. During evaporation, the vapor pressure of the liquid is less than atmospheric pressure. Evaporation is the term used to describe a relatively slow vaporization process that can occur at temperatures below the boiling point.

Question 59-12.

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.

Question 59-13.

A syringe at a temperature of 20 □C is filled with liquid ether in such a way that there is no space for any vapor. If the temperature is kept constant and the plunger is withdrawn to create a volume that can be occupied by vapor, what would be the approximate pressure of the vapor produced? **Solution**
(a) about 450 torr; ether boils at approximately 36 °C; at 20 °C, the vapor pressure will be relatively high

Question 59-14.

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.

Question 59-15.

The enthalpy of vaporization of water is larger than its enthalpy of fusion. Explain why.

Solution

When water melts, the hydrogen bonding in the solid is only partially overcome to yield the liquid. When water evaporates, intermolecular attractions between its molecules must be completely overcome, requiring a greater amount of energy.

Question 59-16.

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.

Question 59-17.

Explain why the enthalpies of vaporization of the following substances increase in the order $CH_4 < NH_3 < H_2O$, even though all three substances have approximately the same molar mass.

Solution

Methane, CH_4, is a nonpolar molecule and thus experiences only relatively weak dispersion forces in the liquid state. Ammonia and water are both polar molecules and, furthermore, are capable of hydrogen bonding. The greater IMFs associated with hydrogen bonding result in higher enthalpies of vaporization for these two substances. Because the electronegativity of O is greater than that for N, it is reasonable to predict that the O-H bond moments are greater than the N-H bond moments, and that hydrogen bonding is more extensive in water than in ammonia, supporting the reported trend in vaporization enthalpies.

Question 59-18.

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.

Question 59-19.

The hydrogen fluoride molecule, HF, is more polar than a water molecule, H_2O (for example, has a greater dipole moment), yet the molar enthalpy of vaporization for liquid hydrogen fluoride is lesser than that for water. Explain.

Solution

Each water molecule has two H atoms that may participate in hydrogen bonding with other water molecules, while a hydrogen fluoride molecule has only one. Less heat is therefore required to overcome hydrogen bonding in liquid HF than in liquid H_2O.

Question 59-20.

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.

Question 59-21.

Which contains the compounds listed correctly in order of increasing boiling points?

(a) $N_2 < CS_2 < H_2O < KCl$
(b) $H_2O < N_2 < CS_2 < KCl$
(c) $N_2 < KCl < CS_2 < H_2O$
(d) $CS_2 < N_2 < KCl < H_2O$
(e) $KCl < H_2O < CS_2 < N_2$

Solution

The trend in boiling points should follow the trend in forces holding the substances (atoms/molecules) together. KCl is an ionic compound, and so the ionic bonding (electrostatic attraction between the potassium cations and chloride anions) is expected to be far stronger than any intermolecular forces within the other covalent compounds. KCl is, therefore, expected to exhibit the greatest boiling point. Of the remaining compounds, only H_2O is polar (and, indeed, it exhibits strong hydrogen bonding), and so its IMFs are predicted to be greater than the other covalent compounds listed. Comparing the remaining nonpolar compounds, CS_2 molecules are larger/more massive than N_2 molecules, and so carbon disulfide will experience greater dispersion forces, and a greater boiling point.

Question 59-22.

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: $\Delta H_1 = mC_s\Delta T = (422 \text{ g})(4.184 \text{ J/g °C})(100.0 - 23.5) = 135{,}000 \text{ J}$

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)(1.86 J/g °C)(150 – 100) = 39,000 J.
Adding ΔH_1, ΔH_2, and ΔH_3: 135,000 J + 951,000 J + 39,000 J = 1,125,000 J = 1125 kJ.

Question 59-23.

Evaporation of sweat requires energy and thus take excess heat away from the body. Some of the water that you drink may eventually be converted into sweat and evaporate. If you drink a 20ounce bottle of water that had been in the refrigerator at 3.8 °C, how much heat is needed to convert all of that water into sweat and then to vapor? (Note: Your body temperature is 36.6 °C. For the purpose of solving this problem, assume that the thermal properties of sweat are the same as for water.

