Chapter 11

States of Matter; Liquids and Solids

Concept Check 11.1

Shown here is a representation of a closed container in which you have just placed 10 L of H_2O. In our experiment, we are going to call this starting point in time $t = 0$ and assume that all of the H_2O is in the liquid phase. We have represented a few of the H_2O molecules in the water as dots.

$t = 0$

a. Consider a time, $t = 1$, at which some time has passed but the system has not reached equilibrium.
   (i) How will the level of the liquid H_2O compare to that at $t = 0$?
   (ii) How will the vapor pressure in the flask compare to that at $t = 0$?
   (iii) How will the number of H_2O molecules in the vapor state compare to that at $t = 0$?
   (iv) How does the rate of evaporation in this system compare to the rate of condensation?
   (v) Draw a picture of the system at $t = 1$.

b. Consider a time, $t = 2$, at which enough time has passed for the system to reach equilibrium.
   (i) How will the level of the liquid H_2O compare to that at $t = 1$?
   (ii) How will the vapor pressure in the flask compare to that at $t = 1$?
   (iii) How will the number of H_2O molecules in the vapor state compare to that at $t = 1$?
   (iv) How does the rate of evaporation in this system compare to the rate of condensation?
   (v) Draw a picture of the system at $t = 2$.

Solution

a. (i) At $t = 0$, since the system is not at equilibrium and there are no H_2O molecules in the gaseous state, you would expect the rate of evaporation to exceed the rate of condensation. At $t = 1$, since evaporation has proceeded at a greater rate than condensation, there must now be fewer molecules in the liquid state resulting in a lower level of H_2O (*l*).

(ii) At $t = 1$, since some of the H_2O has gone into the vapor state, the vapor pressure must be higher.

(iii) At $t = 1$, since evaporation has occurred, there must be more molecules in the vapor state.

(iv) At $t = 0$, since the system is not at equilibrium and there are no H_2O molecules in the gaseous state, you would expect the rate of evaporation to exceed the rate of condensation.

(v)

$t = 1$

b. (i) Between $t = 1$ and $t = 2$, the system is still prior to reaching equilibrium. Therefore, the rate of evaporation continues to exceed the rate of condensation so you would expect the water level to be lower.

(ii) Prior to reaching equilibrium at $t = 2$, you would continue to observe a rate of evaporation greater than the rate of condensation resulting in a higher vapor pressure than $t = 1$.

(iii) Since evaporation has been occurring at a greater rate than condensation between points $t = 1$ and $t = 2$, you would expect more molecules in the vapor state at $t = 2$.

(iv) When the system has reached equilibrium at $t = 2$, the rate of evaporation equals the rate of condensation.

(v)

t = 2

Concept Check 11.2

When camping at high altitude, you need to pay particular attention to changes in cooking times for foods that are boiled in water. If you like eggs that are boiled for 10 minutes near sea level, would you have to cook them for a longer or shorter time at 3200 m to get the egg you like? Be sure to explain your answer.

Solution

You would have to cook the egg for a longer time. The reason is that since there is lower atmospheric pressure at high altitude, water boils at a lower temperature than near sea level. Since the temperature is lower, it would take longer to transfer an equivalent amount of heat to the egg.

Concept Check 11.3

A common misconception is that the following chemical reaction occurs when boiling water: $2H_2O(l) \rightarrow 2H_2(g) + O_2(g)$ instead of $H_2O(l) \rightarrow H_2O(g)$.

a. What physical evidence do you have that the second reaction is correct?
b. How would the enthalpy of the wrong reaction compare with that of the correct reaction?
c. How could you calculate the enthalpy change for the wrong reaction (see Chapter 6)?

