We now have the triple point data for hydrazine. The triple point temperature is 2.0 °C (275.2 K) and the triple point pressure is 3.38 Torr. In our final application of equation (12.2), we use those data as T_2 and P_2. The temperature T_1 is 0 °C (273.2 K) and the unknown sublimation pressure is P_1. The enthalpy change needed in this final calculation must be the enthalpy of sublimation, which is

$$\Delta_{sub}H = \Delta_{fus}H + \Delta_{vap}H$$

$$= \left(12.66\frac{kJ}{mol} \times \frac{1000\,J}{1\,kJ}\right) + 4.30 \times 10^4\,J\,mol^{-1} = 5.57 \times 10^4\,J\,mol^{-1}$$

Finally, we substitute these data into equation (12.2) and solve for P_1, the sublimation pressure of hydrazine at 0 °C.

$$\ln\left(\frac{3.38\,Torr}{P_1}\right) = -\frac{5.57 \times 10^4\,J\,mol^{-1}}{8.3145\,J\,mol^{-1}\,K^{-1}} \times \left(\frac{1}{275.2} - \frac{1}{273.2}\right)K^{-1}$$

$$\ln\left(\frac{3.38\,Torr}{P_1}\right) = -6.70 \times 10^3 \times (-2.66 \times 10^{-5}) = 0.178$$

$$\frac{3.38\,Torr}{P_1} = e^{0.178} = 1.19$$

$$P_1 = \frac{3.38\,Torr}{1.19} = 2.84\,Torr$$

Assess

Observe that, compared with the vapor pressure at 25 °C (14.4 Torr), the calculated triple point pressure (3.38 Torr) is smaller; and the sublimation pressure at 0 °C (2.84 Torr) is smaller still. This is certainly the trend expected for the three values. In the three situations in which equation (12.2) is used, the first one is the most subject to error because the difference between T_2 and T_1 is 89 °C, while in the other two it is 23 °C and 2 °C, respectively. Both $\Delta_{vap}H$ and $\Delta_{sub}H$ are undoubtedly temperature-dependent.

PRACTICE EXAMPLE A: The normal boiling point of isooctane (a gasoline component with a high octane rating) is 99.2 °C, and its $\Delta_{vap}H$ is 35.76 kJ mol^{-1}. Because isooctane and water have nearly identical boiling points, will they have nearly equal vapor pressures at room temperature? If not, which would you expect to be more volatile? Explain.

PRACTICE EXAMPLE B: The *second* electron affinity of oxygen is, by definition, the energy change for adding an electron to O$^-$ to form O^{2-}:

$$O^-(g) + e^- \longrightarrow O^{2-}(g) \quad E_{ea,2} = ?$$
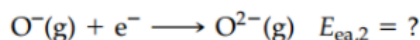
The second electron affinity cannot be measured directly, but it can be obtained indirectly by using the Born–Haber cycle for an ionic compound containing the O^{2-} ion.

(a) Show that $E_{ea,2}$ can be calculated from the enthalpy of formation and lattice energy of MgO(s), the enthalpy of sublimation of Mg(s), the ionization energies of Mg, the bond energy of O$_2$, and the $E_{ea,1}$ for O(g).

(b) The lattice energy of MgO is -3925 kJ mol^{-1}. Combine this with other values in the text to estimate $E_{ea,2}$ for oxygen.


Exercises

Intermolecular Forces

1. For each of the following substances describe the importance of dispersion (London) forces, dipole–dipole interactions, and hydrogen bonding: **(a)** HCl; **(b)** Br$_2$; **(c)** ICl; **(d)** HF; **(e)** CH$_4$.

2. When another atom or group of atoms is substituted for one of the hydrogen atoms in benzene, C$_6$H$_6$, the boiling point changes. Explain the order of the following boiling points: C$_6$H$_6$, 80 °C; C$_6$H$_5$Cl, 132 °C; C$_6$H$_5$Br, 156 °C; C$_6$H$_5$OH, 182 °C.

3. Arrange the liquids represented by the following molecular models in the expected order of increasing viscosity at 25 °C.

(a)   (b)   (c)   (d)
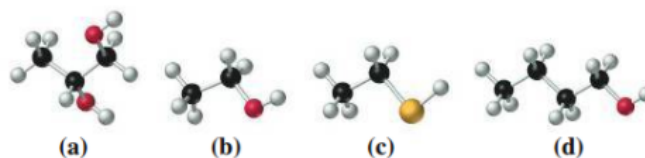
4. Arrange the liquids represented by the following molecular models in the expected order of increasing normal boiling point.

