above that of liquid nitrogen were recently discovered. The structures of these materials are based on the perovskite structure. Were they to have the ideal perovskite structure, the superconductor would have the structure shown in part (a) of the figure below.

![Ideal perovskite structure](image1)

![Actual structure of superconductor](image2)

(a) Ideal perovskite structure  
(b) Actual structure of superconductor

**Phase Changes and Phase Diagrams**

87. Plot the following data and determine $\Delta H_{\text{vap}}$ for magnesium and lithium. In which metal is the bonding stronger?

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Vapor Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Mg</td>
</tr>
<tr>
<td>1. 750.</td>
<td>0.620.</td>
</tr>
<tr>
<td>10. 890.</td>
<td>0.740.</td>
</tr>
<tr>
<td>100. 1080.</td>
<td>0.900.</td>
</tr>
<tr>
<td>400. 1240.</td>
<td>1.040.</td>
</tr>
<tr>
<td>760. 1310.</td>
<td>1.110.</td>
</tr>
</tbody>
</table>

88. From the following data for liquid nitric acid, determine its heat of vaporization and normal boiling point.

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Vapor Pressure (mm Hg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.</td>
<td>14.4</td>
</tr>
<tr>
<td>10.</td>
<td>26.6</td>
</tr>
<tr>
<td>20.</td>
<td>47.9</td>
</tr>
<tr>
<td>30.</td>
<td>81.3</td>
</tr>
<tr>
<td>40.</td>
<td>133</td>
</tr>
<tr>
<td>50.</td>
<td>208</td>
</tr>
<tr>
<td>80.</td>
<td>670.</td>
</tr>
</tbody>
</table>
89. In Breckenridge, Colorado, the typical atmospheric pressure is 520. torr. What is the boiling point of water ($\Delta H_{\text{vap}} = 40.7$ kJ/mol) in Breckenridge?

90. The temperature inside a pressure cooker is 115°C. Calculate the vapor pressure of water inside the pressure cooker. What would be the temperature inside the pressure cooker if the vapor pressure of water was 3.50 atm?

91. Carbon tetrachloride, CCl$_4$, has a vapor pressure of 213 torr at 40.0°C and 836 torr at 80.0°C. What is the normal boiling point of CCl$_4$?

92. The normal boiling point for acetone is 56.5°C. At an elevation of 5300 ft the atmospheric pressure is 630. torr. What would be the boiling point of acetone ($\Delta H_{\text{vap}} = 32.0$ kJ/mol) at this elevation? What would be the vapor pressure of acetone at 25.0°C at this elevation?

93. A substance, X, has the following properties:

<table>
<thead>
<tr>
<th>Specific Heat Capacities</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta H_{\text{vap}}$</td>
</tr>
<tr>
<td>$\Delta H_{\text{vap}}$</td>
</tr>
<tr>
<td>bp</td>
</tr>
<tr>
<td>mp</td>
</tr>
</tbody>
</table>

Sketch a heating curve for substance X starting at −50.0°C.

94. Given the data in Exercise 93 on substance X, calculate the energy that must be removed to convert 250.0 g of substance X from a gas at 100.0°C to a solid at −50.0°C. Assume X has a molar mass of 75.0 g/mol.

95. The molar heat of fusion of sodium metal is 2.60 kJ/mol, whereas its heat of vaporization is 97.0 kJ/mol.
   a. Why is the heat of vaporization so much larger than the heat of fusion?
   b. What quantity of heat would be needed to melt 1.00 g sodium at its normal melting point?
   c. What quantity of heat would be needed to vaporize 1.00 g sodium at its normal boiling point?
   d. What quantity of heat would be evolved if 1.00 g sodium vapor condensed at its normal boiling point?

96. The molar heat of fusion of benzene (C$_6$H$_6$) is 9.92 kJ/mol. Its molar heat of vaporization is 30.7 kJ/mol. Calculate the heat required to melt 8.25 g benzene at its normal melting point. Calculate the heat required to vaporize 8.25 g benzene at its normal boiling point. Why is the heat of vaporization more than three times the heat of fusion?

97. What quantity of energy does it take to convert 0.500 kg ice at −20.0°C to steam at 250.0°C? Specific heat capacities: ice, 2.03 J/g · °C; liquid, 4.2 J/g · °C; steam, 2.0 J/g · °C; $\Delta H_{\text{vap}} = 40.7$ kJ/mol; $\Delta H_{\text{vap}} = 6.02$ kJ/mol.

