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 elec-trons 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 sublimes (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

5. The nature of the forces stay the same. It is the amount of intermolecular forces that differ in the various phases. Solids have the largest amount of intermolecular forces. To convert a solid into a liquid requires breaking about 15-20% of the intermolecular forces; but the types of forces are still the same. To go from a liquid to a gas requires breaking the remaining intermolecular forces in the liquid phase. In the gas phase, no intermolecular forces are assumed to exist.

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

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

21. a. As the strength of the intermolecular forces increase, the rate of evaporation decreases.

b. As temperature increases, the rate of evaporation increases.

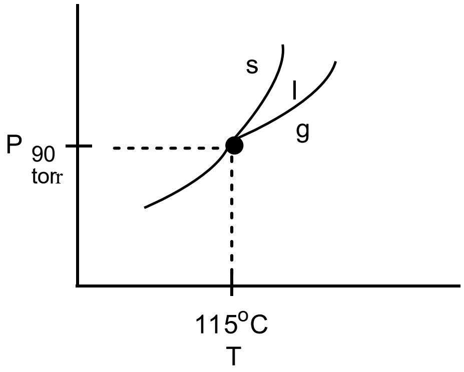
c. As surface area increases, the rate of evaporation increases.

23. $C_2H_5OH(l) \rightarrow C_2H_5OH(g)$ is an endothermic process. Heat is absorbed when liquid ethanol vaporizes; the internal heat from the body provides this heat, which results in the cooling of the body.

24. The phase change $H_2O(g) \rightarrow H_2O(l)$ releases heat that can cause additional damage. Also, steam can be at a temperature greater than 100°C.

27. The strength of intermolecular forces determines relative boiling points. The types of intermolecular forces for covalent compounds are London dispersion forces, dipole forces, and hydrogen bonding. Because the three compounds are assumed to have similar molar mass and shape, the strength of the London dispersion forces will be about equal among the three compounds. One of the compounds will be nonpolar, so it only has London dispersion forces. The other two compounds will be polar, so they have additional dipole forces and will boil at a higher temperature than the nonpolar compound. One of the polar compounds will have an H covalently bonded to either N, O, or F. This gives rise to the strongest type of covalent intermolecular forces, hydrogen bonding. The compound that hydrogen bonds will have the highest boiling point, whereas the polar compound with no hydrogen bonding will boil at a temperature in the middle of the other compounds.

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.

37. a. OCS; OCS is polar and has dipole-dipole forces in addition to London dispersion (LD) forces. All polar molecules have dipole forces. CO_2 is nonpolar and only has LD forces. To predict polarity, draw the Lewis structure and deduce whether the individual bond dipoles cancel.

b. SeO_2; both SeO_2 and SO_2 are polar compounds, so they both have dipole forces as well as LD forces. However, SeO_2 is a larger molecule, so it would have stronger LD forces.

c. $H_2NCH_2CH_2NH_2$; more extensive hydrogen bonding (H-bonding) is possible because two NH_2 groups are present.

d. H_2CO; H_2CO is polar, whereas CH_3CH_3 is nonpolar. H_2CO has dipole forces in addition to LD forces. CH_3CH_3 only has LD forces.

e. CH_3OH; CH_3OH can form relatively strong H-bonding interactions, unlike H_2CO.

39. a. Neopentane is more compact than n-pentane. There is less surface-area contact among neopentane molecules. This leads to weaker London dispersion (LD) forces and a lower boiling point.

b. HF is capable of H-bonding; HCl is not.

c. LiCl is ionic, and HCl is a molecular solid with only dipole forces and LD forces. Ionic forces are much stronger than the forces for molecular solids.

d. n-Hexane is a larger molecule, so it has stronger LD forces.

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.