(a)   (b)   (c)   (d)
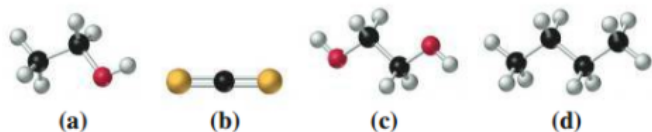
5. One of the following substances is a liquid at room temperature and the others are gaseous: CH_3OH; C_3H_8; N_2; N_2O. Which do you think is the liquid? Explain.

6. In which of the following compounds might intramolecular hydrogen bonding be an important factor? Explain. (a) $CH_3CH_2COCH_3$; (b) $CH_3NH_2CH_2CH_2COOH$; (c) $CH_3CH_2CHFCH_2OH$; (d) *ortho*-phthalic acid.
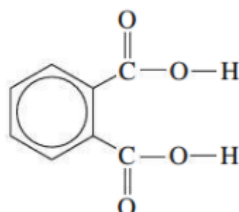
ortho-Phthalic acid

Surface Tension and Viscosity

11. Silicone oils, such as $H_3C[SiO(CH_3)_2]_n Si(CH_3)$, are used in water repellents for treating tents, hiking boots, and similar items. Explain how silicone oils function.

12. Surface tension, viscosity, and vapor pressure are all related to intermolecular forces. Why do surface tension and viscosity decrease with temperature, whereas vapor pressure increases with temperature?

13. Is there any scientific basis for the colloquial expression "slower than molasses in January"? Explain.

14. A television commercial claims that a product makes water "wetter." Can there be any basis to this claim? Explain.

Vaporization

19. As a liquid evaporated from an open container, its temperature was observed to remain roughly constant. When the same liquid evaporated from a thermally insulated container (a vacuum bottle or Dewar flask), its temperature was observed to drop. How would you account for this difference?

20. Explain why vaporization occurs only at the surface of a liquid until the boiling point temperature is reached. That is, why does vapor not form throughout the liquid at all temperatures?

21. The enthalpy of vaporization of benzene, $C_6H_6(l)$, is 33.9 kJ mol^{-1} at 298 K. How many liters of $C_6H_6(g)$, measured at 298 K and 95.1 mmHg, are formed when 1.54 kJ of heat is absorbed by $C_6H_6(l)$ at a constant temperature of 298 K?

7. How many water molecules can hydrogen bond to methanol?

8. What is the maximum number of hydrogen bonds that can form between two acetic acid molecules?

9. In DNA the nucleic acid bases form hydrogen bonds between them, which are responsible for the formation of the double-stranded helix. Arrange the bases guanine and cytosine to give the maximum number of hydrogen bonds.
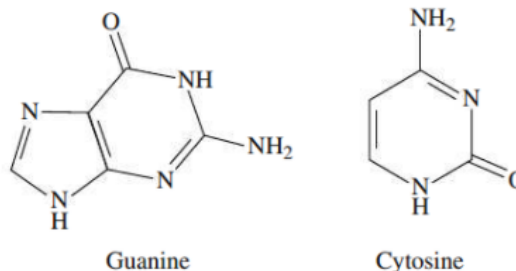
Guanine   Cytosine

10. Water molecules will form small, stable clusters. Draw one possible water cluster by using six water molecules and maximizing the number of hydrogen bonds for each water molecule.

15. Rank the following in order of increasing surface tension (at room temperature): (a) CH_3OH; (b) $HOCH_2CH_2OH$; (c) $CH_3CH_2OCH_2CH_3$.

16. Would you predict the surface tension of t-butyl alcohol, $(CH_3)_3COH$, to be greater than or less than that of n-butyl alcohol, $CH_3CH_2CH_2CH_2OH$? Explain.

17. Butanol and pentane have approximately the same mass, however, the viscosity (at 20 °C) of butanol is $\eta = 2.948$ cP, and the viscosity of pentane is $\eta = 0.240$ cP. Explain this difference.

