

Exercises

Review Questions

- 1. Why do ethanol and dimethyl ether have such different properties even though they have the same chemical formula?
- 2. Why are intermolecular forces important?
- 3. What are the key properties of liquids (in contrast to gases and solids)?
- 4. What are the key properties of solids (in contrast to liquids and gases)?
- 5. What is the fundamental difference between an amorphous solid and a crystalline solid?
- 6. Which factors cause transitions between the solid and liquid state? The liquid and gas state?
- 7. Describe the relationship between the state of a substance, its temperature, and the strength of its intermolecular forces.
- 8. From which kinds of interactions do intermolecular forces originate?
- 9. Why are intermolecular forces generally much weaker than bonding forces?
- 10. What is the dispersion force? What does the magnitude of the dispersion force depend on? How can we predict the magnitude of the dispersion force for closely related elements or compounds?
- 11. What is the dipole-dipole force? How can we predict the presence of dipole-dipole forces in a compound?
- 12. How is the miscibility of two liquids related to their polarity?
- 13. What is hydrogen bonding? How can we predict the presence of hydrogen bonding in a compound?
- 14. What is the ion-dipole force? Why is it important?
- 15. What is surface tension? How does surface tension result from intermolecular forces? How is it related to the strength of intermolecular forces?
- 16. What is viscosity? How does viscosity depend on intermolecular forces? What other factors affect viscosity?
- 17. What is capillary action? How does it depend on the relative strengths of adhesive and cohesive forces?
- 18. Explain what happens during the processes of vaporization and condensation. Why does the rate of vaporization increase with increasing temperature and surface area?
- 19. Why is vaporization endothermic? Why is condensation exothermic?
- 20. How is the volatility of a substance related to the intermolecular forces present within the substance?
- 21. What is the heat of vaporization for a liquid, and why is it useful?
- 22. Explain the process of dynamic equilibrium. How is dynamic equilibrium related to vapor pressure?
- 23. What happens to a system in dynamic equilibrium when it is disturbed in some way?
- 24. How is vapor pressure related to temperature? What happens to the vapor pressure of a substance when the temperature is increased? Decreased?
- 25. Define the terms boiling point and normal boiling point.
- 26. What is the Clausius-Clapeyron equation, and why is it important?
- 27. Explain what happens to a substance when it is heated in a closed container to its critical temperature.
- 28. What is sublimation? Cite a common example of sublimation.
- 29. What is fusion? Is fusion exothermic or endothermic? Why?
- 30. What is the heat of fusion, and why is it important?
- **31.** Examine the heating curve for water in Section 11.7 ☐ (Figure 11.33 ☐). Explain why the curve has two segments in which heat is added to the water but the temperature does not rise.
- 32. Examine the heating curve for water in Section 11.7 [Figure 11.33]. Explain the significance of the slopes of each of the three rising segments. Why are the slopes different?
- 33. What is a phase diagram? What is the significance of crossing a line in a phase diagram?
- 34. Draw a generic phase diagram and label its important features.

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 $Note: Answers\ to\ all\ odd-numbered\ Problems\ can\ be\ found\ in\ Appendix\ III.\ Exercises\ in\ the\ Problems\ by\ Topic\ section\ are$ paired, with each odd-numbered problem followed by a similar even-numbered problem. Exercises in the Cumulative Problems section are also paired but more loosely. Because of their nature, Challenge Problems and Conceptual Problems are unpaired.

