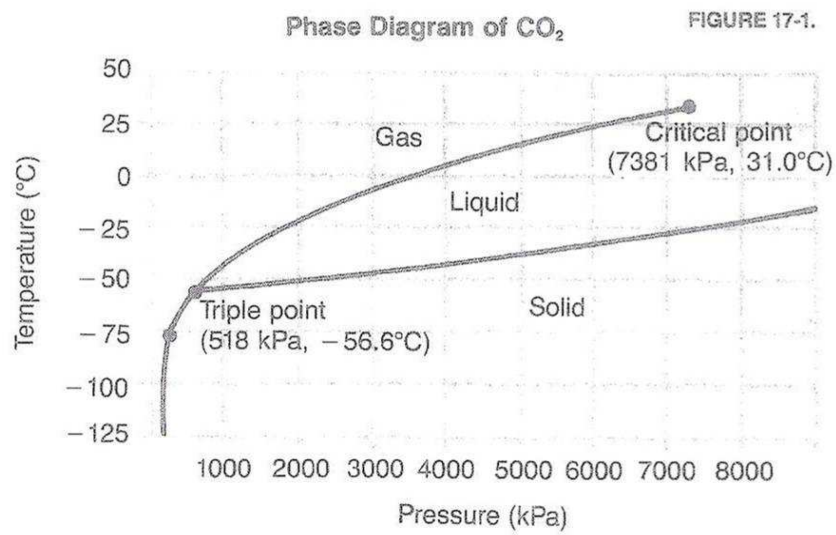
LIQUIDS 17

17:1 PHASE DIAGRAMS

The solid, liquid, and gas phases of a substance exist at different temperatures and pressures. The **phase diagram** is a convenient way to represent graphically the conditions at which a particular phase is stable.

Figure 17-1 is a phase diagram for CO_2, carbon dioxide. There are three lines that divide the diagram into solid, liquid, and gas regions. Each point on a line represents a temperature and pressure at which the two phases are in equilibrium. The normal boiling point and normal melting point occur where the equilibrium line is cut by the standard atmospheric pressure line 101.325 kPa. The **triple point** indicates the temperature and pressure at which all three phases are in equilibrium.

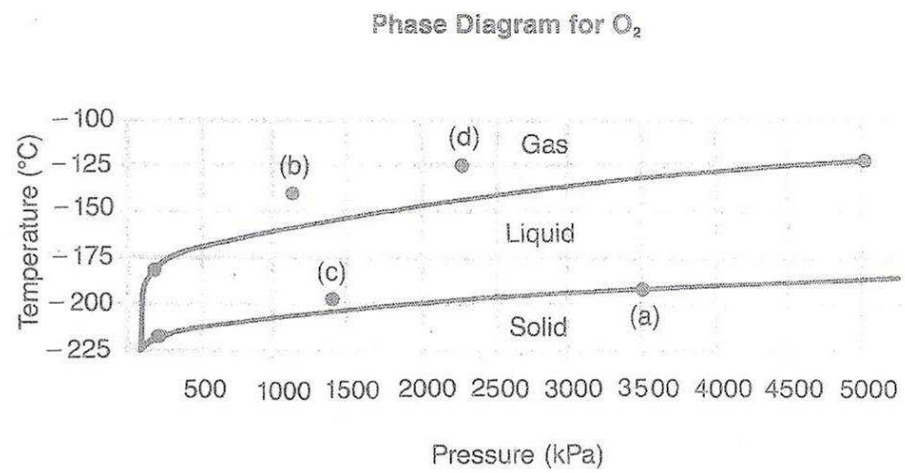
FIGURE 17-1.



In a closed system, liquid and gaseous carbon dioxide can be in equilibrium. Above the critical temperature there is only one phase, gaseous carbon dioxide. The **critical temperature,** T_c, is the temperature above which no amount of pressure will liquefy the gas. At the critical temperature the minimum pressure necessary to liquefy the gas is called the **critical pressure,** P_c. A high critical temperature indicates that the attractive force between the particles is strong. Methyl chloride, CH_3Cl, has a T_c = 144°C

and P_c = 6685 kPa. It can be liquified by increasing the pressure. By compressing the gas the molecules come close enough that van der Waals forces can hold them together.