98. Consider a 75.0-g sample of H$_2$O(g) at 125°C. What phase or phases are present when 215 J of energy is removed from this sample? (See Exercise 97.)

99. An ice cube tray contains enough water at 22.0°C to make 18 ice cubes that each have a mass of 30.0 g. The tray is placed in a freezer that uses CF$_2$Cl$_2$ as a refrigerant. The heat of vaporization of CF$_2$Cl$_2$ is 158 J/g. What mass of CF$_2$Cl$_2$ must be vaporized in the refrigeration cycle to convert all the water at 22.0°C to ice at −5.0°C? The heat capacities for H$_2$O(s) and H$_2$O(l) are 2.03 J/g · °C and 4.18 J/g · °C, respectively, and the enthalpy of fusion for ice is 6.02 kJ/mol.

100. A 0.250-g chunk of sodium metal is cautiously dropped into a mixture of 50.0 g water and 50.0 g ice, both at 0°C. The reaction is

\[ 2Na(s) + 2H_2O(l) \rightarrow 2NaOH(aq) + H_2(g) \quad \Delta H = -368 \text{ kJ} \]

Will the ice melt? Assuming the final mixture has a specific heat capacity of 4.18 J/g · °C, calculate the final temperature. The enthalpy of fusion for ice is 6.02 kJ/mol.

101. Consider the phase diagram given below. What phases are present at points A through H? Identify the triple point, normal boiling point, normal freezing point, and critical point. Which phase is denser, solid or liquid?

102. Sulfur exhibits two solid phases, rhombic and monoclinic. Use the accompanying phase diagram for sulfur to answer the following questions. (The phase diagram is not to scale.)

   a. How many triple points are in the phase diagram?
   b. What phases are in equilibrium at each of the triple points?
   c. What is the stable phase at 1 atm and 100.0°C?
   d. What are the normal melting point and the normal boiling point of sulfur?
   e. Which is the densest phase?
f. At a pressure of $1.0 \times 10^{-5}$ atm, can rhombic sulfur sublime?
g. What phase changes occur when the pressure on a sample of sulfur at 100°C is increased from $1.0 \times 10^{-8}$ atm to 1500 atm?

103. Use the accompanying phase diagram for carbon to answer the following questions.
   a. How many triple points are in the phase diagram?
   b. What phases can coexist at each triple point?
   c. What happens if graphite is subjected to very high pressures at room temperature?
   d. If we assume that the density increases with an increase in pressure, which is more dense, graphite or diamond?

104. Like most substances, bromine exists in one of the three typical phases. Br$_2$ has a normal melting point of $-7.2°C$ and a normal boiling point of 59°C. The triple point for Br$_2$ is $-7.3°C$ and 40 torr, and the critical point is 320°C and 100 atm. Using this information, sketch a phase diagram for bromine indicating the points described above. Based on your phase diagram, order the three phases from least dense to most dense. What is the stable phase of Br$_2$ at room temperature and 1 atm? Under what temperature conditions can liquid bromine never exist? What phase changes occur as the temperature of a sample of bromine at 0.10 atm is increased from $-50°C$ to 200°C?

105. The melting point of a fictional substance X is 225°C at 10.0 atm. If the density of the solid phase of X is 2.67 g/cm$^3$ and the density of the liquid phase is 2.78 g/cm$^3$ at 10.0 atm, predict whether the normal melting point of X will be less than, equal to, or greater than 225°C. Explain.

106. Consider the following data for xenon:
   - Triple point: $-121°C$, 280 torr
   - Normal melting point: $-112°C$
   - Normal boiling point: $-107°C$

Which is more dense, Xe(s) or Xe(l)? How do the melting point and boiling point of xenon depend on pressure?

107. Consider two different organic compounds, each with the formula C$_2$H$_6$O. One of these compounds is a liquid at room conditions and the other is a gas. Write Lewis structures consistent with this observation, and explain your answer. (Hint: The oxygen atom in both structures satisfies the octet rule with two bonds and two lone pairs.)

108. Rationalize the differences in physical properties in terms of intermolecular forces for the following organic compounds. Compare the first three substances with each other, compare the last three with each other, and then compare all six. Can you account for any anomalies?

