

Chapter 9 Review Questions and Text Homework Solutions

Review Questions

1. Intermolecular forces are the relatively weak forces between molecules that hold the molecules together in the solid and liquid phases. Intramolecular forces are the forces within a molecule. These are the covalent bonds in a molecule. Intramolecular forces (covalent bonds) are much stronger than intermolecular forces.

Dipole forces are the forces that act between polar molecules. The electrostatic attraction between the positive end of one polar molecule and the negative end of another is the dipole force. Dipole forces are generally weaker than hydrogen bonding. Both of these forces are due to dipole moments in molecules. Hydrogen bonding is given a separate name from dipole forces because hydrogen bonding is a particularly strong dipole force. Any neutral molecule that has a hydrogen covalently bonded to N, O, or F exhibits the relatively strong hydrogen bonding intermolecular forces.

London dispersion forces are accidental-induced dipole forces. Like dipole forces, London dispersion forces are electrostatic in nature. Dipole forces are the electrostatic forces between molecules having a permanent dipole. London dispersion forces are the electrostatic forces between molecules having an accidental or induced dipole. All covalent molecules (polar and nonpolar) have London dispersion forces, but only polar molecules (those with permanent dipoles) exhibit dipole forces.

As the size of a molecule increases, the strength of the London dispersion forces increases. This is because, as the electron cloud about a molecule gets larger, it is easier for the electrons to be drawn away from the nucleus. The molecule is said to be more polarizable.

London dispersion (LD) < dipole-dipole < H bonding < metallic bonding, covalent network, ionic.

Yes, there is considerable overlap. Consider some of the examples in Exercise 9.136 of the text. Benzene (only LD forces) has a higher boiling point than acetone (dipole-dipole forces). Also, there is even more overlap among the stronger forces (metallic, covalent, and ionic).

2.
 - c. Melting point: The temperature (at constant pressure) where a solid converts entirely to a liquid if heat is applied. A more detailed definition is the temperature at which the solid and liquid states have the same vapor pressure under conditions where the total pressure is constant.
 - d. Boiling point: The temperature (at constant pressure) where a liquid converts entirely to a gas if heat is applied. The detailed definition is the temperature at which the vapor pressure of the liquid is exactly equal to the external pressure.
 - e. Vapor pressure: The pressure of the vapor over a liquid at equilibrium.

As the strengths of intermolecular forces increase, surface tension, viscosity, melting point and boiling point increase, while vapor pressure decreases.

3. Solid: Rigid; has fixed volume and shape; slightly compressible

Liquid: Definite volume but no specific shape; assumes shape of the container; slightly compressible

Gas: No fixed volume or shape; easily compressible

- 9.
- a. Evaporation: Process where liquid molecules escape the liquid's surface to form a gas.
 - b. Condensation: Process where gas molecules hit the surface of a liquid and convert to a liquid.
 - c. Sublimation: Process where a solid converts directly to a gas without passing through the liquid state.
 - d. Boiling: The temperature and pressure at which a liquid completely converts to a gas as long as heat is applied.
 - e. Melting: Temperature and pressure at which a solid completely converts to a liquid as long as heat is applied.
 - f. Enthalpy of vaporization (ΔH_{vap}): The enthalpy change that occurs at the boiling point when a liquid converts into a gas.
 - g. Enthalpy of fusion (ΔH_{fus}): The enthalpy change that occurs at the melting point when a solid converts into a liquid.
 - h. Heating curve: A plot of temperature versus time as heat is applied at a constant rate to some substance.

10. Fusion refers to a solid converting to a liquid, and vaporization refers to a liquid converting to a gas. Only a fraction of the hydrogen bonds in ice are broken in going from the solid phase to the liquid phase. Most of the hydrogen bonds in water are still present in the liquid phase and must be broken during the liquid to gas phase transition. Thus, the enthalpy of vaporization is much larger than the enthalpy of fusion because more intermolecular forces are broken during the vaporization process.

A volatile liquid is one that evaporates relatively easily. Volatile liquids have large vapor pressures because the intermolecular forces that prevent evaporation are relatively weak.