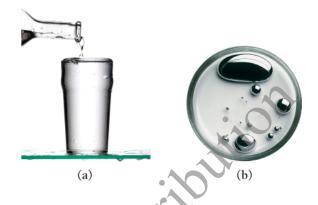
Intermolecular Forces
35. Determine the kinds of intermolecular forces that are present in each element or compound.
a. N_2
b. NH_3
c. CO
$\mathbf{d.} \ \mathrm{CCl}_4$
36. Determine the kinds of intermolecular forces that are present in each element or compound.
a. Kr
b. NCl_3
c. $\mathrm{SiH_4}$
d. HF
37. Determine the kinds of intermolecular forces that are present in each element or compound.
a. HCl
b. $\mathrm{H}_2\mathrm{O}$
${f c.}~{ m Br}_2$
d. He
38. Determine the kinds of intermolecular forces that are present in each element or compound.
a. PH_3
b. HBr
c. CH ₃ OH
$\mathbf{d}.~\mathbf{I}_2$
39. Arrange these compounds in order of increasing boiling point. Explain your reasoning.
a. CH_4
b. $\mathrm{CH_{3}CH_{3}}$
c. CH ₃ CH ₂ Cl
d. CH ₃ CH ₂ OH
40. Arrange these compounds in order of increasing boiling point. Explain your reasoning.
a. $\mathrm{H}_2\mathrm{S}$
b. $\mathrm{H}_2\mathrm{Se}$
c. H ₂ O
41. Pick the compound with the highest boiling point in each pair. Explain your reasoning.
a. CH ₃ OH or CH ₃ SH
b. $\mathrm{CH_{3}OCH_{3}}$ or $\mathrm{CH_{2}CH_{2}OH}$
c. $\mathrm{CH_4}$ or $\mathrm{CH_3CH_3}$
42. Pick the compound with the highest boiling point in each pair. Explain your reasoning.
a. $\mathrm{NH_3}$ or $\mathrm{CH_4}$
b. CS_2 or CO_2
${f c.~CO_2}$ or ${f NO_2}$
43. In each pair of compounds, pick the one with the higher vapor pressure at a given temperature. Explain you
reasoning.
a. Br_2 or I_2
b. H_2S or H_2O
${f c.}~{ m NH_3}~{ m or}~{ m PH_3}$
44. In each pair of compounds, pick the one with the higher vapor pressure at a given temperature. Explain you
reasoning.
a. $\mathrm{CH_4}$ or $\mathrm{CH_3Cl}$
b. $\mathrm{CH_{3}CH_{2}CH_{2}OH}$ or $\mathrm{CH_{3}OH}$
c. $\mathrm{CH_3OH}\ \mathrm{or}\ \mathrm{H_2CO}$
45. Determine if each pair of compounds forms a homogeneous solution when combined. For those that form

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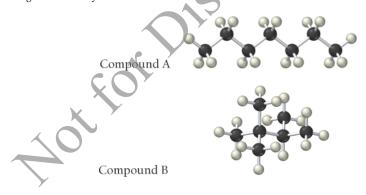
- a. CCl_4 and H_2O
- b. KCl and H_2O
- c. Br_2 and CCl_4
- d. CH₃CH₂OH and H₂O
- **46.** Determine if each pair of compounds forms a homogeneous solution when combined. For those that form homogeneous solutions, indicate the type of forces that are involved.
 - a. $CH_3CH_2CH_2CH_2CH_3$ and $CH_3CH_2CH_2CH_2CH_3$
 - **b.** CBr_4 and H_2O
 - c. $LiNO_3$ and H_2O
 - d. CH_3OH and $CH_3CH_2CH_2CH_2CH_3$

Surface Tension, Viscosity, and Capillary Action

- 47. Which compound would you expect to have greater surface tension: acetone $[(CH_3)_2CO]$ or water (H_2O) ? Explain.
- **48.** Water (a) "wets" some surfaces and beads up on others. Mercury (b), in contrast, beads up on almost all surfaces. Explain this difference.



49. The structures of two isomers of heptane are shown here. Which of these two compounds would you expect to have the greater viscosity?



- **50.** The viscosity of a multigrade motor oil (such as one rated 10W-40) is less temperature dependent than the viscosities of most substances. These oils contain polymers (long molecules composed of repeating units) that coil up at low temperatures but unwind at higher temperatures. Explain how the addition of these polymers to the motor oil might make the viscosity less temperature dependent than a normal liquid.
- **51.** Water in a glass tube that contains grease or oil residue displays a flat meniscus (the tube on the left in the accompanying photo), whereas water in a clean glass tube displays a concave meniscus (the tube on the right). Explain this observation.



52. When a thin glass tube is put into water, the water rises 1.4 cm. When the same tube is put into hexane, the hexane rises only 0.4 cm. Explain.