18. Carbon tetrachloride (CCl_4) and mercury have similar viscosities at 20 °C. Explain.

22. A vapor volume of 1.17 L forms when a sample of liquid acetonitrile, CH_3CN, absorbs 1.00 kJ of heat at its normal boiling point (81.6 °C and 1 atm). What is $\Delta_{vap}H$ in kilojoules per mole of CH_3CN?

23. Use data from the Integrative Example (page 566) to determine how much heat is required to convert 25.00 mL of liquid hydrazine at 25.0 °C to hydrazine vapor at its normal boiling point.

24. How much heat is required to raise the temperature of 215 g $CH_3OH(l)$ from 20.0 to 30.0 °C and then vaporize it at 30.0 °C? Use data from Table 12.4 and a molar heat capacity of $CH_3OH(l)$ of 81.1 J mol^{-1}K^{-1}.

25. How many liters of $CH_4(g)$, measured at 23.4 °C and 768 mmHg, must be burned to provide the heat needed to vaporize 3.78 L of water at 100 °C? For CH_4, $\Delta_{comb}H =$

-8.90×10^2 kJ mol^{-1}. For H$_2$O(l) at 100 °C, $d = 0.958$ g cm^{-3}, and $\Delta_{vap}H = 40.7$ kJ mol^{-1}.

26. A 50.0 g piece of iron at 152 °C is dropped into 20.0 g H$_2$O(l) at 89 °C in an open, thermally insulated container. How much water would you expect to vapor-ize, assuming no water splashes out? The specific heats of iron and water are 0.45 and 4.21 J g^{-1} °C^{-1}, respectively, and $\Delta_{vap}H = 40.7$ kJ mol^{-1}H$_2$O.

Vapor Pressure and Boiling Point

27. From Figure 12-18, estimate **(a)** the vapor pressure of C$_6$H$_5$NH$_2$ at 100 °C; **(b)** the normal boiling point of C$_6$H$_5$CH$_3$.

28. Use data in Figure 12-20 to estimate **(a)** the normal boiling point of aniline; **(b)** the vapor pressure of diethyl ether at 25 °C.

29. Equilibrium is established between Br$_2$(l) and Br$_2$(g) at 25.0 °C. A 250.0 mL sample of the vapor weighs 0.486 g. What is the vapor pressure of bromine at 25.0 °C, in millimeters of mercury?

30. The density of acetone vapor in equilibrium with liq-uid acetone, (CH$_3$)$_2$CO, at 32 °C is 0.876 g L^{-1}. What is the vapor pressure of acetone at 32 °C, expressed in kilopascals?

31. A double boiler is used when a careful control of tem-perature is required in cooking. Water is boiled in an outside container to produce steam, and the steam condenses on the outside walls of an inner container in which cooking occurs. (A related laboratory device is called a steam bath.) **(a)** How is heat energy conveyed to the food to be cooked in a double boiler? **(b)** What is the maximum temperature that can be reached in the inside container?

32. One popular demonstration in chemistry labs is per-formed by boiling a small quantity of water in a metal can (such as a used soda can), picking up the can with tongs and quickly submerging it upside down in cold water. The can collapses with a loud and satisfying pop. Give an explanation of this crushing of the can. (Note: If you try this demonstration, do not heat the can over an open flame.)

33. Pressure cookers achieve a high cooking temperature to speed the cooking process by heating a small amount of water under a constant pressure. If the pressure is set at 2 atm, what is the boiling point of the water? Use information from Table 12.5.

34. Use data from Table 12.5 to estimate **(a)** the boiling point of water in Santa Fe, New Mexico, if the prevailing atmospheric pressure is 640 mmHg; **(b)** the prevailing atmospheric pressure at Lake Arrowhead, California, if the observed boiling point of water is 94 °C.

35. A 25.0 L volume of He(g) at 30.0 °C is passed through 6.220 g of liquid aniline (C$_6$H$_5$NH$_2$) at 30.0 °C. The liquid remaining after the experiment weighs 6.108 g. Assume that the He(g) becomes saturated with ani-line vapor and that the total gas volume and tempera-ture remain constant. What is the vapor pressure of aniline at 30.0 °C?

36. A 7.53 L sample of N$_2$(g) at 742 mmHg and 45.0 °C is bubbled through CCl$_4$(l) at 45.0 °C. Assuming the gas becomes saturated with CCl$_4$(g), what is the vol-ume of the resulting gaseous mixture if the total pres-sure remains at 742 mmHg and the temperature remains at 45 °C? The vapor pressure of CCl$_4$ at 45 °C is 261 mmHg.