<table>
<thead>
<tr>
<th>bp (°C)</th>
<th>mp (°C)</th>
<th>$\Delta H_{vap}$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene, C$_6$H$_6$</td>
<td>80</td>
<td>6</td>
</tr>
<tr>
<td>Naphthalene, C$_{10}$H$_8$</td>
<td>218</td>
<td>80</td>
</tr>
<tr>
<td>Carbon tetrachloride</td>
<td>76</td>
<td>-23</td>
</tr>
<tr>
<td>Acetone, CH$_3$COCH$_3$</td>
<td>56</td>
<td>-95</td>
</tr>
<tr>
<td>Acetic acid, CH$_3$CO$_2$H</td>
<td>118</td>
<td>17</td>
</tr>
<tr>
<td>Benzoic acid, C$_6$H$_5$CO$_2$H</td>
<td>249</td>
<td>122</td>
</tr>
</tbody>
</table>

109. Oil of wintergreen, or methyl salicylate, has the following structure:

Methyl 4-hydroxybenzoate is another molecule with exactly the same molecular formula; it has the following structure:

Account for the large difference in the melting points of the two substances.

110. Amino acids are the building blocks of the body’s worker molecules called proteins. When two amino acids bond together, they do so through the formation of a peptide linkage, and a dipeptide is formed. Consider the following tripeptide formed when three alanine amino acids bond together:

What types of interparticle forces could be present in a sample of this tripeptide?
111. When a person has a severe fever, one therapy used to reduce the fever is an “alcohol rub.” Explain how the evaporation of alcohol from a person’s skin removes heat energy from the body.

112. A common response to hearing that the temperature in New Mexico is 105°F is, “It’s not that bad; it’s a dry heat,” whereas at the same time the summers in Atlanta, Georgia, are characterized as “dreadful,” even though the air temperature is typically lower. What role does humidity play in how our bodies regulate temperature?

113. Why is a burn from steam typically much more severe than a burn from boiling water?

114. Diethyl ether (CH₃CH₂OCH₂CH₃) was one of the first chemicals used as an anesthetic. At 34.6°C, diethyl ether has a vapor pressure of 760 torr, and at 17.9°C, it has a vapor pressure of 400 torr. What is the ΔH of vaporization for diethyl ether?

115. Some of the physical properties of H₂O and D₂O are as follows:

<table>
<thead>
<tr>
<th>Property</th>
<th>H₂O</th>
<th>D₂O</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density at 20°C (g/mL)</td>
<td>0.997</td>
<td>1.108</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>100.00</td>
<td>101.41</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>0.00</td>
<td>3.79</td>
</tr>
<tr>
<td>ΔH°vap (kJ/mol)</td>
<td>40.7</td>
<td>41.61</td>
</tr>
<tr>
<td>ΔH°fus (kJ/mol)</td>
<td>6.01</td>
<td>6.3</td>
</tr>
</tbody>
</table>

Account for the differences. (Note: D is a symbol often used for ²H, the deuterium isotope of hydrogen.)

116. Rationalize the following boiling points:

\[
\begin{align*}
\text{CH₃C}=\text{O} & \quad 118°C \\
\text{ClCH₂C}=\text{O} & \quad 189°C \\
\text{CH₃C}=\text{O} & \quad 57°C
\end{align*}
\]

117. Consider the following vapor pressure versus temperature plot for three different substances A, B, and C.

If the three substances are CH₄, SiH₄, and NH₃, match each curve to the correct substance.

118. Consider the following enthalpy changes:

\[
\begin{align*}
\text{F}^- + \text{HF} & \rightarrow \text{FHF}^- & \Delta H &= -155 \text{ kJ/mol} \\
(\text{CH₃})₂\text{C}=\text{O} + \text{HF} & \rightarrow (\text{CH₃})₂\text{C}=\text{O}--\text{HF} & \Delta H &= -46 \text{ kJ/mol} \\
\text{H₂O(g)} + \text{HOH(g)} & \rightarrow \text{H₂O}--\text{HOH (in ice)} & \Delta H &= -21 \text{ kJ/mol}
\end{align*}
\]

How do the strengths of hydrogen bonds vary with the electronegativity of the element to which hydrogen is bonded? Where in the preceding series would you expect hydrogen bonds of the following type to fall?

