Sample Exercise 11.1 Identifying Substances That Can Form Hydrogen Bonds

In which of these substances is hydrogen bonding likely to play an important role in determining physical properties: methane (CH_4), hydrazine (H_2NNH_2), methyl fluoride (CH_3F), hydrogen sulfide (H_2S)?

Solution

Analyze We are given the chemical formulas of four compounds and asked to predict whether they can participate in hydrogen bonding. All the compounds contain H, but hydrogen bonding usually occurs only when the hydrogen is covalently bonded to N, O, or F.

Plan We analyze each formula to see if it contains N, O, or F directly bonded to H. There also needs to be a nonbonding pair of electrons on an electronegative atom (usually N, O, or F) in a nearby molecule, which can be revealed by drawing the Lewis structure for the molecule.

Solve The foregoing criteria eliminate CH_4 and H_2S, which do not contain H bonded to N, O, or F. They also eliminate CH_3F, whose Lewis structure shows a central C atom surrounded by three H atoms and an F atom. (Carbon always forms four bonds, whereas hydrogen and fluorine form one each.) Because the molecule contains a C — F bond and not an H — F bond, it does not form hydrogen bonds. In H_2NNH_2, however, we find N — H bonds, and the Lewis structure shows a nonbonding pair of electrons on each N atom, telling us hydrogen bonds can exist between the molecules:
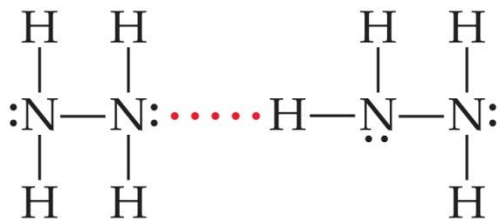
Sample Exercise 11.1 Identifying Substances That Can Form Hydrogen Bonds

Continued

Check Although we can generally identify substances that participate in hydrogen bonding based on their containing N, O, or F covalently bonded to H, drawing the Lewis structure for the interaction provides a way to check the prediction.

Practice Exercise 1

Which of the following substances is most likely to be a liquid at room temperature?
(a) formaldehyde, H_2CO
(b) fluoromethane, CH_3F
(c) hydrogen cyanide, HCN
(d) hydrogen peroxide, H_2O_2
(e) hydrogen sulfide, H_2S

Practice Exercise 2

In which of these substances is significant hydrogen bonding possible: methylene chloride (CH_2Cl_2), phosphine (PH_3), chloramine (NH_2Cl), acetone (CH_3COCH_3)?

Sample Exercise 11.2 Predicting Types and Relative Strengths of Intermolecular Attractions

List the substances $BaCl_2$, H_2, CO, HF, and Ne in order of increasing boiling point.

Solution

Analyze We need to assess the intermolecular forces in these substances and use that information to determine the relative boiling points.

Plan The boiling point depends in part on the attractive forces in each substance. We need to order these substances according to the relative strengths of the different kinds of intermolecular attractions.

Solve The attractive forces are stronger for ionic substances than for molecular ones, so $BaCl_2$ should have the highest boiling point. The intermolecular forces of the remaining substances depend on molecular weight, polarity, and hydrogen bonding. The molecular weights are H_2, 2 amu; CO, 28 amu; HF, 20 amu; and Ne, 20 amu. The boiling point of H_2 should be the lowest because it is nonpolar and has the lowest molecular weight. The molecular weights of CO, HF, and Ne are similar. Because HF can hydrogen-bond, it should have the highest boiling point of the three. Next is CO, which is slightly polar and has the highest molecular weight. Finally, Ne, which is nonpolar, should have the lowest boiling point of these three. The predicted order of boiling points is, therefore,

$$H_2 < Ne < CO < HF < BaCl_2$$
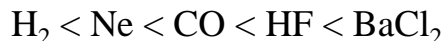
Check The boiling points reported in the literature are H_2, 20 K; Ne, 27 K; CO, 83 K; HF, 293 K; and $BaCl_2$, 1813 K—in agreement with our predictions.