FIGURE 17-2.



PROBLEMS

1. Using Figure 17-2, determine the following for oxygen.
   a. critical temperature
   b. critical pressure
   c. normal melting point
   d. normal boiling point
2. Using Figure 17-1, determine the state of matter that exists for CO_2 under the following conditions.
   a. 4000 kPa and −100°C
   b. 1000 kPa and 10°C
   c. 3000 kPa and −25°C
   d. 101.3 kPa and 0°C
3. What transition would occur at the labeled points on Figure 17-2 when the following changes occur?
   a. at point A if temperature increased
   b. at point B if temperature decreased
   c. at point C if pressure increased
   d. at point D if pressure decreased

17:2 ENERGY AND CHANGE OF STATE

When a substance is heated, the energy of its particles is increased. If the kinetic energy is increased, the result is an increase in the temperature of the substance. If the increase is in potential energy, the physical state of the substance will change. The change, or combination of changes, that will take place depends upon the starting temperature of the substance. Similar considerations can be applied to removing energy from (cooling) a substance.

The changes of state from solid to liquid and liquid to solid take place at the same temperature, which is labeled the **melting point** or **freezing point.** The changes from liquid to gas and gas to liquid take place at the same temperature, which is labeled the **boiling point** or **condensing point.** The amount of energy required for a state change depends on the nature and amount of a substance. If we use q to represent the quantity of energy needed to melt a substance, then

$$q = m(\Delta H_{fus})$$

where m is the mass of the substance and H_{fus} is a property of a substance called **enthalpy of fusion.** Similarly, to boil a substance, the relationship is

$$q = m(\Delta H_{vap})$$

where H_{vap} is a property of a substance called its **enthalpy of vaporization.** Table 17-1 lists the enthalpies of fusion and vaporization for several substances.

Table 17-1

Molar Enthalpies of Fusion and Vaporization for Some Substances (in kJ/mol)

Fusion(H_{fus})		Vaporization (H_{vap})	
aluminum	10.71	aluminum	290.8
arsenic	27.7	benzene	30.8
gold	12.4	gold	324.4
indium	3.26	helium	0.084
iron	13.8	iron	350
steel	13.8	selenium	26.3
titanium	14.146	sodium	97.4
water	6.012	water	40.7

Example 1

How much energy is required to melt 86.3 g of iron at its melting point?

Solving Process:

The energy required for this phase change depends upon the mass, 86.3 g, and enthalpy of fusion, 13.8 kJ/mol. To make use of the H_{fus} value, the quantity of iron must be in units of moles. Thus, the solution is

$$q = \textit{mass} \times \textit{enthalpy of fusion} \times \textit{mole conversion}$$

$$= \frac{86.3\ \cancel{\text{g Fe}}}{} \left| \frac{13.8\ \text{kJ}}{1\ \cancel{\text{mol Fe}}} \right| \frac{1\ \cancel{\text{mol Fe}}}{55.8\ \cancel{\text{g Fe}}} = 21.3\ \text{kJ}$$

The amount of energy required to change the temperature of a substance depends upon the amount and nature of the substance as well as the extent of the temperature change. The energy required is calculated by

$$q = m(\Delta T)C_p$$

where q is the energy added (or removed), m is the mass of the substance, ΔT is the change in temperature, and C_p is a property of the substance called its **specific heat.** Review Section 3:5 for an example problem.

You may be asked to do calculations that involve both temperature and state changes. For such problems, each step involving a temperature or state change is solved separately. The sum of the energy changes for all the steps is the solution to the problem. For example, suppose you are asked to start with a solid substance below its melting point and determine the energy required to change that substance to a gas above its boiling point. The following steps must be taken.

a. heat the solid to its melting point
b. melt the solid
c. heat the liquid to its boiling point
d. boil the liquid
e. heat the gas to the required temperature