\[
\begin{align*}
\text{N}--\text{HO} & \quad \text{and} \quad \text{N}--\text{H}--\text{N}
\end{align*}
\]

119. The unit cell for a pure xenon fluoride compound is shown below. What is the formula of the compound?

120. Boron nitride (BN) exists in two forms. The first is a slippery solid formed from the reaction of BCl₃ with NH₃, followed by heating in an ammonia atmosphere at 750°C. Subjecting the first form of BN to a pressure of 85,000 atm at 1800°C produces a second form that is the second hardest substance known. Both forms of BN remain solids to 3000°C. Suggest structures for the two forms of BN.

121. Consider the following data concerning four different substances.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conducts Electricity as a Solid</th>
<th>Other Properties</th>
</tr>
</thead>
<tbody>
<tr>
<td>B₂H₆</td>
<td>no</td>
<td>gas at 25°C</td>
</tr>
<tr>
<td>SiO₂</td>
<td>no</td>
<td>high mp</td>
</tr>
<tr>
<td>CsI</td>
<td>no</td>
<td>aqueous solution</td>
</tr>
<tr>
<td>W</td>
<td>yes</td>
<td>conducts electricity</td>
</tr>
</tbody>
</table>

Label the four substances as either ionic, network, metallic, or molecular solids.

122. Argon has a cubic closest packed structure as a solid. Assuming that argon has a radius of 190 pm, calculate the density of solid argon.

123. Dry nitrogen gas is bubbled through liquid benzene (C₆H₆) at 20.0°C. From 100.0 L of the gaseous mixture of nitrogen and benzene, 24.7 g benzene is condensed by passing the mixture through a trap at a temperature where nitrogen is gaseous and the vapor pressure of benzene is negligible. What is the vapor pressure of benzene at 20.0°C?
124. A 20.0-g sample of ice at \(-10.0^\circ\text{C}\) is mixed with 100.0 g water at 80.0\(^\circ\text{C}\). Calculate the final temperature of the mixture assuming no heat loss to the surroundings. The heat capacities of \(\text{H}_2\text{O}(s)\) and \(\text{H}_2\text{O}(l)\) are 2.03 and 4.18 J/g·\(^\circ\text{C}\), respectively, and the enthalpy of fusion for ice is 6.02 kJ/mol.

125. In regions with dry climates, evaporative coolers are used to cool air. A typical electric air conditioner is rated at 1.00 \(\times 10^5\) Btu/h (1 Btu, or British thermal unit = amount of energy to raise the temperature of 1 lb water by 1°F). What quantity of water must be evaporated each hour to dissipate as much heat as a typical electric air conditioner?

126. The critical point of \(\text{NH}_3\) is 132\(^\circ\text{C}\) and 111 atm, and the critical point of \(\text{N}_2\) is \(-147^\circ\text{C}\) and 34 atm. Which of these substances cannot be liquefied at room temperature no matter how much pressure is applied? Explain.

### Challenge Problems

127. When 1 mol benzene is vaporized at a constant pressure of 1.00 atm and at its boiling point of 353.0 K, 30.79 kJ of energy (heat) is absorbed and the volume change is +28.90 L. What are \(\Delta E\) and \(\Delta H\) for this process?

128. You and a friend each synthesize a compound with the formula \(\text{XeCl}_2\text{F}_3\). Your compound is a liquid and your friend’s compound is a gas (at the same conditions of temperature and pressure). Explain how the two compounds with the same formulas can exist in different phases at the same conditions of pressure and temperature.

129. Using the heats of fusion and vaporization for water given in Exercise 97, calculate the change in enthalpy for the sublimation of water:

\[
\text{H}_2\text{O}(s) \rightarrow \text{H}_2\text{O}(g)
\]

Using the \(\Delta H\) value given in Exercise 118 and the number of hydrogen bonds formed with each water molecule, estimate what portion of the intermolecular forces in ice can be accounted for by hydrogen bonding.

130. Consider a perfectly insulated and sealed container. Determine the minimum volume of a container such that a gallon of water at 25\(^\circ\text{C}\) will evaporate completely. If the container is a cube, determine the dimensions in feet. Assume the density of water is 0.998 g/cm\(^3\).