Solution

$$20\text{ oz } H_2O \times \frac{29.6\text{ g}}{1\text{ oz}} = 590\text{ mL } H_2O$$

590 mL H_2O $\times$ 1.00 g/mL = 590 g H_2O

$$590\text{ g } H_2O \times \frac{1\text{ mol}}{18.02\text{ g } H_2O} = 32.7\text{ mol } H_2O$$

or 33 mol H_2O using the correct number of significant figures. The amount of heat needed to increase the temperature of water from 3.8 °C to 36.6 °C is $\Delta H_1 = mC_s\Delta T$ = (590 g)(4.184 J/g °C)(36.6 – 3.8) = 81,000 J. Heat needed to vaporize this amount of water: $\Delta H_2 = n\Delta H_{vap}$ = (33 mol)(40,650 J/mol) =1,340,000 J. The total heat required for the process is 81,000 J + 1,340,000 J = 1,420,000 J = 1420 kJ.

Question 59-24.

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) $263.1\text{ g } TiCl_4 \times \frac{1\text{ mol}}{\text{g}}$ = 1.385 mol $TiCl_4$. Heat required to melt this amount of $TiCl_4$ is 189.9 $n\Delta H_{fusion}$ = 1.385 mol $\times$ 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.

UNIT 60 Phase Diagrams

Question 60-1.

From the phase diagram for water (Figure 10.31), determine the state of water at:

(a) 35 °C and 85 kPa
(b) –15 °C and 40 kPa
(c) –15 °C and 0.1 kPa
(d) 75 °C and 3 kPa
(e) 40 °C and 0.1 kPa (f) 60 °C and 50 kPa

Solution

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

Question 60-2.

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.

Question 60-3.

Pressure cookers allow food to cook faster because the higher pressure inside the pressure cooker increases the boiling temperature of water. A particular pressure cooker has a safety valve that is set to vent steam if the pressure exceeds 3.4 atm. What is the approximate maximum temperature that can be reached inside this pressure cooker? Explain your reasoning.

Solution

From looking at a phase diagram for water, the maximum temperature would be around 150 °C. Increased pressure from the pressure cooker allows water to boil at higher temperatures.

Question 60-4.

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

So Question lution

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

Question 60-5.

Determine the phase changes that carbon dioxide undergoes as pressure is increased at a constant temperature of (a) –50 °C and (b) 50 °C? (See the phase diagram in Figure 10.34.) **Solution**

(a) At –50 °C and low pressures, carbon dioxide is gaseous. Increasing the pressure at this temperature will result in condensation (gas-to-liquid phase transition) at ~700 kPa and freezing (liquid-to-solid phase transition) at ~10,000 kPa.

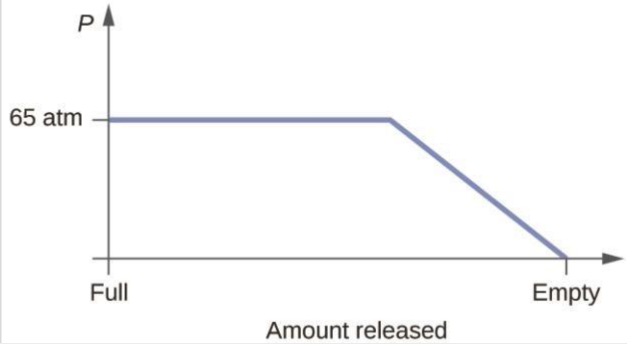
(b) Since 50 °C is above the critical temperature for carbon dioxide (31 °C), increasing the pressure cannot cause condensation, but instead a transition to the supercritical fluid state occurs at ~7000 kPa.

Question 60-6.

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:



Question 60-7.

Dry ice, $CO_2(s)$, does not melt at atmospheric pressure. It sublimes at a temperature of –78 °C. What is the lowest pressure at which $CO_2(s)$ will melt to give $CO_2(l)$? At approximately what temperature will this occur? (See Figure 10.34 for the phase diagram.)

Solution

The lowest pressure at which a solid may melt is that corresponding to its triple point. Dry ice, $CO_2(s)$, will melt to give $CO_2(l)$ at ~500 kPa and –60°C.

Question 60-8.

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.

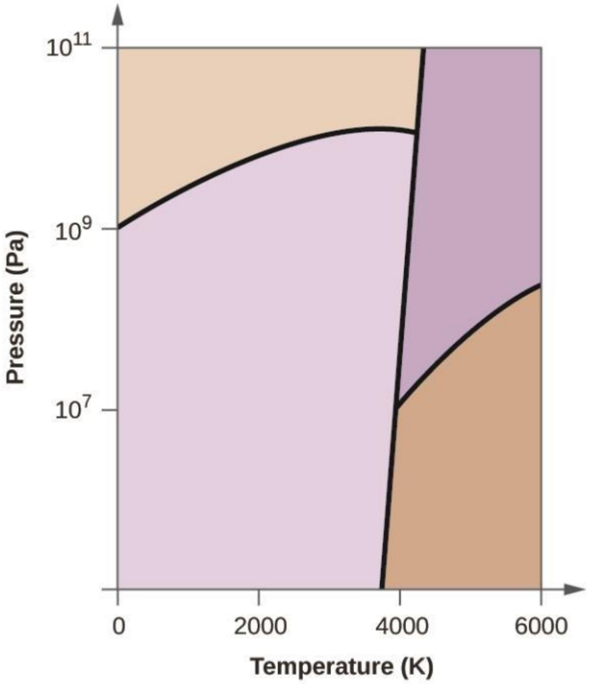
Question 60-9.