11. See Figures 9.21 and 9.22 of the text for the phase diagrams of H_2O and CO_2 . Most substances exhibit only three different phases: solid, liquid, and gas. This is true for H_2O and CO_2 . Also typical of phase diagrams is the positive slopes for both the liquid-gas equilibrium line and the solid-gas equilibrium line. This is also true for both H_2O and CO_2 . The solid-liquid equilibrium line also generally has a positive slope. This is true for CO_2 , but not for H_2O . In the H_2O phase diagram, the slope of the solid-liquid line is negative. The determining factor for the slope of the solid-liquid line is the relative densities of the solid and liquid phases. The solid phase is denser than the liquid phase in most substances; for these substances, the slope of the solid-liquid equilibrium line is

positive. For water, the liquid phase is denser than the solid phase which corresponds to a negative sloping solid-liquid equilibrium line. Another difference between H_2O and CO_2 is the normal melting points and normal boiling points. The term normal just dictates a pressure of 1 atm. H_2O has a normal melting point (0°C) and a normal boiling point (100°C), but CO_2 does not. At 1 atm pressure, CO_2 only sublimates (goes from the solid phase directly to the gas phase). There are no temperatures at 1 atm for CO_2 where the solid and liquid phases are in equilibrium or where the liquid and gas phases are in equilibrium. There are other differences, but those discussed above are the major ones.

The relationship between melting points and pressure is determined by the slope of the solid-liquid equilibrium line. For most substances (CO_2 included), the positive slope of the solid-liquid line shows a direct relationship between the melting point and pressure. As pressure increases, the melting point increases. Water is just the opposite since the slope of the solid-liquid line in water is negative. Here the melting point of water is inversely related to the pressure.

For boiling points, the positive slope of the liquid-gas equilibrium line indicates a direct relationship between the boiling point and pressure. This direct relationship is true for all substances including H_2O and CO_2 .

The critical temperature for a substance is defined as the temperature above which the vapor cannot be liquefied no matter what pressure is applied. The critical temperature, like the boiling point temperature, is directly related to the strength of the intermolecular forces. Since H_2O exhibits relatively strong hydrogen bonding interactions and CO_2 only exhibits London dispersion forces, one would expect a higher critical temperature for H_2O than for CO_2 .

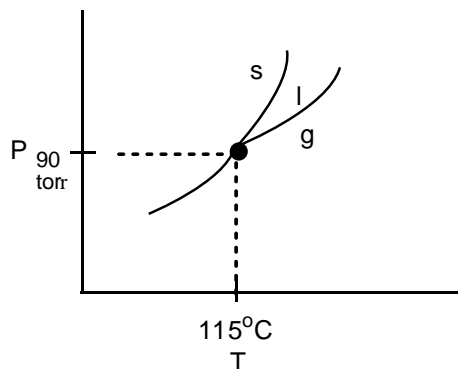
Text Homework

20. Equilibrium: There is no change in composition; the vapor pressure is constant.

Dynamic: Two processes, vapor \rightarrow liquid and liquid \rightarrow vapor, are both occurring but with equal rates, so the composition of the vapor is constant.

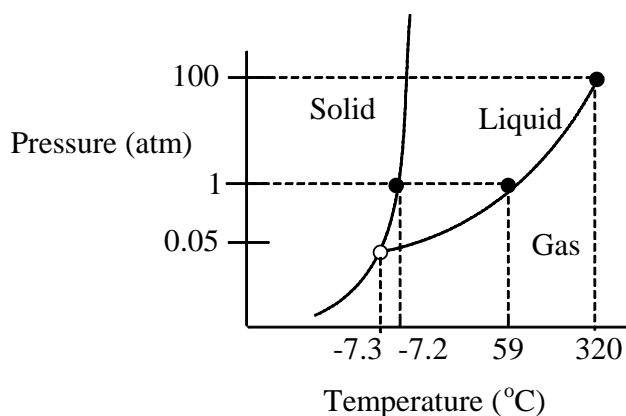
24. The phase change $\text{H}_2\text{O}(\text{g}) \rightarrow \text{H}_2\text{O}(\text{l})$ releases heat that can cause additional damage. Also, steam can be at a temperature greater than 100°C .

34. The typical phase diagram for a substance shows three phases and has a positive-sloping solid-liquid equilibrium line (water is atypical). A sketch of the phase diagram for I_2 would look like this:



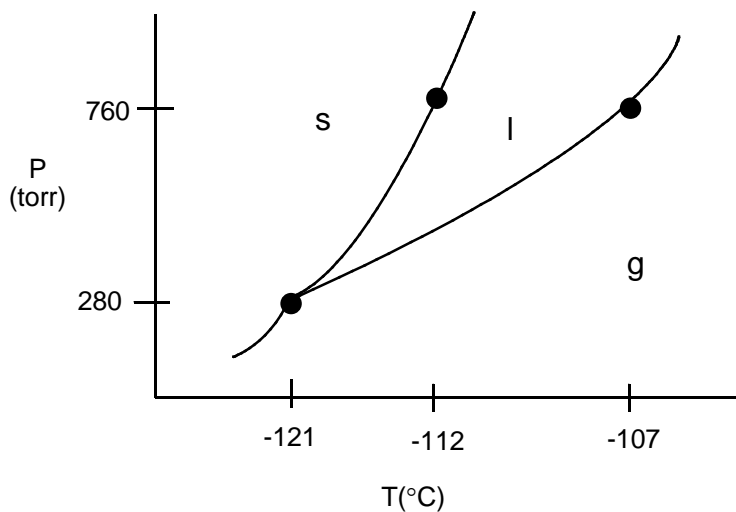
Statements a and e are true. For statement a, the liquid phase is always more dense than the gaseous phase (gases are mostly empty space). For statement e, because the triple point is at 90 torr, the liquid phase cannot exist at any pressure less than 90 torr, no matter what the temperature. For statements b, c, and d, examine the phase diagram to prove to yourself that they are false.