131. Consider the following melting point data:

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaCl</th>
<th>MgCl(_2)</th>
<th>AlCl(_3)</th>
<th>SiCl(_4)</th>
<th>PCl(_3)</th>
<th>SCl(_2)</th>
<th>Cl(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mp (^\circ\text{C})</td>
<td>801</td>
<td>708</td>
<td>190</td>
<td>70</td>
<td>91</td>
<td>78</td>
<td>101</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compound</th>
<th>NaF</th>
<th>MgF(_2)</th>
<th>AlF(_3)</th>
<th>SiF(_4)</th>
<th>PFS cans</th>
<th>SF(_6)</th>
<th>F(_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>mp (^\circ\text{C})</td>
<td>997</td>
<td>1396</td>
<td>1040</td>
<td>90</td>
<td>94</td>
<td>56</td>
<td>220</td>
</tr>
</tbody>
</table>

132. Some ionic compounds contain a mixture of different charged cations. For example, wüsite is an oxide that contains both Fe\(^{2+}\) and Fe\(^{3+}\) cations and has a formula of Fe\(_{0.950}\)O\(_{1.00}\). Calculate the fraction of iron ions present as Fe\(^{3+}\). What fraction of the sites normally occupied by Fe\(^{2+}\) must be vacant in this solid?

133. Some ionic compounds contain a mixture of different charged cations. For example, some titanium oxides contain a mixture of Ti\(^{4+}\) and Ti\(^{3+}\) ions. Consider a certain oxide of titanium that is 28.31% oxygen by mass and contains a mixture of Ti\(^{2+}\) and Ti\(^{3+}\) ions. Determine the formula of the compound and the relative numbers of Ti\(^{2+}\) and Ti\(^{3+}\) ions.

134. Spinel is a mineral that contains 37.9% aluminum, 17.1% magnesium, and 45.0% oxygen, by mass, and has a density of 3.57 g/cm\(^3\). The edge of the cubic unit cell measures 809 pm. How many of each type of ion are present in the unit cell?

135. Mn crystallizes in the same type of cubic unit cell as Cu. Assuming that the radius of Mn is 5.6% larger than the radius of Cu and the density of copper is 8.96 g/cm\(^3\), calculate the density of Mn.

136. You are asked to help set up a historical display in the park by stacking some cannonballs next to a Revolutionary War cannon. You are told to stack them by starting with a triangle in which each side is composed of four touching cannonballs. You are to continue stacking them until you have a single ball on the top centered over the middle of the triangular base.

**a.** How many cannonballs do you need?

**b.** What type of closest packing is displayed by the cannonballs?

**c.** The four corners of the pyramid of cannonballs form the corners of what type of regular geometric solid?

137. Some water is placed in a sealed glass container connected to a vacuum pump (a device used to pump gases from a container), and the pump is turned on. The water appears to boil and then freezes. Explain these changes using the phase diagram for water. What would happen to the ice if the vacuum pump was left on indefinitely?

138. The molar enthalpy of vaporization of water at 373 K and 1.00 atm is 40.7 kJ/mol. What fraction of this energy is used to change the internal energy of the water, and what fraction is used to do work against the atmosphere? (Hint: Assume that water vapor is an ideal gas.)

139. For a simple cubic array, solve for the volume of an interior sphere (cubic hole) in terms of the radius of a sphere in the array.

140. Rubidium chloride has the sodium chloride structure at normal pressures but assumes the cesium chloride structure at high pressures. (See Exercise 67.) What ratio of densities is expected for these two forms? Does this change in structure make sense on the basis of simple models? The ionic radius is 148 pm for Rb\(^+\) and 181 pm for Cl\(^-\).

### Integrative Problems

These problems require the integration of multiple concepts to find the solutions.

141. A 0.132-mol sample of an unknown semiconducting material with the formula XY has a mass of 19.0 g. The element X has an electron configuration of \([\text{Kr}]5s^24d^{10}\). What is this semiconducting material? A small amount of the Y atoms in the semiconductor is replaced with an equivalent amount of atoms with an electron configuration of \([\text{Ar}]4s^23d^{10}4p^3\). Does this correspond to n-type or p-type doping?

142. A metal burns in air at 600\(^\circ\text{C}\) under high pressure to form an oxide with formula MO\(_2\). This compound is 23.72% oxygen by mass. The distance between touching atoms in a cubic closest