Sample Exercise 11.1 Identifying Substances That Can Form Hydrogen Bonds
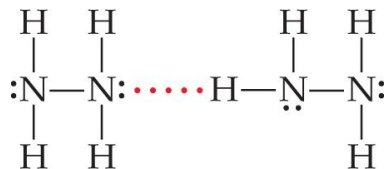
In which of these substances is hydrogen bonding likely to play an important role in determining physical properties: methane (CH_4), hydrazine (H_2NNH_2), methyl fluoride (CH_3F), hydrogen sulfide (H_2S)?

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 a 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:

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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

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

Answer: HOOH

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 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), CO (28), HF (20), and Ne (20). 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, however, 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,

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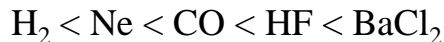
Check The boiling points reported in the literature are H_2 (20 K), Ne (27 K), CO (83 K), HF (293 K), and $BaCl_2$ (1813 K)—in agreement with our predictions.

Continued

Practice Exercise

(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.

Answers: **(a)** CH_3CH_3 has only dispersion forces, whereas the other two substances have both dispersion forces and hydrogen bonds, **(b)** CH_3CH_2OH

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Sample Exercise 11.3 Calculating ΔH 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 J/g-K, 4.18 J/g-K, 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 segment *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:
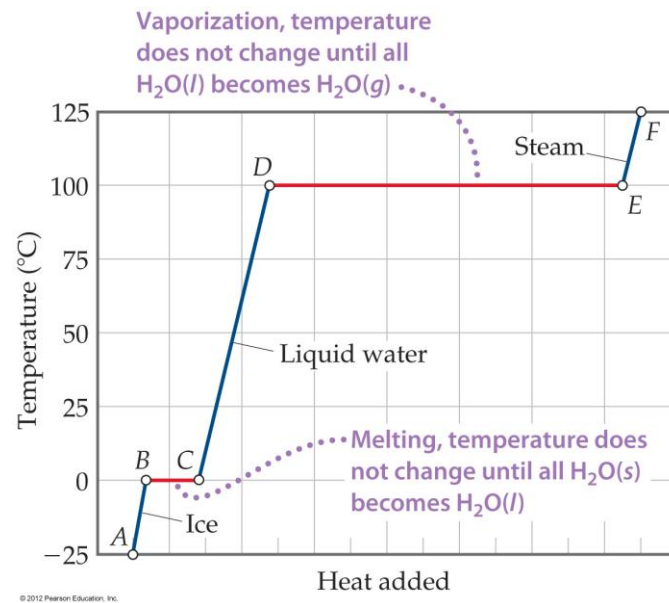
AB: $\Delta H = (1.00 \text{ mol})(18.0 \text{ g/mol})(2.03 \text{ J/g-K})(25 \text{ K})$
$= 914 \text{ J} = 0.91 \text{ kJ}$

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For segment *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 segments *CD*, *DE*, and *EF* can be calculated in similar fashion:
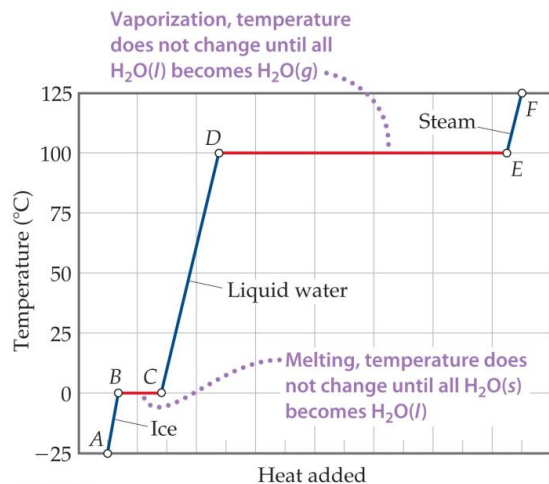
CD: $\Delta H = (1.00 \text{ mol})(18.0 \text{ g/mol})(4.18 \text{ J/g-K})(100 \text{ K}) = 7520 \text{ J} = 7.52 \text{ kJ}$
DE: $\Delta H = (1.00 \text{ mol})(40.67 \text{ kJ/mol}) = 40.7 \text{ kJ}$
EF: $\Delta H = (1.00 \text{ mol})(18.0 \text{ g/mol})(1.84 \text{ J/g-K})(25 \text{ K}) = 830 \text{ J} = 0.83 \text{ kJ}$