Is it possible to liquefy nitrogen at room temperature (about 25 °C)? Is it possible to liquefy sulfur dioxide at room temperature? Explain your answers.

Solution
From Table 10.3, the critical temperature of nitrogen is 126.0 K. Since this value is below room temperature, nitrogen cannot be liquefied at room temperature. The critical temperature is 430.5 K for sulfur dioxide, which is above room temperature. It can be liquefied at room temperature.

Question 60-10.

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

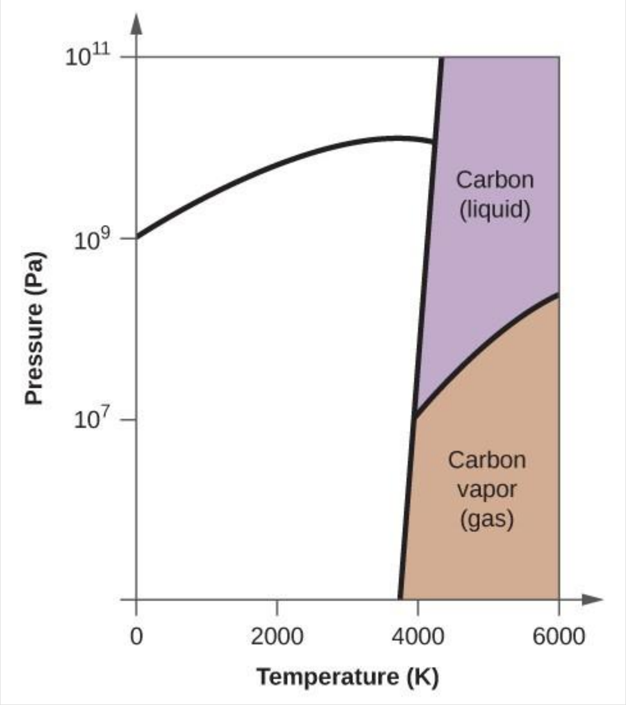


(a) On the phase diagram, label the gas and liquid regions.
(b) Graphite is the most stable phase of carbon at normal conditions. On the phase diagram, label the graphite phase.
(c) If graphite at normal conditions is heated to 2500 K while the pressure is increased to 10^{10} Pa, it is converted into diamond. Label the diamond phase.
(d) Circle each triple point on the phase diagram.

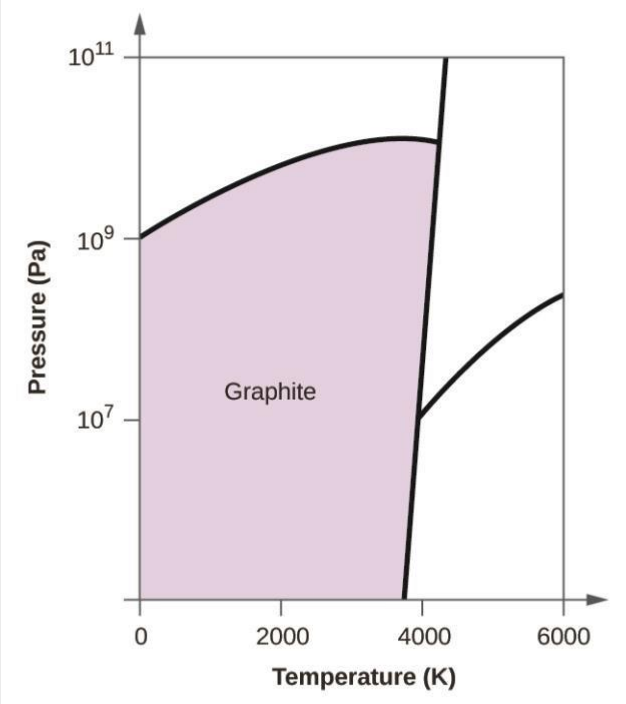
(e) In what phase does carbon exist at 5000 K and 10^8 Pa?
(f) If the temperature of a sample of carbon increases from 3000 K to 5000 K at a constant pressure of 10^6 Pa, which phase transition occurs, if any?