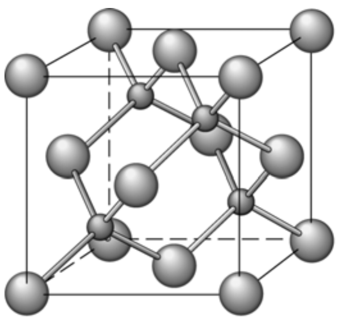
Solution

a. If the first reaction occurred, the mixture of hydrogen and oxygen that resulted would form an explosive mixture.
b. Since you would be breaking strong chemical bonds and forming relatively weak bonds, the enthalpy for the first reaction (the wrong reaction) would be many times greater (more positive) than for the second reaction.

c. Apply Hess's law. The enthalpy for the wrong reaction would be equal to two times ΔH_f^o for $H_2O(l)$, plus the heat required to raise the temperature of two moles of water from 25°C to 100°C.

Concept Check 11.4

Shown here is a representation of a unit cell for a crystal. The large balls (they are orange in the text) are atom A, and the small black balls are atom B.



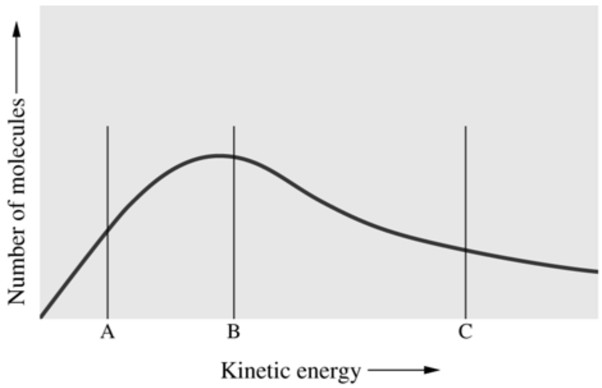
a. What is the chemical formula of the compound that has this unit cell ($A_?B_?$)?
b. Consider the configuration of the A atoms. Is this a cubic unit cell? If so, which type?

Solution

a. First, consider the B balls (small). There are four atoms, each completely inside the cell. Thus, there are four B atoms per cell. Next, there are 14 A atoms (large). Of these, eight are in corners and contribute 1/8 to the cell. Six atoms are in faces and contribute 1/2 to the cell. Thus, there are 8 x (1/8) + 6 x (1/2) = 4 A atoms per cell. The ratio of A atoms to B atoms is 4 to 4, or 1 to 1. Thus the formula of the compound is AB.
b. Since all of the B atoms are completely within the cell, the shape of the cell is determined by the A atoms only. It is a face-centered cubic unit cell.

Conceptual Problem 11.21

Shown here is a curve of the distribution of kinetic energies of the molecules in a liquid at an arbitrary temperature *T*.



The lines marked A, B, and C represent the point where each of the molecules for three different liquids (liquid A, liquid B, and liquid C) has enough kinetic energy to escape into the gas phase (see Figure 11.5 for more information). Write a brief explanation for each of your answers to the following questions.

a. Which of the molecules – A, B, or C – would have the majority of the molecules in the gas phase at temperature *T*?
b. Which of the molecules – A, B, or C – has the strongest intermolecular attractions?
c. Which of the molecules would have the lowest vapor pressure at temperature *T*?

Solution

a. The number of molecules in the gas phase is directly related to the kinetic energy needed to escape into the gas phase. The molecules with the most kinetic energy will have the most molecules in the gas phase. Since molecules of C have the highest kinetic energy, they will have the majority of molecules in the gas phase.
b. The molecules with the strongest intermolecular attractions will have the lowest kinetic energy. Since molecules of A have the lowest kinetic energy, they will have the strongest intermolecular attractions.
c. The molecules with the strongest intermolecular attractions will have the lowest vapor pressure. Thus, molecules of A would have the lowest vapor pressure.

Conceptual Problem 11.22

Consider a substance X with a ΔH_{vap} = 20.3 kJ/mol and ΔH_{fus} = 9.0 kJ/mol. The melting point, freezing point, and heat capacities of both the solid and liquid X are identical to those of water.

a. If you placed one beaker containing 50 g of X at -10°C and another beaker with 50 g of H_2O at -10°C on a hot plate and started heating them, which material would reach the boiling point first?
b. Which of the materials from part a., X or H_2O, would completely boil away first?

c. On a piece of graph paper, draw the heating curve for H_2O and X. How do the heating curves reflect your answers from parts a. and b. of this problem?