Example 2

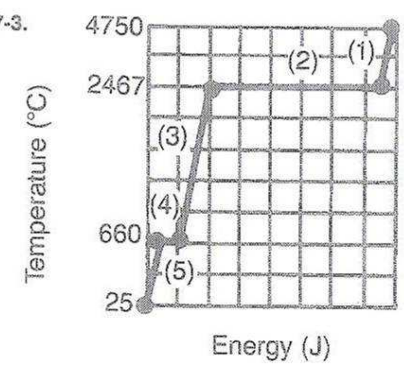
How much energy is released when 42.5 g of aluminum vapor are cooled from 4750°C to 25.0°C?

freezing point	= 660.0°C	boiling point	= 2467°C
H_{vap}	= 291 kJ/mol	H_{fus}	= 10.7 kJ/mol
C_p(g)	= 1.05 J/g · C°	C_p(l)	= 0.869 J/g · C°
C_p(cr)	= 0.903 J/g · C°		

Solving Process:

It is often helpful in problems of this type to draw a graph to indicate the steps in changing the vapor to solid.

FIGURE 17-3.



Step 1: Calculate the energy released as the Al gas is cooled to the condensing point, 2467°C. Convert joules to kilojoules so the units in each step will be the same.

$$q = m(\Delta T)C_p$$

$$= \frac{42.5\,\cancel{\text{g}} \;\big|\; 2283\,\cancel{\text{C}^\circ} \;\big|\; 1.05\,\cancel{\text{J}} \;\big|\; 1\text{ kJ}}{\;\big|\; \;\big|\; \cancel{\text{g}\cdot\text{C}^\circ} \;\big|\; 1000\,\cancel{\text{J}}} = 102\text{ kJ}$$

Step 2: Calculate the energy released as the Al gas is condensed. You must convert grams of Al to moles because H_{vap} is given in kJ/mol.

$$q = \textit{mass} \times \textit{mole conversion} \times \textit{enthalpy of vaporization}$$

$$= \frac{42.5\,\cancel{\text{g}} \;\big|\; 1\,\cancel{\text{mol}} \;\big|\; 291\text{ kJ}}{\;\big|\; 27.0\,\cancel{\text{g}} \;\big|\; 1\,\cancel{\text{mol}}} = 458\text{ kJ}$$

Step 3: Calculate the energy released as the liquid Al is cooled to the freezing point, 660.0°C.

$$q = \frac{42.5\,\cancel{\text{g}} \;\big|\; 1807\,\cancel{\text{C}^\circ} \;\big|\; 0.869\,\cancel{\text{J}} \;\big|\; 1\text{ kJ}}{\;\big|\; \;\big|\; \cancel{\text{g}\cdot\text{C}^\circ} \;\big|\; 1000\,\cancel{\text{J}}} = 66.7\text{ kJ}$$

Step 4: Calculate the energy released as the liquid Al is frozen.

$$q = \textit{mass} \times \textit{mole conversion} \times \textit{enthalpy of vaporization}$$

$$= \frac{42.5\,\cancel{\text{g}} \;\big|\; 1\,\cancel{\text{mol}} \;\big|\; 10.7\text{ kJ}}{\;\big|\; 27.0\,\cancel{\text{g}} \;\big|\; 1\,\cancel{\text{mol}}} = 16.9\text{ kJ}$$

Step 5: Calculate the energy released as the solid Al is cooled to 25.0°C.

$$q = \frac{42.5\,\cancel{\text{g}} \;\big|\; 635\,\cancel{\text{C}^\circ} \;\big|\; 0.903\,\cancel{\text{J}} \;\big|\; 1\text{ kJ}}{\;\big|\; \;\big|\; \cancel{\text{g}\cdot\text{C}^\circ} \;\big|\; 1000\,\cancel{\text{J}}} = 24.4\text{ kJ}$$

The total energy released is the sum of all five steps.

$$102\text{ kJ} + 458\text{ kJ} + 66.7\text{ kJ} + 16.9\text{ kJ} + 24.4\text{ kJ} = 668\text{ kJ}$$