Solution

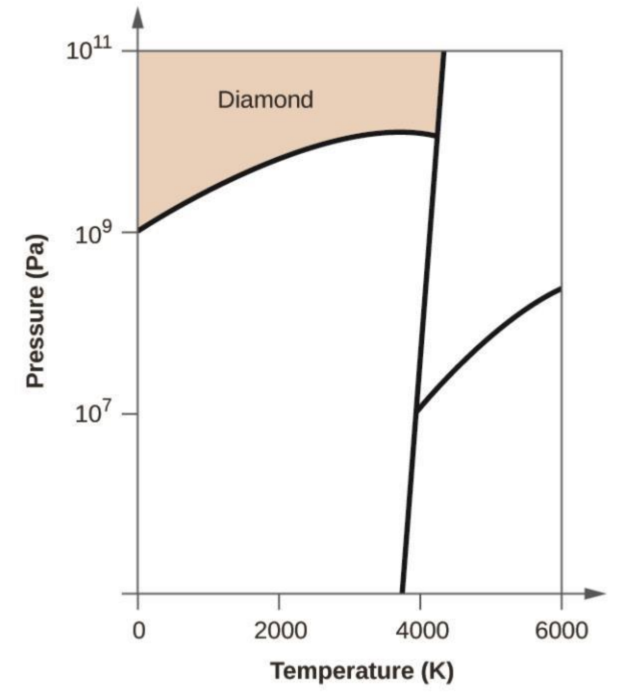
(a)



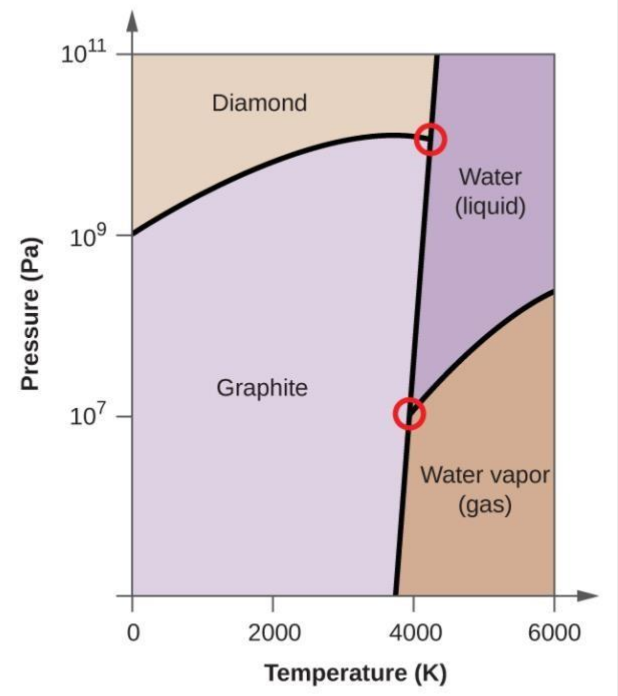
(b)



(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.

UNIT 61 The Solid State of Matter

Question 61-1.

What types of liquids typically form amorphous solids?

Solution

Amorphous solids lack an ordered internal structure. Liquid materials that contain large, cumbersome molecules that cannot move readily into ordered positions generally form such solids.

Question 61-2.

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

Question 61-3.

As it cools, olive oil slowly solidifies and forms a solid over a range of temperatures. Which best describes the solid?

(a) ionic
(b) covalent network
(c) metallic
(d) amorphous
(e) molecular crystals

Solution

(d) amorphous

Question 61-4.

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.

Question 61-5.

Identify the type of crystalline solid (metallic, network covalent, ionic, or molecular) formed by each of the following substances: (a) SiO_2

(b) KCl
(c) Cu
(d) CO_2
(e) C (diamond)
(f) $BaSO_4$
(g) NH_3
(h) NH_4F
(i) C_2H_5OH

Solution

(a) SiO_2, covalent network; (b) KCl, ionic; (c) Cu, metallic; (d) CO, molecular; (e) C (diamond), covalent network; (f) $BaSO_4$, ionic; (g) NH_3, molecular; (h) NH_4F, ionic; (i) C_2H_5OH, molecular

Question 61-8.

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

Question 61-9.

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	lustrous, malleable	1500 °C	high	insoluble
Y	soft, yellow	113 °C	none	insoluble
Z	hard, white	800 °C	only if melted/dissolved	soluble

Solution

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

Question 61-10.

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

Substance	Appearance	Melting Point	Electrical	Solubility in
			Conductivity	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

Question 61-11.