Solution

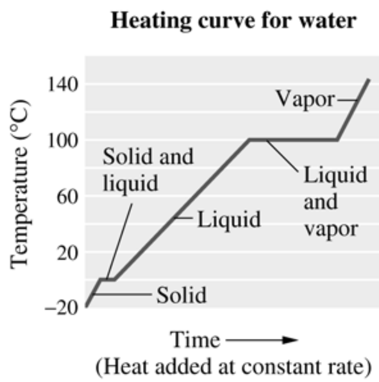
You will need to compare the heats of fusion and vaporization of substance X (ΔH_{fus} = 9.0 kJ/mol and ΔH_{vap} = 20.3 kJ/mol) with the values for water, which are ΔH_{fus} = 6.01 kJ/mol and ΔH_{vap} = 40.7 kJ/mol. Comparing values shows that ΔH_{fus} is 1.5 times larger for substance X, and ΔH_{vap} is 2.0 times larger for H_2O.

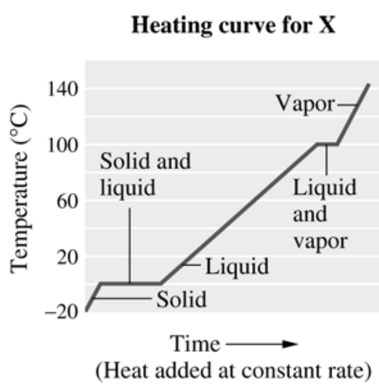
Heating the substance, or water, from -10°C to the boiling point is a three step process. Step 1 is to heat the solid from -10°C to 0°C, the freezing point. The heat required for this step is equal to mass x specific heat capacity x temperature change. Step 2 is to melt the solid to liquid at 0°C. The heat required for this step is equal to moles x ΔH_{fus}. Step 3 is to heat the liquid from 0°C to 100°C. The heat required for this step is equal to mass x specific heat capacity x temperature change.

a. Since the masses, heat capacities, and temperature changes for water and for substance X are all equal, the heat required for step 1 and step 3 are the same for both. Since ΔH_{fus} is larger for substance X (per mole), step 2 will require more heat for substance X, and thus take longer. Therefore, H_2O will reach the boiling point first.

b. To completely boil away the substance, an additional step is required. Step 4 is to boil the liquid to vapor at 100°C. The heat required for this step is equal to moles x ΔH_{vap}. Since the ΔH_{vap} values are much larger than the ΔH_{fus} values, step 4 will require much more heat than step 2 for both substance X and H_2O. Since ΔH_{vap} is smaller for substance X (per mole), step 4 will require less heat for substance X, and thus take less time. The total heat required for the four steps is directly proportional to the time it would take to completely boil away the substance. Steps 1 and 3 are the same for both. Step 2 takes 1.5 times as long for substance X, but step 4 takes 2.0 times as long for water. Since step 4 requires the most heat, water will require more time to complete this step, so substance X will boil away first.

c. The heating curves for substance X and for water are shown below.





Conceptual Problem 11.23

Using the information presented in this chapter, explain why farmers spray water above and on their fruit trees on still nights when they know the temperature is going to drop below 0°C. (*Hint*: Totally frozen fruit is what the farmers are trying to avoid).

Solution

The water that the farmers spray above and on their fruit will be warmer than the temperature of the fruit on the trees. Therefore, as the temperature of the air drops, it absorbs heat from the water, converting it into ice, before absorbing any heat from the fruit. The heat released when the liquid to solid phase change occurs prevents the fruit from freezing.