PROBLEMS

4. Compute the energy changes associated with the following transitions.
   a. melting 55.8 g Ti at 1666°C
   b. condensing 14.2 g H_2O at 100.0°C
   c. boiling 53.5 g C_6H_6, benzene, at 80.1°C
   d. freezing 27.3 g Al at 660°C
   e. melting 76.4 g Au at 1064°C
5. Compute the energy changes associated with the following transitions.
   a. heating 49.2 g acetic acid, CH_3COOH, from 24.1°C to 67.3°C
   b. heating 9.61 g toluene, $C_6H_5CH_3$, from 19.6°C to 75.0°C
   c. heating 2.47 g kerosene from 17.1°C to 46.7°C
   d. cooling 31.9 g chalk from 83.2°C to 55.5°C
   e. cooling 63.6 g glass from 95.5°C to 42.3°C

17:3 HYDROGEN BONDING

Water, H_2O, has a molecular mass of 18 u. Hydrogen sulfide, H_2S, has a molecular mass of 34 u. At 25°C, hydrogen sulfide is a gas. If you did not already know that water is a liquid at 25°C, you might predict it to be gas on the basis of its smaller molecular mass compared to H_2S. How can you explain the fact that water is, instead, a liquid? The explanation lies in the existence of an attractive force between water molecules called **hydrogen bonding**.

The hydrogen bond is not a chemical bond. It is an intermolecular attractive force. When hydrogen is covalently bonded to a highly electronegative element, such as fluorine, nitrogen, or oxygen, a strongly polar molecule results. The dipole-dipole interaction between these molecules is strong because the hydrogen has a partial positive charge. Hydrogen is the only element to exhibit this property.

The effects of hydrogen bonding can be observed when water freezes and melts. When water freezes, hydrogen bonding between water causes the molecules to become arranged in an open crystal structure. This arrangement results in a decrease in density. When ice melts, many of the hydrogen bonds are broken and the lattice collapses. The water molecules move closer together. Water is most dense at 3.98°C. Because ice is less dense than the liquid, it floats..

CHAPTER REVIEW PROBLEMS

1. In a closed, insulated system, ice is floating in water. The temperature is 0°C. Will all of the water freeze?
2. Water is boiling at 100°C. The hot plate's surface temperature is increased. Will the water now boil at a higher temperature?
3. Will a gas liquefy above the critical temperature when the pressure increases a large amount?
4. Are the vapor pressure of the liquid phase and the vapor pressure of the gas phase equal at the boiling point?
5. Are the attractive forces between the particles strong or weak when the vapor pressure of a substance is high?
6. Gas can be liquified when what temperature and pressure changes occur?
7. Using the phase diagram for compound x, Figure 17-4, answer the following questions.
   a. At what temperature does the vapor pressure of the solid equal atmospheric pressure?
   b. What is the temperature of the triple point?
   c. What is the critical temperature?

d. What is the critical pressure?
e. At what labeled point does boiling occur?
f. At what point do solid and liquid phases exist in equilibrium?

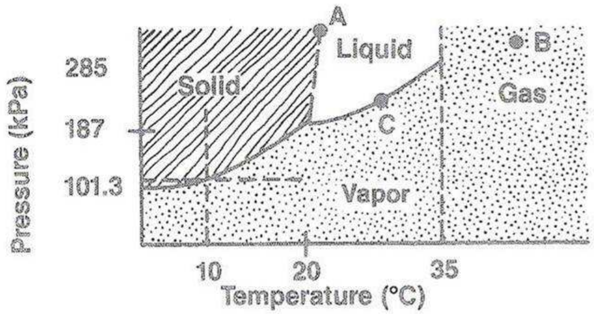


FIGURE 17-4.

Use Tables 17-1 and A-8 to answer the following questions.

8. How much energy is required to raise the temperature of 91.4 g solid steel from 25.0°C to 76.1°C?
9. How much energy is required to raise the temperature of 4.66 g kerosene from 10.9°C to 26.8°C?
10. How much energy is required to raise the temperature of 175 g H_2O from −11.0°C to 140.0°C?
11. If 100.0 g of pure water at 27°C are placed into an insulated flask, how many grams of ice at 0.0°C must be added to lower the temperature of the water to 5.0°C? (recall: energy lost = energy gained)
12. When hydrogen is bonded to a highly electronegative element, what intermolecular attractive force results?
13. List three elements that bond with hydrogen to produce hydrogen bonds between the molecules?
14. Why does ice float in liquid water when most solids sink in their liquids?
15. A hydrogen bond is not a true chemical bond. True or false?