37. Some vapor pressure data for Freon-12, CCl$_2$F$_2$, once a common refrigerant, are -12.2 °C, 2.0 atm; 16.1 °C, 5.0 atm; 42.4 °C, 10.0 atm; 74.0 °C, 20.0 atm. Also, bp $= -29.8$ °C, $T_c = 111.5$ °C, $P_c = 39.6$ atm. Use these data to plot the vapor pressure curve of Freon-12. What approximate pressure would be required in the compressor of a refrigeration system to convert Freon-12 vapor to liquid at 25.0 °C?

38. A 10.0 g sample of liquid water is sealed in a 1515 mL flask and allowed to come to equilibrium with its vapor at 27 °C. What is the mass of H$_2$O(g) present when equilibrium is established? Use vapor pressure data from Table 12.5.

The Clausius–Clapeyron Equation

39. Cyclohexanol has a vapor pressure of 10.0 mmHg at 56.0 °C and 100.0 mmHg at 103.7 °C. Calculate its enthalpy of vaporization, $\Delta_{vap}H$.

40. The vapor pressure of methyl alcohol is 40.0 mmHg at 5.0 °C. Use this value and other information from the text to estimate the normal boiling point of methyl alcohol.

41. The normal boiling point of acetone, an important laboratory and industrial solvent, is 56.2 °C and its $\Delta_{vap}H$ is 25.5 kJ mol^{-1}. At what temperature does ace-tone have a vapor pressure of 375 mmHg?

42. The vapor pressure of trichloromethane (chloroform) is 40.0 Torr at -7.1 °C. Its enthalpy of vaporization is 29.2 kJ mol^{-1}. Calculate its normal boiling point.

43. Benzaldehyde, C$_6$H$_5$CHO, has a normal boiling point of 179.0 °C and a critical point at 422 °C and 45.9 atm. Estimate its vapor pressure at 100.0 °C.

44. With reference to Figure 12-20, which is the more volatile liquid, benzene or toluene? At approximately what temperature does the less volatile liquid have the same vapor pressure as the more volatile one at 65 °C?

Critical Point

45. Which substances listed in Table 12.6 can exist as liq-uids at room temperature (about 20.0 °C)? Explain.

46. Can SO$_2$ be maintained as a liquid under a pressure of 100 atm at 0 °C? Can liquid methane be obtained under the same conditions?

Melting and Freezing

47. The normal melting point of copper is 1357 K, and $\Delta_{fus}H$ of Cu is 13.05 kJ mol^{-1}. **(a)** How much heat, in kilojoules, is evolved when a 3.78 kg sample of molten Cu freezes? **(b)** How much heat, in kilojoules, must be absorbed at 1357 K to melt a bar of copper that is 75 cm × 15 cm × 12 cm? (Assume $d = 8.92$ g/cm^3 for Cu.)

48. An ice calorimeter measures quantities of heat by the quantity of ice melted. How many grams of ice would be melted by the heat released in the complete combustion of 1.60 L of propane gas, $C_3H_8(g)$, measured at 20.0 °C and 735 mmHg? [*Hint:* What is the standard molar enthalpy of combustion of $C_3H_8(g)$?]

States of Matter and Phase Diagrams

49. An 80.0 g piece of dry ice, $CO_2(s)$, is placed in a 0.500 L container, and the container is sealed. If this container is held at 25 °C, what state(s) of matter must be present? [*Hint:* Refer to Table 12.6 and Figure 12-28.]

50. Sketch a plausible phase diagram for hydrazine (N_2H_4) from the following data: triple point (2.0 °C and 3.4 mmHg), the normal melting point (2 °C), the normal boiling point (113.5 °C), and the critical point (380 °C and 145 atm). The density of the liquid is less than that of the solid. Label significant data points on this diagram. Are there any features of the diagram that remain uncertain? Explain.