40. The electrostatic potential diagrams indicate that ethanol and acetone are polar substances, and that propane is a nonpolar substance. Ethanol, with the O–H covalent bond, will exhibit relatively strong hydrogen bonding intermolecular forces in addition to London dispersion forces. The polar acetone will exhibit dipole forces in addition to London dispersion forces, and the nonpolar propane will only exhibit London dispersion (LD) forces. Therefore, ethanol (with the H-bonding capacity) should have the highest boiling point, with polar acetone having the next highest boiling point, and the nonpolar propane, with the weakest intermolecular forces, will have the lowest boiling point.
62. a. 3
- b. Triple point at 95.31°C: rhombic, monoclinic, gas
Triple point at 115.18°C: monoclinic, liquid, gas
Triple point at 153°C: rhombic, monoclinic, liquid
- c. From the phase diagram, the monoclinic solid phase is stable at $T = 100.^{\circ}\text{C}$ and $P = 1$ atm.
- d. Normal melting point = 115.21°C; normal boiling point = 444.6°C; the normal melting and boiling points occur at $P = 1.0$ atm.
- e. Rhombic is the densest phase because the rhombic-monoclinic equilibrium line has a positive slope, and because the solid-liquid equilibrium lines also have positive slopes.
- f. No; $P = 1.0 \times 10^{-5}$ atm is at a pressure somewhere between the 95.31 and 115.18°C triple points. At this pressure, the rhombic and gas phases are never in equilibrium with each other, so rhombic sulfur cannot sublime at $P = 1.0 \times 10^{-5}$ atm. However, monoclinic sulfur can sublime at this pressure.
- g. From the phase diagram, we would start off with gaseous sulfur. At 100.°C and $\sim 1 \times 10^{-5}$ atm, S(g) would convert to the solid monoclinic form of sulfur. Finally at 100.°C and some large pressure less than 1420 atm, S(s, monoclinic) would convert to the solid rhombic form of sulfur. Summarizing, the phase changes are $S(\text{g}) \rightarrow S(\text{monoclinic}) \rightarrow S(\text{rhombic})$.
64. The following sketch of the Br₂ phase diagram is not to scale. Because the triple point of Br₂ is at a temperature below the freezing point of Br₂, the slope of the solid-liquid line is positive.



The positive slopes of all the lines indicate that $\text{Br}_2(\text{s})$ is denser than $\text{Br}_2(\text{l})$, which is more dense than $\text{Br}_2(\text{g})$. At room temperature ($\sim 22^\circ\text{C}$) and 1 atm, $\text{Br}_2(\text{l})$ is the stable phase. $\text{Br}_2(\text{l})$ cannot exist at a temperature below the triple-point temperature of -7.3°C or at a temperature above the critical-point temperature of 320°C . The phase changes that occur as temperature is increased at 0.10 atm are solid \rightarrow liquid \rightarrow gas.

66.



From the three points given, the slope of the solid-liquid boundary line is positive, so $\text{Xe}(\text{s})$ is more dense than $\text{Xe}(\text{l})$. Also, the positive slope of this line tells us that the melting point of Xe increases as pressure increases. The same direct relationship exists for the boiling point of Xe because the liquid-gas boundary line also has a positive slope.

112. At any temperature, the plot tells us that substance A has a higher vapor pressure than substance B, with substance C having the lowest vapor pressure. Therefore, the substance with the weakest intermolecular forces is A, and the substance with the strongest intermolecular forces is C.

NH_3 can form hydrogen-bonding interactions, whereas the others cannot. Substance C is NH_3 . The other two are nonpolar compounds with only London dispersion forces. Because CH_4 is smaller than SiH_4 , CH_4 will have weaker LD forces and is substance A. Therefore, substance B is SiH_4 .

130. The critical temperature is the temperature above which the vapor cannot be liquefied no matter what pressure is applied. Since N_2 has a critical temperature below room temperature ($\sim 22^\circ\text{C}$), it cannot be liquefied at room temperature. NH_3 , with a critical temperature above room temperature, can be liquefied at room temperature.