41. Boiling points and freezing points are assumed directly related to the strength of the intermolecular forces, whereas vapor pressure is inversely related to the strength of the intermolecular forces.

a. HBr; HBr is polar, whereas Kr and Cl_2 are nonpolar. HBr has dipole forces unlike Kr and Cl_2. So HBr has the stronger intermolecular forces and the highest boiling point.

b. NaCl; the ionic forces in NaCl are much stronger than the intermolecular forces for molecular substances, so NaCl has the highest melting point.

c. I_2; all are nonpolar, so the largest molecule (I_2) will have the strongest LD (London Dispersion) forces and the lowest vapor pressure.

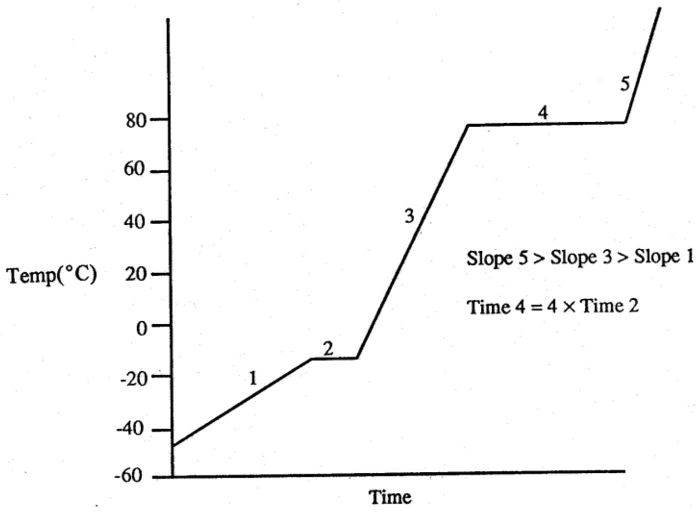
d. N_2; nonpolar and smallest, so it has the weakest intermolecular forces.

e. CH_4; smallest, nonpolar molecule, so it has the weakest LD forces.

f. HF; HF can form relatively strong H-bonding interactions, unlike the others.

g. $CH_3CH_2CH_2OH$; H-bonding, unlike the others, so it has strongest intermolecular forces.

53.



61. A: solid B: liquid C: vapor

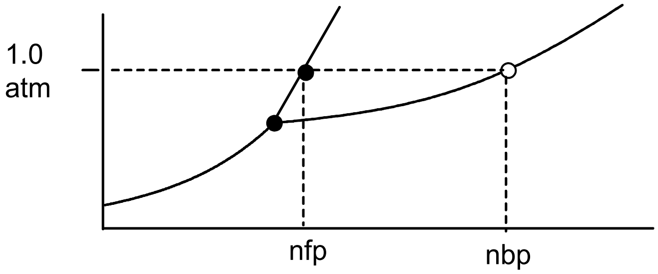
D: solid + vapor E: solid + liquid + vapor

F: liquid + vapor G: liquid + vapor H: vapor

triple point: E critical point: G

Normal freezing point: Temperature at which solid-liquid line is at 1.0 atm (see following plot).

Normal boiling point: Temperature at which liquid-vapor line is at 1.0 atm (see following plot).



Because the solid-liquid line equilibrium has a positive slope, the solid phase is denser than the liquid phase.

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.°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(g) $\rightarrow$ S(monoclinic) $\rightarrow$ S(rhombic).

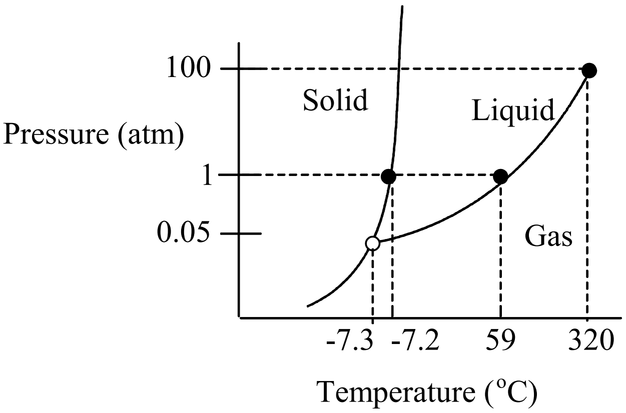
63. a. two

b. Higher-pressure triple point: graphite, diamond and liquid; lower-pressure triple point at $\sim 10^7$ Pa: graphite, liquid and vapor

c. It is converted to diamond (the more dense solid form).

d. Diamond is more dense, which is why graphite can be converted to diamond by applying pressure.