Identify the following substances as ionic, metallic, covalent network, or molecular solids: Substance A is malleable, ductile, conducts electricity well, and has a melting point of 1135 °C. Substance B is brittle, does not conduct electricity as a solid but does when molten, and has a melting point of 2072 °C. Substance C is very hard, does not conduct electricity, and has a melting point of 3440 °C. Substance D is soft, does not conduct electricity, and has a melting point of 185 °C.

Solution

A = metallic; B = ionic; C = covalent network; D = molecular

Question 61-12.

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

Question 61-13.

Substance B is hard, does not conduct electricity, and melts at 1200 °C. Substance B is likely a(n):

(a) ionic solid
(b) metallic solid
(c) molecular solid
(d) covalent network solid **Solution**
(d) covalent network solid

UNIT 62 Lattice Structures in Crystalline Solids

Question 62-1.

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.

Question 62-2.

Describe the crystal structure of Pt, which crystallizes with four equivalent metal atoms in a cubic unit cell.

Solution

Each of the eight corners of a cube has $\frac{1}{8}$ Pt atom contributing to the cube. In addition, each of the six faces includes $\frac{1}{2}$ Pt atom. The total is $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$. The structure, therefore, is face-centered cubic, or cubic closest packed.

Question 62-3.

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.

Question 62-4.

What is the coordination number of an aluminum atom in the face-centered cubic structure of aluminum? **Solution**

Face-centered cubic structures occur with cubic closest packing in which each atom touches 12 nearest neighbors: six in its own layer and three in each adjacent layer. The coordination number, therefore, is 12.

Question 62-5.

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.

Question 62-6.

Nickel metal crystallizes in a cubic closest packed structure. What is the coordination number of a nickel atom? **Solution**

Cubic closest packed structures are packed with each atom touching 12 nearest neighbors: six in its own layer, and three in each adjacent layer. The coordination number, therefore, is 12.

Question 62-7.

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

$d = 2\sqrt{e}$

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

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

$= 2e^2 + e^2 = 3e^2$

diagonal = $3\ e =$

$4r$ $\sqrt{\ }$

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

(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):

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

3.170 □ 10-23 cm3 −23 3 −1

V(atom) = = 1.585 × 10 cm atom

2 atoms

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

183.85 g mol^{-1}

density = $\quad ^{3} \quad ^{-1}$

9.546 cm mol

= 19.26 g/cm

Question 62-8.

Platinum (atomic radius = 1.38 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of platinum.

Solution

In a face-centered cube containing identical atoms or radius, r, the edge length it 2r 2 . For platinum, r =1.38 Å

edge length = 2(1.38) 2 = 3.90 The volume of a unit cell is:

3

□ 10^{-8} cm □

□

V (unit cell) = 3.90 Å × □ ______ Å

□ Å □

= 5.93 □ 10^{-23} cm^3

One unit cell contains four atoms, so 1 mol of Pt contains:

6.022 □ 10 $atoms^{23}$ 1 unit cell $\quad ^{23} \quad ^{-1}$

□ = 1.506 □ 10 unit cells mol

1 mol 4 atoms

The mass of 1 mol of Pt is 195.09 g. The density is:

mass 195.09 g mol^{-1} $\quad ^{-3}$

density = = $\quad ^{23} \quad ^{-1} \quad ^{-23} \quad ^{3}$ = 21.8 g cm

volume (1.506 × 10 cells mol) (5.93 □ 10 cm)

Question 62-9.

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

$d = 2\ e$

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

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

$= 4r = 3e$

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

(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):

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

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

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

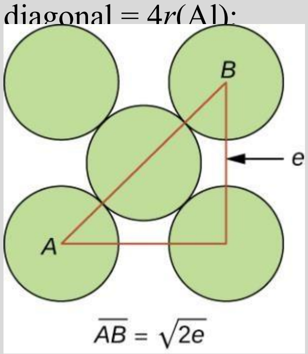
$$d(\text{Ba}) = \frac{137.33\ \text{g}}{38.204\ \text{cm}^3} = 3.595\ \text{g/cm}^3$$

Question 62-10.

Aluminum (atomic radius = 1.43 Å) crystallizes in a cubic closely packed structure. Calculate the edge length of the face-centered cubic unit cell and the density of aluminum.