Vaporization and Vapor Pressure

- 53. Which evaporates more quickly: 55 mL of water in a beaker with a diameter of 4.5 cm or 55 mL of water in a dish with a diameter of 12 cm? Is the vapor pressure of the water different in the two containers? Explain.
- **54.** Which evaporates more quickly: 55 mL of water (H_2O) in a beaker or 55 mL of acetone $[(CH_3)_2CO]$ in an identical beaker under identical conditions? Is the vapor pressure of the two substances different? Explain.
- 55. Spilling room-temperature water over your skin on a hot day cools you down. Spilling room-temperature vegetable oil over your skin on a hot day does not. Explain the difference.
- **56.** Why is the heat of vaporization of water greater at room temperature than it is at its boiling point?
- 57. The human body obtains 915 kJ of energy from a candy bar. If this energy were used to vaporize water at 100 °C, how much water (in liters) could be vaporized? (Assume the density of water is 1.00 g/mL.)
- 58. A 100.0 mL sample of water is heated to its boiling point. How much heat (in kJ) is required to vaporize it? (Assume a density of 1.00 g/mL.)
- 59. Suppose that 0.95 g of water condenses on a 75.0 g block of iron that is initially at 22 °C. If the heat released during condensation is used only to warm the iron block, what is the final temperature (in °C) of the iron block? (Assume a constant enthalpy of vaporization for water of 44.0 kJ/mol.)
- **60.** Suppose that 1.15 g of rubbing alcohol (C_3H_8O) evaporates from a 65.0 g aluminum block. If the aluminum block is initially at 25 °C, what is the final temperature of the block after the evaporation of the alcohol? Assume that the heat required for the vaporization of the alcohol comes only from the aluminum block and that the alcohol vaporizes at 25 $^{\circ}$ C.
- 61. This table displays the vapor pressure of ammonia at several different temperatures. Use the data to determine the heat of vaporization and normal boiling point of ammonia.

Temperature (K)	Pressure (torr)	
200	65.3	
210	134.3	
220	255.7	
230	456.0	
235	597.0	

62. This table displays the vapor pressure of nitrogen at several different temperatures. Use the data to determine the heat of vaporization and normal boiling point of nitrogen.

Temperature (K)	Pressure (torr)
65	130.5
70	289.5
75	570.8
80	1028
85	1718

- 63. Ethanol has a heat of vaporization of 38.56 kJ/mol and a normal boiling point of 78.4 °C. What is the vapor pressure of ethanol at 15 °C?
- 64. Benzene has a heat of vaporization of 30.72 kJ/mol and a normal boiling point of 80.1 °C. At what temperature does benzene boil when the external pressure is 445 torr?

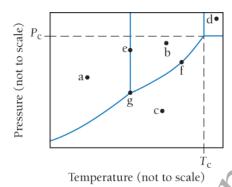
Sublimation and Fusion

- 65. How much energy is released when 65.8 g of water freezes?
- 66. Calculate the amount of heat required to completely sublime 50.0 g of solid dry ice (CO₂) at its sublimation

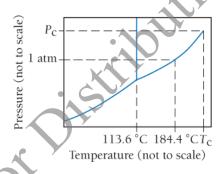
- temperature. The heat of sublimation for carbon dioxide is 32.3 kJ/mol.
- **67.** An 8.5 g ice cube is placed into 255 g of water. Calculate the temperature change in the water upon the complete melting of the ice. Assume that all of the energy required to melt the ice comes from the water.
- **68.** How much ice (in grams) would have to melt to lower the temperature of 352 mL of water from 25 $^{\circ}$ C to 5 $^{\circ}$ C? (Assume the density of water is 1.0 g/mL.)
- **69.** How much heat (in kJ) is required to warm 10.0 g of ice, initially at -10.0 °C, to steam at 110.0 °C? The heat capacity of ice is $2.09 \text{ J/g} \cdot ^{\circ}\text{C}$, and that of steam is $2.01 \text{ J/g} ^{\circ}\text{C}$.
- 70. How much heat (in kJ) is evolved in converting 1.00 mol of steam at 145 °C to ice at -50 °C? The heat capacity of steam is 2.01 J/g °C, and that of ice is 2.09 J/g · °C.

Phase Diagrams

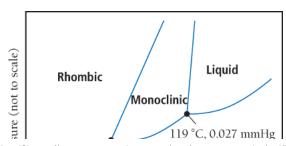
71. Identify the states present at points a through g in the phase diagram shown here.



72. Consider the phase diagram for iodine shown here.

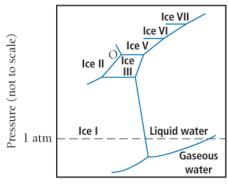


- a. What is the normal boiling point for iodine?
- **b.** What is the melting point for iodine at 1 atm?
- c. Which state is present at room temperature and normal atmospheric pressure?
- d. Which state is present at 186 °C and 1.0 atm?
- 73. Nitrogen has a normal boiling point of 77.3 K and a melting point (at 1 atm) of 63.1 K. Its critical temperature is 126.2 K, and its critical pressure is 2.55×10^4 torr. It has a triple point at 63.1 K and 94.0 torr. Sketch the phase diagram for nitrogen. Does nitrogen have a stable liquid state at 1 atm?
- **74.** Argon has a normal boiling point of 87.2 K and a melting point (at 1 atm) of 84.1 K. Its critical temperature is 150.8 K, and its critical pressure is 48.3 atm. It has a triple point at 83.7 K and 0.68 atm. Sketch the phase diagram for argon. Which has the greater density, solid argon or liquid argon?
- **75.** Consider the phase diagram for sulfur shown here. The rhombic and monoclinic states are two solid states with different structures.