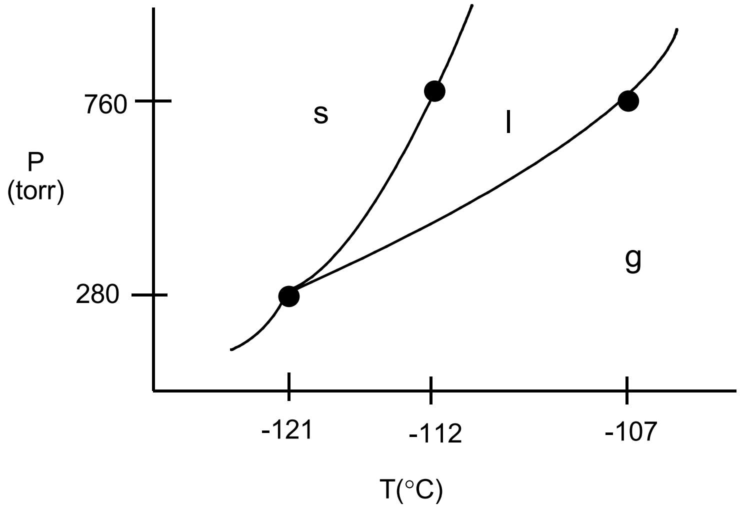
64. The following sketch of the Br_2 phase diagram is not to scale. Because the triple point of Br_2 is at a temperature below the freezing point of Br_2, the slope of the solid-liquid line is positive.



The positive slopes of all the lines indicate that $Br_2(s)$ is denser than $Br_2(l)$, which is more dense than $Br_2(g)$. At room temperature (~22°C) and 1 atm, $Br_2(l)$ is the stable phase. $Br_2(l)$ 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 → liquid → gas.

65. Because the density of the liquid phase is greater than the density of the solid phase, the slope of the solid-liquid boundary line is negative (as in H_2O). With a negative slope, the melting points increase with a decrease in pressure, so the normal melting point of X should be greater than 225°C.

66.



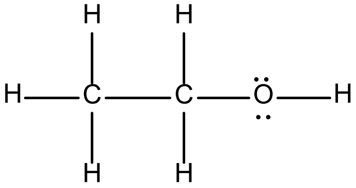
From the three points given, the slope of the solid-liquid boundary line is positive, so Xe(s) is more dense than Xe(l). Also, the positive slope of this line tells us that the melting point of Xe increases as pressure increases. The same direct relationship exists for the boiling point of Xe because 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 sub-stance 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.

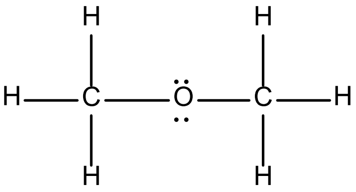
NH_3 can form hydrogen-bonding interactions, whereas the others cannot. Substance C is NH_3. The other two are nonpolar compounds with only London dispersion forces. Because CH_4 is smaller than SiH_4, CH_4 will have weaker LD forces and is substance A. Therefore, substance B is SiH_4.

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 (~22°C), it cannot be liquefied at room temperature. NH_3, with a critical temperature above room temperature, can be liquefied at room temperature.

135. The structures of the two C_2H_6O compounds (20 valence e^-) are:



exhibits relatively strong hydrogen bonding



does not exhibit hydrogen bonding

The liquid will have the stronger intermolecular forces. Therefore, the first compound (ethanol) with hydrogen bonding is the liquid and the second compound (dimethyl ether) with the weaker intermolecular forces is the gas.