Practice Exercise 1

List the substances Ar, Cl_2, CH_4, and CH_3COOH in order of increasing strength of intermolecular attractions.
(a) $CH_4 < Ar < CH_3COOH < Cl_2$
(b) $Cl_2 < CH_3COOH < Ar < CH_4$
(c) $CH_4 < Ar < Cl_2 < CH_3COOH$
(d) $CH_3COOH < Cl_2 < Ar < CH_4$
(e) $Ar < Cl_2 < CH_4 < CH_3COOH$

Practice Exercise 2

(a) Identify the intermolecular attractions present in the following substances and **(b)** select the substance with the highest boiling point: CH_3CH_3, CH_3OH, and CH_3CH_2OH.

Sample Exercise 11.3 Calculating Δ*H* for Temperature and Phase Changes

Calculate the enthalpy change upon converting 1.00 mol of ice at –25 °C to steam at 125 °C under a constant pressure of 1 atm. The specific heats of ice, liquid water, and steam are 2.03, 4.18, and 1.84 J/g-K, respectively. For H_2O, $\Delta H_{fus} = 6.01$ kJ/mol and $\Delta H_{vap} = 40.67$ kJ/mol.

Solution

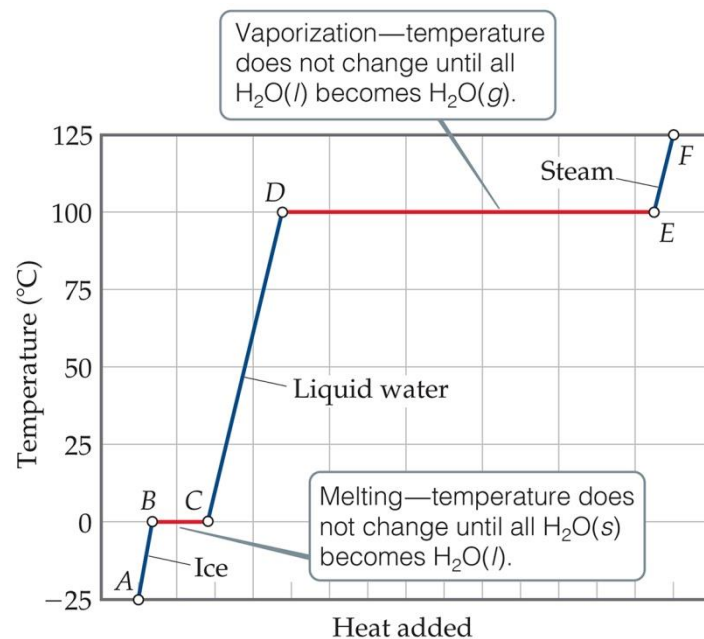**Analyze** Our goal is to calculate the total heat required to convert 1 mol of ice at –25 °C to steam at 125 °C.

Plan We can calculate the enthalpy change for each segment and then sum them to get the total enthalpy change (Hess's law, Section 5.6).

Solve
For line *AB* in Figure 11.22, we are adding enough heat to ice to increase its temperature by 25 °C. A temperature change of 25 °C is the same as a temperature change of 25 K, so we can use the specific heat of ice to calculate the enthalpy change during this process:

$$AB: \Delta H = (1.00\,\text{mol})(18.0\,\text{g/mol})(2.03\,\text{J/g-K})(25\,\text{K})$$
$$= 914\,\text{J} = 0.91\,\text{kJ}$$

Vaporization—temperature does not change until all $H_2O(l)$ becomes $H_2O(g)$.

Steam

Liquid water

Melting—temperature does not change until all $H_2O(s)$ becomes $H_2O(l)$.

Ice

Heat added

Continued

For line *BC* in Figure 11.22, in which we convert ice to water at 0 °C, we can use the molar enthalpy of fusion directly:

$$BC: \Delta H = (1.00 \text{ mol})(6.01 \text{ kJ/mol}) = 6.01 \text{ kJ}$$

The enthalpy changes for lines *CD*, *DE*, and *EF* can be calculated in similar fashion:

$$CD: \Delta H = (1.00 \text{ mol})(18.0 \text{ g/mol})(4.18 \text{ J/g-K})(100 \text{ K})$$
$$= 7520 \text{ J} = 7.52 \text{ kJ}$$

$$DE: \Delta H = (1.00 \text{ mol})(40.67 \text{ kJ/mol}) = 40.7 \text{ kJ}$$

$$EF: \Delta H = (1.00 \text{ mol})(18.0 \text{ g/mol})(1.84 \text{ J/g-K})(25 \text{ K})$$
$$= 830 \text{ J} = 0.83 \text{ kJ}$$