Temperature (not to scale)

- a. Below what pressure does solid sulfur sublime?
- b. Which of the two solid states of sulfur is most dense?
- **76.** The high-pressure phase diagram of ice is shown here. Notice that, under high pressure, ice can exist in several different solid forms. Which three forms of ice are present at the triple point marked O? What is the density of ice II compared to ice I (the familiar form of ice)? Would ice III sink or float in liquid water?



Temperature (not to scale)

The Uniqueness of Water

- 77. Water has a high boiling point given its relatively low molar mass. Explain.
- 78. Water is a good solvent for many substances. What is the molecular basis for this property, and why is it significant?
- 79. Explain the role water plays in moderating Earth's climate.
- **80.** How is the density of solid water compared to that of liquid water atypical among substances? Why is this significant?

Cumulative Problems

81. Explain the observed trend in the melting points of the hydrogen halides.



82. Explain the observed trend in the boiling points of these compounds.

$$\begin{array}{ll} {\rm H_2Te} & -2\,^{\circ}{\rm C} \\ {\rm H_2Se} & -41.5\,^{\circ}{\rm C} \, . \\ {\rm H_2S} & -60.7\,^{\circ}{\rm C} \\ {\rm H_2O} & 100\,^{\circ}{\rm C} \end{array}$$

- 83. The vapor pressure of water at $25 \,^{\circ}$ C is 23.76 torr. If 1.25 g of water is enclosed in a 1.5 L container, is any liquid present? If so, what is the mass of the liquid?
- **84.** The vapor pressure of CCl₃F at 300 K is 856 torr. If 11.5 g of CCl₃F is enclosed in a 1.0 L container, is any liquid present? If so, what is the mass of the liquid?
- **85.** Four ice cubes at exactly 0 °C with a total mass of 53.5 g are combined with 115 g of water at 75 °C in an insulated container. If no heat is lost to the surroundings, what is the final temperature of the mixture?
- **86.** A sample of steam with a mass of 0.552 g at a temperature of 100 °C condenses into an insulated container holding 4.25 g of water at 5.0 °C. Assuming that no heat is lost to the surroundings, what is the final

87. Draw a heating curve (such as the one in Figure 11.33) for 1 mole of methanol beginning at 170 K and ending at 350 K. Assume that the values given here are constant over the relevant temperature ranges.

Melting point	176 K	
Boiling point	338 K	
ΔH_{fus}	2.2 kJ/mol	
ΔH_{vap}	35.2 kJ/mol	
$C_{s, solid}$	105 J/mol⋅K	
$C_{\rm s,liquid}$	81.3 J/mol·K	
C _{s, gas}	48 J/mol·K	

88. Draw a heating curve (such as the one in Figure 11.33) for 1 mol of benzene beginning at 0 °C and ending at 100 °C. Assume that the values given here are constant over the relevant temperature ranges.

Melting point	5.4°C
Boiling point	90.1°C
ΔH_{fus}	9.9 kJ/mol
ΔH_{vap}	30.7 kJ/mol
$C_{\rm s, solid}$	118 J/mol·K
$C_{ m s,\ liquid}$	135 J/mol·K
C _{s, gas}	104 J/mol · K

- 89. Air conditioners not only cool air but dry it as well. A room in a home measures $6.0~\mathrm{m} \times 10.0~\mathrm{m} \times 2.2~\mathrm{m}$. If the outdoor temperature is 30 °C and the vapor pressure of water in the air is 85% of the vapor pressure of water at this temperature, what mass of water must be removed from the air each time the volume of air in the room cycles through the air conditioner? The vapor pressure for water at 30 °C is 31.8 torr.
- 90. A sealed flask contains 0.55 g of water at 28 °C. The vapor pressure of water at this temperature is 28.36 mmHg. What is the minimum volume of the flask in order that there is no liquid water present in the flask?