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

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

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

Temperature (°C)

Heat added

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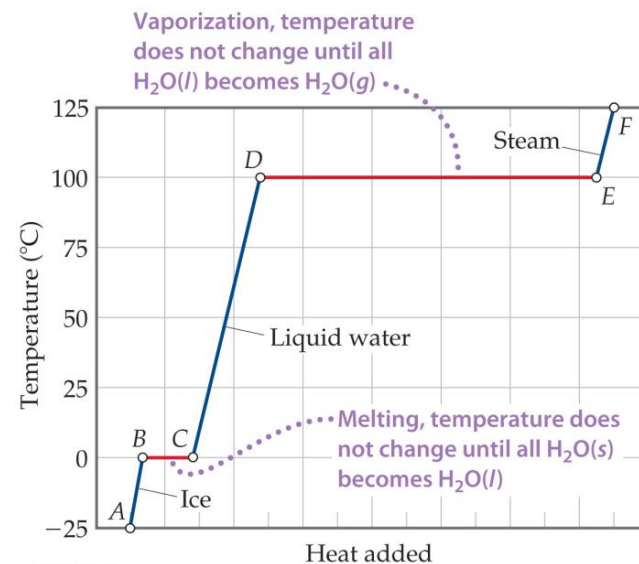# Sample Exercise 11.3 Calculating ΔH for Temperature and Phase Changes

Continued

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

Practice Exercise

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.)

Answer: −20.9 kJ − 33.4 kJ − 6.09 kJ = −60.4 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

Temperature (°C)

Heat added

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Sample Exercise 11.4 Relating Boiling Point to Vapor Pressure

Use Figure 11.25 to estimate the boiling point of diethyl ether under an
external pressure of 0.80 atm.
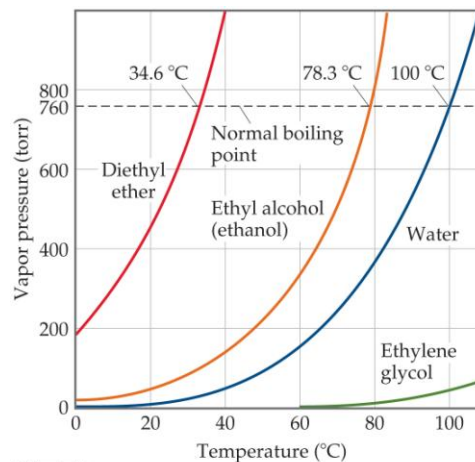
Solution

Analyze We are asked to read a graph of vapor pressure versus temperature to determine the boiling point of
a substance at a particular pressure. The boiling point is the temperature at which the vapor pressure is equal
to the external pressure.

Plan We need to convert 0.80 atm to torr because that is the pressure scale on the graph. We estimate the
location of that pressure on the graph, move horizontally to the vapor pressure curve, and then drop vertically
from the curve to estimate the temperature.

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Sample Exercise 11.4 Relating Boiling Point to Vapor Pressure

Continued

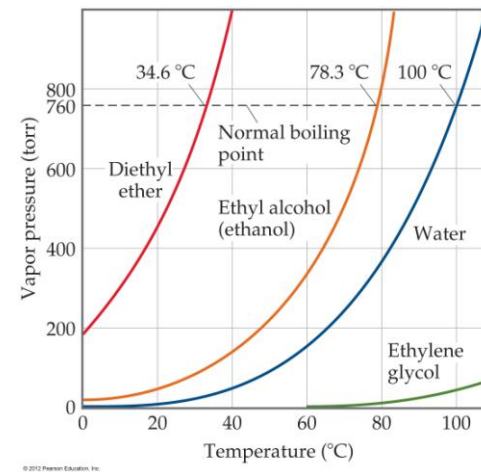**Solve** The pressure equals (0.80 atm)(760 torr/atm) = 610 torr. From Figure 11.25 we see that the boiling point at this pressure is about 27 °C, which is close to room temperature.