The total enthalpy change is the sum of the changes of the individual steps:

$$\Delta H = 0.91 \text{ kJ} + 6.01 \text{ kJ} + 7.52 \text{ kJ} + 40.7 \text{ kJ} + 0.83 \text{ kJ} = 56.0 \text{ kJ}$$

Check The components of the total enthalpy change are reasonable relative to the horizontal lengths (heat added) of the lines in Figure 11.22. Notice that the largest component is the heat of vaporization.

Sample Exercise 11.3 Calculating Δ*H* for Temperature and Phase Changes

Continued

Practice Exercise 1

What information about water is needed to calculate the enthalpy change for converting 1 mol $H_2O(g)$ at 100 °C to $H_2O(l)$ at 80 °C?
(a) heat of fusion **(b)** heat of vaporization **(c)** heat of vaporization and specific heat of $H_2O(g)$ **(d)** heat of vaporization and specific heat of $H_2O(l)$ **(e)** heat of fusion and specific heat of $H_2O(l)$

Practice Exercise 2

What is the enthalpy change during the process in which 100.0 g of water at 50.0 °C is cooled to ice at –30.0 °C? (Use the specific heats and enthalpies for phase changes given in Sample Exercise 11.3.)

Sample Exercise 11.5 Interpreting a Phase Diagram

Use the phase diagram for methane, CH_4, shown in Figure 11.30 to answer the following questions. **(a)** What are the approximate temperature and pressure of the critical point? **(b)** What are the approximate temperature and pressure of the triple point? **(c)** Is methane a solid, liquid, or gas at 1 atm and 0 °C? **(d)** If solid methane at 1 atm is heated while the pressure is held constant, will it melt or sublime? **(e)** If methane at 1 atm and 0 °C is compressed until a phase change occurs, in which state is the methane when the compression is complete?
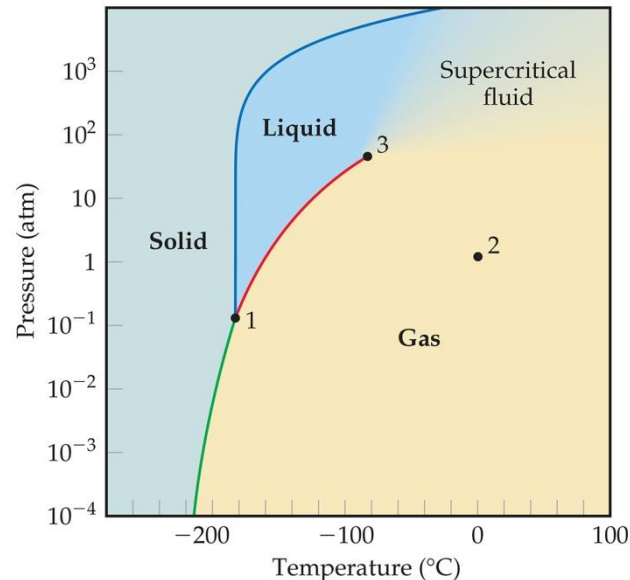

Figure 11.30 Phase diagram of CH_4. Note that a linear scale is used to represent temperature and a logarithmic scale to represent pressure.

Solution

Analyze We are asked to identify key features of the phase diagram and to use it to deduce what phase changes occur when specific pressure and temperature changes take place.

Plan We must identify the triple and critical points on the diagram and also identify which phase exists at specific temperatures and pressures.

Sample Exercise 11.5 Interpreting a Phase Diagram

Continued

Solve
(a) The critical point is the point where the liquid, gaseous, and supercritical fluid phases coexist. It is marked point 3 in the phase diagram and located at approximately –80 °C and 50 atm.
(b) The triple point is the point where the solid, liquid, and gaseous phases coexist. It is marked point 1 in the phase diagram and located at approximately –180 °C and 0.1 atm.
(c) The intersection of 0 °C and 1 atm is marked point 2 in the phase diagram. It is well within the gaseous region of the phase diagram.
(d) If we start in the solid region at $P = 1$ atm and move horizontally (this means we hold the pressure constant), we cross first into the liquid region, at $T \approx -180$ °C, and then into the gaseous region, at $T \approx -160$ °C. Therefore, solid methane melts when the pressure is 1 atm. (For methane to sublime, the pressure must be below the triple point pressure.)
(e) Moving vertically up from point 2, which is 1 atm and 0 °C, the first phase change we come to is from gas to supercritical fluid. This phase change happens when we exceed the critical pressure (~50 atm).