Challenge Problems

91. Two liquids, A and B, have vapor pressures at a given temperature of 24 mmHg and 36 mmHg, respectively. We prepare solutions of A and B at a given temperature and measure the total pressures above the solutions. We obtain these data:

Solution	Amt A (mol)	Amt B (mol)	P (mmHg)
1	1	1	30
2	2	1	28
3	1	2	32
4	1	3	33

Predict the total pressure above a solution of 5 mol A and 1 mol B.

- 92. Butane (C_4H_{10}) has a heat of vaporization of 22.44 kJ/mol and a normal boiling point of -0.4 °C. A 250.0 mL sealed flask contains 0.55 g of butane at -22 °C. How much liquid butane is present? If the butane is warmed to 25 °C, how much liquid butane is present?
- 93. Liquid nitrogen can be used as a cryogenic substance to obtain low temperatures. Under atmospheric pressure, liquid nitrogen boils at 77 K, allowing low temperatures to be reached. However, if the nitrogen is placed in a sealed, insulated container connected to a vacuum pump, even lower temperatures can be reached. Why? If the vacuum pump has sufficient capacity and is left on for an extended period of time, the liquid nitrogen starts to freeze. Explain.
- 94. Given that the heat of fusion of water is -6.02 kJ/mol, the heat capacity of $H_2O(l)$ is $75.2 \text{ J/mol} \cdot \text{K}$, and the heat canacity of H. O (e) is 37.7 I/mol. K. calculate the heat of fusion of water at =10 °C

- 95. The heat of combustion of CH_4 is 890.4 kJ/mol, and the heat capacity of H_2O is 75.2J/mol · K. Find the volume of methane measured at 298 K and 1.00 atm required to convert 1.00 L of water at 298 K to water vapor at 373 K.
- 96. Three 1.0-L flasks, maintained at 308 K, are connected to each other with stopcocks. Initially, the stopcocks are closed. One of the flasks contains 1.0 atm of N_2 ; the second, 2.0 g of H_2O ; and the third, 0.50 g of ethanol, C_2H_6O . The vapor pressure of H_2O at 308 K is 42 mmHg, and that of ethanol is 102 mmHg. When the stopcocks are opened and the contents mix freely, what is the pressure?

Conceptual Problems

- 97. One prediction of global warming is the melting of global ice, which may result in coastal flooding. A criticism of this prediction is that the melting of icebergs does not increase ocean levels any more than the melting of ice in a glass of water increases the level of liquid in the glass. Is this a valid criticism? Does the melting of an ice cube in a cup of water raise the level of the liquid in the cup? Why or why not? In response to this criticism, scientists have asserted that they are not worried about melting icebergs, but rather the melting of ice sheets that sit on the continent of Antarctica. Would the melting of this ice increase ocean levels? Why or why not?
- **98.** The rate of vaporization depends on the surface area of the liquid. However, the vapor pressure of a liquid does not depend on the surface area. Explain.
- **99.** Substance A has a smaller heat of vaporization than substance B. Which of the two substances undergoes a larger change in vapor pressure for a given change in temperature?
- 100. A substance has a heat of vaporization of ΔH_{vap} and heat of fusion of ΔH_{fus} . Express the heat of sublimation in terms of ΔH_{vap} and ΔH_{fus} .
- **101.** Examine the heating curve for water in Section 11.7 (Figure 11.33). If heat is added to the water at a constant rate, which of the three segments in which temperature is rising will have the least steep slope? Why?
- **102.** A root cellar is an underground chamber used to store fruits, vegetables, and sometimes meats. In extreme cold, farmers put large vats of water into the root cellar to prevent fruits and vegetables from freezing. Explain why this works.
- **103.** Suggest an explanation for the observation that the heat of fusion of a substance is always smaller than its heat of vaporization.
- **104.** Refer to Figure 11.33 to answer each question.
 - **a.** A sample of steam begins on the line segment labeled 5 on the graph. Is heat absorbed or released in moving from the line segment labeled 5 to the line segment labeled 3? What is the sign of *q* for this change?
 - **b.** In moving from left to right along the line segment labeled 2 on the graph, heat is absorbed, but the temperature remains constant. Where does the heat go?
 - c. How would the graph charge if it were for another substance (other than water)?
- **105.** The following image is an electrostatic potential map for ethylene oxide, $(CH_2)_2O$, a polar molecule. Use the electrostatic potential map to predict the geometry for how one ethylene oxide molecule interacts with another. Draw structural formulas, using the three-dimensional bond notation introduced in Section 5.9 , to show the geometry of the interaction.