Solution

Aluminum atoms are in contact along the diagonal of the cube face:
diagonal = $4r(\text{Al})$:



The diagonal $\overline{AB}$ or d is given by $4r$ or 4 × 1.43Å. The edge length is found from the Pythagorean theorem where $d = \sqrt{2}e$.

$$e = \frac{d}{\sqrt{2}} = \frac{5.72\ \text{Å}}{\sqrt{2}} = 4.05\ \text{Å}$$

$$V(\text{cell}) = e^3 = (4.05 \times 10^{-8}\ \text{cm})^3 = 6.643 \times 10^{-23}\ \text{cm}^3$$

$$V(\text{mol}) = 6.643 \times 10^{-23}\ \frac{\text{cm}^3}{\text{cell}} \times \frac{1\ \text{cell}}{4\ \text{atoms}} \times 6.022 \times 10^{23}\ \frac{\text{atoms}}{\text{mol}}$$

$= 10.001\ \text{cm}^3/\text{mol}$

$$d(\text{Al}) = 26.9815\frac{\text{g}}{\text{mol}} \times \frac{1\ \text{mol}}{10.001\ \text{cm}^3} = 2.70\ \text{g cm}^{-3}$$

Question 62-11.

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).

Question 62-12.

The free space in a metal may be found by subtracting the volume of the atoms in a unit cell from the volume of the cell. Calculate the percentage of free space in each of the three cubic lattices if all atoms in each are of equal size and touch their nearest neighbors. Which of these structures represents the most efficient packing? That is, which packs with the least amount of unused space?

Solution

A simple cubic crystal lattice of side $2r$ contains one atom of radius r.
free space = volume of cube – volume of atom

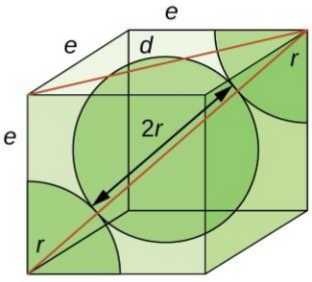
$= (2r)^3 - \frac{4}{3}\square r^3$

$= 8r^3 - 4.1888\ r^3$

$= 3.8112\ r^3$

percent free space = $\frac{3.8112r^3}{8r^3} \times 100 = 47.64\%$

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



The diagonal of the cube is $4r$.

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

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

so $(4r)^2 = 3e^2$

$e = 4r/\sqrt{3}$ (length of edge)

free space = $(4r/\sqrt{3})^3 - 2\left(\frac{4}{3}\pi r^3\right)$

$= 12.3168r^3 - 8.3776r^3$

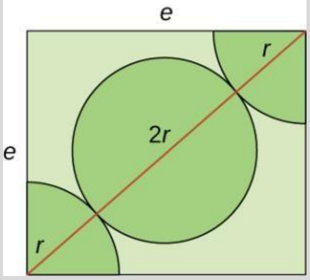
$= 3.9392r^3$

percent free space = $\frac{3.9392r^3}{12.3168r^3} \times 100 = 31.98\%$

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

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

$e = 2\sqrt{2}r$:



free space = $(2\sqrt{2}r)^3 - 4\left(\frac{4}{3}\pi r^3\right)$

$= 22.624r^3 - 16.7552r^3$

$= 5.8722r^3$

percent free space = $\frac{5.8722r^3}{22.6274r^3} \times 100 = 25.95\%$

The face-centered cube has the least amount of unused space.

Question 62-13.

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.

Question 62-14.

A compound of cadmium, tin, and phosphorus is used in the fabrication of some semiconductors. It crystallizes with cadmium occupying one-fourth of the tetrahedral holes and tin occupying one-fourth of the tetrahedral holes in a closest packed array of phosphide ions. What is the formula of the compound? 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. When one-fourth of the holes are occupied, there is one cation for two phosphide ions. Therefore, there is one cadmium and one tin for every two phosphide ions. The formula for the compound is $CdSnP_2$.

Question 62-15.

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.

Question 62-16.

A compound containing zinc, aluminum, and sulfur crystallizes with a closest-packed array of sulfide ions. Zinc ions are found in one-eighth of the tetrahedral holes and aluminum ions in onehalf of the octahedral holes. What is the empirical formula of the compound?

Solution

The ratio of Zn:Al:S is determined from the ratio of holes to the sulfur anions. In this case, two tetrahedral:one octahedral: 1 S. Given the filling order $\frac{1}{8}:\frac{1}{2}:1$, the empirical formula is

$$\mathrm{Zn}\frac{1}{8}\times 2:\mathrm{Al}\frac{1}{2}\times 1:\mathrm{S};\ \text{or}\ \mathrm{Zn}\frac{1}{4}:\mathrm{Al}\frac{1}{2}:\mathrm{S}$$

After multiplying through by 4, the equation is ZnAlS.

Question 62-17.

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.

Question 62-18.

Which of the following elements reacts with sulfur to form a solid in which the sulfur atoms form a closest-packed array with all of the octahedral holes occupied: Li, Na, Be, Ca, or Al?