Comment We can make a flask of diethyl ether boil at room temperature by using a vacuum pump to lower the pressure above the liquid to about 0.8 atm.

Practice Exercise

At what external pressure will ethanol have a boiling point of 60 °C?

Answer: about 340 torr (0.45 atm)

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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?
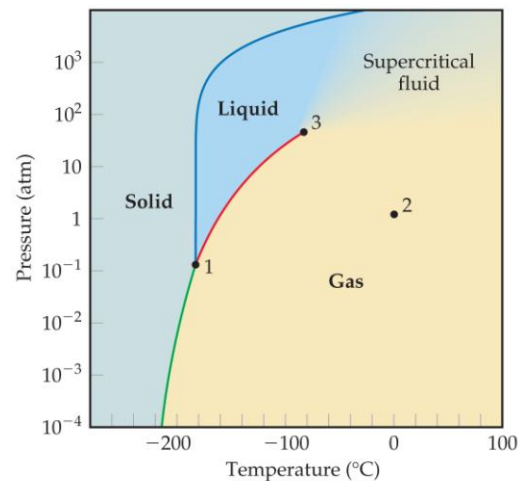
Solution

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.

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.

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Sample Exercise 11.5 Interpreting a Phase Diagram

Continued

(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. (In order 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.

Practice Exercise

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)** Liquid methane does not exist above what temperature?

Answer: **(a)** −162 °C; **(b)** It sublimes whenever the pressure is less than 0.1 atm; **(c)** The highest temperature at which a liquid can exist is defined by the critical temperature. So we do not expect to find liquid methane when the temperature is higher than −80 °C.

Sample Exercise 11.6 Properties of Liquid Crystals

Which of these substances is most likely to exhibit liquid crystalline behavior?

(i)

(ii)

(iii)
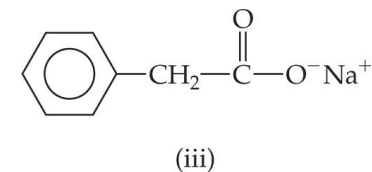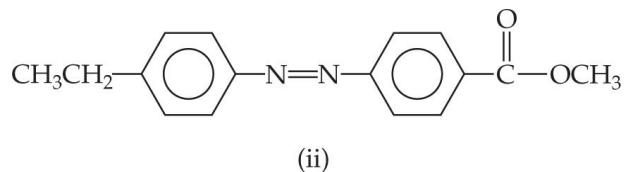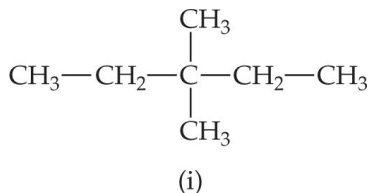
Solution

Analyze We have three molecules with different structures, and we are asked to determine which one is most likely to be a liquid crystalline substance.

Plan We need to identify all structural features that might induce liquid crystalline behavior.

Solve Molecule (i) is not likely to be liquid crystalline because the absence of double and/or triple bonds make this molecule flexible rather than rigid. Molecule (iii) is ionic and the generally high melting points of ionic materials make it unlikely that this substance is liquid crystalline. Molecule (ii) possesses the characteristic long axis and the kinds of structural features often seen in liquid crystals: The molecule has a rodlike shape, the double bonds and benzene rings provide rigidity, and the polar $COOCH_3$ group creates a dipole moment.

Sample Exercise 11.6 Properties of Liquid Crystals

Continued

Practice Exercise

Suggest a reason why decane

$$CH_3CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_2CH_3$$
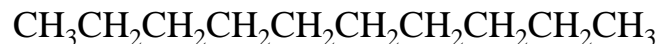
does not exhibit liquid crystalline behavior.

Answer: Because rotation can occur about carbon–carbon single bonds, molecules whose backbone consists predominantly of C − C single bonds are too flexible; the molecules tend to coil in random ways and, thus, are not rodlike.