106. A substance has a triple point at a temperature of 17 °C and a pressure of 3.2 atmospheres. In which states can the substance exist on the surface of Earth at sea level (open to the atmosphere)?

Questions for Group Work

Active Classroom Learning

Discuss these questions with the group and record your consensus answer.

107. The boiling points of three compounds are tabulated here.

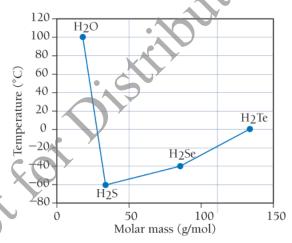
	Molar Mass	Boiling Point
2-hexanone	100.16	128°C
heptane	100.20	98°C
1-hexanol	102.17	156°C

Answer the following questions without looking up the structures for these molecules: Which compound experiences hydrogen bonding? Which compound is polar but does not experience hydrogen bonding? Which is neither polar nor capable of hydrogen bonding? Explain your answers.

- 108. The vapor pressure for pure water and pure acetone is measured as a function of temperature. In each case, a graph of the log of the vapor pressure versus 1/T is found to be a straight line. The slope of the line for water is -4895 K, and the slope of the line for acetone is -6748 K. Determine $\Delta H_{\rm vap}$ for each substance. Account for the difference by discussing the molecular structure of the two molecules.
- 109. Based on the heating curve for water, does it take more energy to melt a mole of water or to boil a mole of water? Does it take more energy to warm the solid, the liquid, or the gas by 10 °C? Explain your answers clearly.
- **110.** Sketch the phase diagram for carbon dioxide. If you have carbon dioxide at 1.0 atm and 25 °C, could you turn it into a liquid by cooling it down? How could you make it a liquid at 25 °C? If you increase the pressure of carbon dioxide that is at body temperature (37 °C), will it ever liquefy?

Data Interpretation and Analysis

111. We have seen that molar mass and molecular structure influence the boiling point. We can see these two factors at work in the boiling points of the Group 6A hydrides shown in the graph.



Boiling Point versus Molar Mass for Group 6A Hydrides

In order to disentangle the effects of molar mass and molecular structure on boiling point, consider the data in the table.

Compound	Molar Mass	<i>n</i> -Boiling Point (°C)	Dipole Moment (D)	Polarizability (10 ⁻²⁴ cm ³)
H ₂ O	18.01	100	1.85	1.45
H ₂ S	34.08	-60	1.10	3.81
H₂Se	80.98	-42.2	0.41	4.71
H ₂ Te	129.6	-2.2	0.22	5.01

Use the information in the graph and the table to answer the questions.

- a. Does molar mass alone correlate with the trend in the boiling points for the Group 6A hydrides?
- b. Which boiling points in the graph correlate with polarizability? Which type of intermolecular force correlates with polarizability?
- c. Use the data in the table to explain the anomalously high boiling point of water.

Answers to Conceptual Connections

Cc 11.1 [a] When water boils, it simply changes state from liquid to gas. Water molecules do not decompose during boiling.

Cc 11.2 (c) I₂ has the highest boiling point because it has the highest molar mass. Because the halogens are

all similar in other ways, you would expect I_2 to have the greatest dispersion forces and therefore the highest

boiling point (and in fact it does).

Cc 11.3 -

$$\begin{array}{ccc}
H & & H \\
H & & H
\end{array}$$

$$\begin{array}{ccc}
H & & H \\
H & & H
\end{array}$$

Cc 11.4 [□] (a) CH₃OH. The compounds all have similar molar masses, so the dispersion forces are similar in all

three. CO is polar, but because $\mathrm{CH_3OH}$ contains H directly bonded to O, it has hydrogen bonding, resulting in

the highest boiling point.

Cc 11.5 (b) Although the rate of vaporization increases with increasing surface area, the vapor pressure of a liquid is independent of surface area. An increase in surface area increases both the rate of vaporization and the rate of condensation—the effects exactly cancel, and the vapor pressure does not change.

Cc 11.6 The warming of the ice from −10 °C to 0 °C absorbs only 20.9 J/g of ice. The melting of the ice, however, absorbs about 334 J/g of ice. (You can obtain this value by dividing the heat of fusion of water by its molar mass.) Therefore, the melting of the ice produces a larger temperature decrease in the water than the warming of the ice.

Cc 11.7 [6] (b) The solid will sublime into a gas. Since the pressure is below the triple point, the liquid state is not stable. Hotrof

Aot for Distribution

Aot for Distribution