Solution

There is one octahedral hole for each anion in a closest-packed array. If all of the octahedral holes are occupied, the substance contains one sulfur ion for each other ion. Only the elements Be and Ca are expected to form a compound with the formula ES, where E is a doubly charged cation and S is the anion. The radius ratios are:

Be^{2+}: $r^+/r^- = 0.31/1.84 = 0.17$

Ca^{2+}: $r^+/r^- = 0.99/1.84 = 0.54$

Only Ca^{2+} has a ratio within the 0.414 to 0.732 range expected for a coordination number of six. The answer is Ca.

Question 62-19.

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.

Question 62-20.

Explain why the chemically similar alkali metal chlorides NaCl and CsCl have different structures, whereas the chemically different NaCl and MnS have the same structure.

Solution

Structures are determined from charge and size and are not directly related to chemical similarity. In this case, the r^+/r^- value for CsCl is sufficiently greater than that of NaCl so that a different structure is required.

Question 62-21.

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+}.

Question 62-22.

Rubidium iodide crystallizes with a cubic unit cell that contains iodide ions at the corners and a rubidium ion in the center. What is the formula of the compound?

Solution

Because an iodide ion is located at each corner, the unit cell contains one-eighth of each of the eight anions, or one iodide ion. Because one rubidium ion appears at the center of the cell, the ratio of ions contained in the cell is 1:1. The formula is RbI.

Question 62-23.

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.

Question 62-24.

NaH crystallizes with the same crystal structure as NaCl. The edge length of the cubic unit cell of NaH is 4.880 Å.

(a) Calculate the ionic radius of H^-. (The ionic radius of Li^+ is 0.0.95 Å.) (b) Calculate the density of NaH.

Solution

(a) Assume a face-centered arrangement with the hydride ions in contact along the diagonal face. Sodium ions fill the space along the edge, giving an edge length of $2r_{\text{Na}^+} + 2r_{\text{H}^-}$. The radius of the hydride is computed from the edge length and the reported radius of Na^+:

$$e = 4.880\ \text{Å} = 2(0.95\ \text{Å}) + 2r_{\text{H}^-}$$

$$\frac{4.880\ \text{Å} - 1.90\ \text{Å}}{2};\quad r_{\text{H}^-} = = 1.49\ \text{Å}$$

(b) To find the density of NaH, consider that the system is face-centered cubic; there are four NaH units per cell.

$V\,(\text{cell}) = (4.880 \times 10^{-8}\ \text{cm})^3 = 1.162 \times 10^{-22}\ \text{cm}^3$

$$V\,(\text{NaH unit cell}) = \frac{1.162 \times 10^{-22}\ \text{cm}^3}{4} = 2.905 \times 10^{-23}\ \text{cm}^3$$

$V\,(\text{mol}) = 2.905 \times 10^{-23}\ \text{cm}^3 \times 6.022 \times 10^{23}\ \text{units/mol} = 17.496\ \text{cm}^3/\text{mol}$

The formula weight of NaH is 24.00 g/mol.

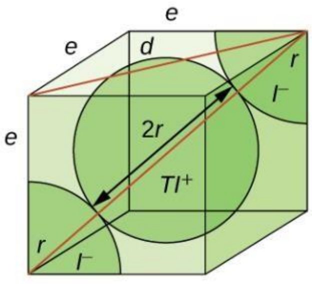
$$d(\text{NaH}) = \frac{24.00\ \text{g mol}^{-1}}{17.496\ \text{cm}^3\ \text{mol}^{-1}} = 1.372\ \text{g cm}$$

Question 62-25.

At temperatures above ~175 °C, thallium(I) iodide crystallizes with the same structure as CsCl. The edge length of the unit cell of TlI is 4.20 Å. Assuming contact between the body-centered Tl^+ ion and the cube-corner I^- ions of a unit cell, calculate the ionic radius of TI^+. (The ionic radius of I^- is 2.16 Å.)

Solution

Though the TlI unit cell is not truly a BCC structure (the body-centered and corner atoms/ions are not identical), the geometry of this structure is appropriate here and may be used to calculate approximate values for ionic radii.



The diagonal of the cube is $2r_{I^-} + 2r_{Tl^+}$. The Pythagorean theorem gives

$(2r_{I^-} + 2r_{Tl^+})^2 = d^2 + e^2$.