Conceptual Problem 11.24

You are presented with three bottles, each containing a different liquid: bottle A, bottle B, and bottle C. Bottle A's label states that it is an ionic compound with a boiling point of 35°C. Bottle B's label states that it is a molecular compound with a boiling point of 29.2°C. Bottle C's label states that it is a molecular compound with a boiling point of 67.1°C.

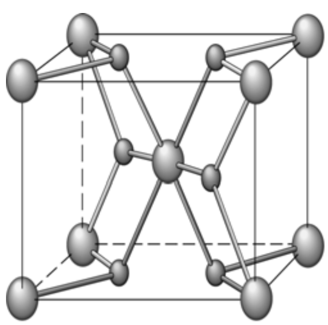
a. Which of the compounds is most likely to be incorrectly identified?
b. If Bottle A were a molecular compound, which of the compounds has the strongest intermolecular attractions?
c. If Bottle A were a molecular compound, which of the compounds would have the highest vapor pressure?

Solution

a. Bottle A is most likely mislabeled. If it is an ionic compound, the boiling point should be higher than 35°C. Most ionic compounds are solids, with high melting points.
b. The substance with the highest boiling point will have the strongest intermolecular attractions. Thus, the compound in bottle C has the strongest intermolecular attractions.
c. The substance with the lowest boiling point will have the highest vapor pressure. Thus the substance in bottle B will have the highest vapor pressure.

Conceptual Problem 11.25

Shown here is a representation of a unit cell for a crystal. The large balls are atom A (they are orange in text), and the small black balls are atom B.



a. What is the chemical formula of the compound that has this unit cell ($A_?B_?$)?
b. Consider the configuration of the A atoms. Is this a cubic unit cell? If so, which type?

Solution

a. Considering the A atoms, there are nine per cell. Of these, eight are in corners and contribute 1/8 per cell, and one is completely inside the cell. Thus there are 8 x (1/8) + 1 x (1) = 2 A atoms per cell. Next, considering the B atoms, there are six per cell. Of these, four are in faces and contribute 1/2 per cell, and two are completely inside the cell. Thus, there are 4 x (1/2) + 2 x (1) = 4 B atoms per unit cell. The ratio of A atoms to B atoms is 2 to 4, or 1 to 2. Thus, the formula of the compound is AB_2.

b. The A atoms are in the arrangement of a body-centered cell.

Conceptual Problem 11.26

Assuming normal winter conditions (-1.5°C and 1.0 atm pressure), consult the phase diagram for water (Fig. 11.11) and come up with a reason why ice skates and sleds slide so well on solid water. Keep in mind that sleds and ice skates do not typically slide well on other solid surfaces (concrete and metal, for example).

Solution

Consulting the phase diagram for water (Figure 11.11), you see that by increasing the pressure on the solid ice at constant temperature, you will convert solid ice into liquid water. The film of liquid that forms allows the skates and sleds to slide so well.

Conceptual Problem 11.27

If you place room temperature water in a well-insulated cup and allow some of the water to evaporate, the temperature of the water in the cup will drop lower than room temperature. Come up with an explanation for this observation.

Solution

As the water evaporates, the molecules with higher kinetic energy escape the liquid, leaving behind the molecules with lower energy. The result is a drop in temperature of the liquid. Since the cup is well insulated, the energy lost with the evaporated molecules is not rapidly replaced.

Conceptual Problem 11.28

The heats of vaporization for water and carbon disulfide are 40.7 kJ/mol and 26.8 kJ/mol, respectively. A vapor (steam) burn occurs when the concentrated vapor of a substance condenses on your skin. Which of these substances, water or carbon disulfide, would result in the most severe burn if identical quantities of each vapor at a temperature just above their boiling point came in contact with your skin?

Solution

The heat released when the vapor of a substance condenses to liquid is equal to the negative (opposite) of the heat of vaporization for the substance. Due to its strong intermolecular attractions, water has a larger heat of vaporization, so it releases more heat when condensing on the skin causing a more severe burn.