Check The pressure and temperature at the critical point are higher than those at the triple point, which is expected. Methane is the principal component of natural gas. So it seems reasonable that it exists as a gas at 1 atm and 0 °C.

Sample Exercise 11.5 Interpreting a Phase Diagram

Continued

Practice Exercise 1

Based on the phase diagram for methane (Figure 11.30), what happens to methane as it is heated from –250 to 0 °C at a pressure of 10^{-2} atm?
(a) It sublimes at about –200 °C.
(b) It melts at about –200 °C.
(c) It boils at about –200 °C.
(d) It condenses at about –200 °C.
(e) It reaches the triple point at about –200 °C.

Practice Exercise 2

Use the phase diagram of methane to answer the following questions.
(a) What is the normal boiling point of methane?
(b) Over what pressure range does solid methane sublime?
(c) Above what temperature does liquid methane not exist?

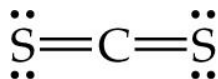# Sample Integrative Exercise Putting Concepts Together

The substance CS_2 has a melting point of –110.8 °C and a boiling point of 46.3 °C. Its density at 20 °C is 1.26 g/cm³. It is highly flammable. **(a)** What is the name of this compound? **(b)** List the intermolecular forces that CS_2 molecules exert on one another. **(c)** Write a balanced equation for the combustion of this compound in air. (You will have to decide on the most likely oxidation products.) **(d)** The critical temperature and pressure for CS_2 are 552 K and 78 atm, respectively. Compare these values with those for CO_2 in Table 11.5 and discuss the possible origins of the differences.

TABLE 11.5   Critical Temperatures and Pressures of Selected Substances

Substance	Critical Temperature (K)	Critical Pressure (atm)
Nitrogen, N_2	126.1	33.5
Argon, Ar	150.9	48.0
Oxygen, O_2	154.4	49.7
Methane, CH_4	190.0	45.4
Carbon dioxide, CO_2	304.3	73.0
Phosphine, PH_3	324.4	64.5
Propane, $CH_3CH_2CH_3$	370.0	42.0
Hydrogen sulfide, H_2S	373.5	88.9
Ammonia, NH_3	405.6	111.5
Water, H_2O	647.6	217.7

Solution

(a) The compound is named carbon disulfide, in analogy with the naming of other binary molecular compounds such as carbon dioxide. ∞∞∞ (Section 2.8)

(b) Because there is no H atom, there can be no hydrogen bonding. If we draw the Lewis structure, we see that carbon forms double bonds with each sulfur:

$$\ddot{S}{=}C{=}\ddot{S}$$

Sample Integrative Exercise Putting Concepts Together

Continued

Using the VSEPR model ⟨⟨⟨ (Section 9.2), we conclude that the molecule is linear and therefore has no dipole moment. ⟨⟨⟨ (Section 9.3) Thus, there are no dipole–dipole forces. Only dispersion forces operate between the CS_2 molecules.

(c) The most likely products of the combustion will be CO_2 and SO_2. ⟨⟨⟨ (Section 3.2) Under some conditions, SO_3 might be formed, but this would be the less likely outcome. Thus, we have the following equation for combustion:

$$CS_2(l) + 3\ O_2(g) \longrightarrow CO_2(g) + 2\ SO_2(g)$$
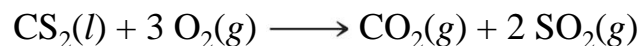
(d) The critical temperature and pressure of CS_2 (552 K and 78 atm, respectively) are both higher than those given for CO_2 in Table 11.5 (304 K and 73 atm, respectively). The difference in critical temperatures is especially notable. The higher values for CS_2 arise from the greater dispersion attractions between the CS_2 molecules compared with CO_2. These greater attractions are due to the larger size of the sulfur compared to oxygen and, therefore, its greater polarizability.