Since $d^2 = e^2 + e^2$,

$(2r_{I^-} + 2r_{Tl^+})^2 = 3e^2$

$2r_{I^-} + 2r_{Tl^+} = \sqrt{3e}$

Substituting the provided cell edge length and I^- radius values yields:

$$(2)(2.16\,\mathring{A}) + 2r_{Tl^+} = \sqrt{3}(4.20\,\mathring{A})$$

$$r_{Tl^+} = \frac{\sqrt{3}(4.20\,\mathring{A}) - 2(2.16)\,\mathring{A}}{2} = 1.48\,\mathring{A}$$

Question 62-26.

A cubic unit cell contains manganese ions at the corners and fluoride ions at the center of each edge.

(a) What is the empirical formula of this compound? Explain your answer.
(b) What is the coordination number of the Mn^{3+} ion?
(c) Calculate the edge length of the unit cell if the radius of a Mn^{3+} ion is 0.65 A.
(d) Calculate the density of the compound.

Solution

(a) Mn (corners) $8 \times \frac{1}{8} = 1$

F (edges) $12 \times \frac{1}{4} = 3$

The formula is MnF_3.

(b) There are six edges radiating from each Mn^{3+}. Each edge contains a nearest-neighbor F^- ion, so the coordination number of the Mn^{3+} ion is 6.

(c) The edge length is:

$$\begin{aligned} r_{Mn} + 2r_F + r_{Mn} &= 2(r_{Mn} + r_F) \\ &= 2(0.65 + 1.36) \\ &= 4.02 \text{ Å} \end{aligned}$$

(d) Each unit cell contains one Mn^{3+} ion, so 1 mol of MnF_3 contains 6.022×10^{23} unit cells:

$$V\text{(unit cell)} = \left(4.02 \text{ Å} \times \frac{10^{-8} \text{ cm}}{1 \text{ Å}}\right)^3$$

$= 6.50 \times 10^{-23}$ cm^3/cell

The mass of 1 mol of MnF_3 is 111.9375 g/mol.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{111.9375 \text{ g mol}^{-1}}{(6.022 \times 10^{23} \text{ cell mol}^{-1}) \times \left(\frac{6.50 \times 10^{-23} \text{ cm}^3}{\text{cell}}\right)}$$

$$= 2.68 \text{ g cm}^{-3}$$

Question 62-27.

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

Solution

The Bragg equation is:

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

where d is the spacing between planes.

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

$= 2.874$ Å

Question 62-28.

A diffractometer using X-rays with a wavelength of 0.2287 nm produced first-order diffraction peak for a crystal angle $\theta = 16.21°$. Determine the spacing between the diffracting planes in this crystal.

Solution

$$d = \frac{n\lambda}{2\sin\theta} = \frac{(1)(0.2287 \text{ nm})}{(2)(\sin 16.21)} = 0.41 \text{ nm}$$

Question 62-29.

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

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

Question 62-30.

Gold crystallizes in a face-centered cubic unit cell. The second-order reflection (n = 2) of X-rays for the planes that make up the tops and bottoms of the unit cells is at $\theta = 22.20^\circ$. The wavelength of the X-rays is 1.54 Å. What is the density of metallic gold?

Solution

The unit cell edge is *d* (from the Bragg equation), the spacing between planes. Calculate *d* and use it to compute unit cell volumes. Given that the face-centered cell contains four atoms, calculate the molar volume and then the density.

$$e = d = \frac{n\lambda}{2\sin\square} = \frac{2(1.54 \square 10^{-8}\text{ cm})}{2\sin 22.20\square} = 4.0758 \square 10^{\circ}\text{ cm}$$

$$V\text{(cell)} = (4.0758 \times 10^{-8}\text{ cm})^3 = 6.7707 \times 10^{-23}\text{ cm}$$

$$V\text{(atom)} = \frac{V\text{(cell)}}{4} = 1.6927 \times 10^{-23}\text{ cm}^3$$

$$V\text{(mol)} = \frac{1.69271\ 0^{-23}\text{ cm}^3}{\text{atom}} \times 6.022 \times 10^{23}\text{ atom/mol}$$

$$= 10.1933\text{ cm}^3\text{ mol}^{-1}$$

$$\text{density (Au)} = \frac{196.9665\text{ g}}{10.1933\text{ cm}^3} = 19.3\text{ g cm}^{-3}$$

Question 62-31.

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 $n = 1$, $\lambda = 2$

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

Then hc $(6.626 \square 10^{-34}\text{ J s})(2.998 \square 10\text{ m s}$

$)^{8\ -1}$

$$E = \ = {}_{-10}\ \lambda\ 0.712 \times 10\text{ m}$$

$$= 2.79 \square 10^{-15}\text{ J} = 1.74 \square 10\text{ eV}^4$$