51. Shown here is a portion of the phase diagram for phosphorus.
(a) Indicate the phases present in the regions labeled with a question mark.
(b) A sample of solid red phosphorus cannot be melted by heating in a container open to the atmosphere. Explain why this is so.
(c) Trace the phase changes that occur when the pressure on a sample is reduced from point A to B, at constant temperature.
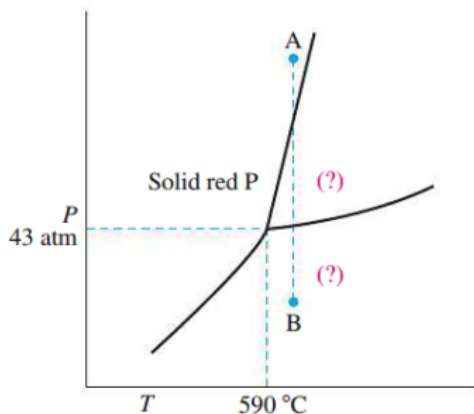
52. Describe what happens to the following samples in situations like those pictured in Figure 12-31. Be as specific as you can about the temperatures and pressures at which changes occur.
(a) A sample of water is heated from −20 to 200 °C at a constant pressure of 600 Torr.
(b) The pressure on a sample of iodine is increased from 90 mmHg to 100 atm at a constant temperature of 114 °C.

(c) A sample of carbon dioxide at 35 °C is cooled to −100 °C at a constant pressure of 50 atm. [*Hint:* Refer also to Table 12.6.]

53. A 0.240 g sample of $H_2O(l)$ is sealed into an evacuated 3.20 L flask. What is the pressure of the vapor in the flask if the temperature is **(a)** 30.0 °C; **(b)** 50.0 °C; **(c)** 70.0 °C?

54. A 2.50 g sample of $H_2O(l)$ is sealed in a 5.00 L flask at 120.0 °C.
(a) Show that the sample exists completely as vapor.
(b) Estimate the temperature to which the flask must be cooled before liquid water condenses.

55. Use appropriate phase diagrams and data from Table 12.6 to determine whether any of the following is likely to occur naturally at or near Earth's surface anywhere on Earth. Explain. **(a)** $CO_2(s)$; **(b)** $CH_4(l)$; **(c)** $SO_2(g)$; **(d)** $I_2(l)$; **(e)** $O_2(l)$.

56. Trace the phase changes that occur as a sample of $H_2O(g)$, originally at 1.00 mmHg and −0.10 °C, is compressed at constant temperature until the pressure reaches 100 atm.

57. To an insulated container with 100.0 g $H_2O(l)$ at 20.0 °C, 175 g steam at 100.0 °C and 1.65 kg of ice at 0.0 °C are added.
(a) What mass of ice remains unmelted after equilibrium is established?
(b) What *additional* mass of steam should be introduced into the insulated container to just melt all of the ice?

58. A 54 cm^3 ice cube at −25.0 °C is added to a thermally insulated container with 400.0 mL $H_2O(l)$ at 32.0 °C. What will be the final temperature in the container and what state(s) of matter will be present? (Specific heats: $H_2O(s)$, 2.01 J g^{-1} °C^{-1}; $H_2O(l)$, 4.18 J g °C^{-1}. Densities: $H_2O(s)$, 0.917 g/cm^3; $H_2O(l)$, 0.998 g/cm^3. Also, $\Delta_{fus}H$ of ice = 6.01 kJ mol^{-1}.)

59. You decide to cool a can of soda pop quickly in the freezer compartment of a refrigerator. When you take out the can, the soda pop is still liquid; but when you open the can, the soda pop immediately freezes. Explain why this happens.

60. Why is the triple point of water (ice–liquid–vapor) a better fixed point for establishing a thermometric scale than either the melting point of ice or the boiling point of water?

Network Covalent Solids

61. Based on data presented in the text, would you expect diamond or graphite to have the greater density? Explain.

62. Diamond is often used as a cutting medium in glass cutters. What property of diamond makes this possible? Could graphite function as well?

63. Silicon carbide, SiC, crystallizes in a form similar to diamond, whereas boron nitride, BN, crystallizes in a form similar to graphite.
(a) Sketch the SiC structure as in Figure 12-32(b).
(b) Propose a bonding scheme for BN.

64. Are the fullerenes network covalent solids? What makes them different from diamond and graphite? It has been shown that carbon can form chains in which every other carbon atom is bonded to the next carbon atom by a triple bond. Is this allotrope of carbon a network covalent solid? Explain.

Ionic Bonding and Properties

65. The melting points of NaF, NaCl, NaBr, and NaI are 988, 801, 755, and 651 °C, respectively. Are these data consistent with ideas developed in Section 12-5? Explain.

66. Use Coulomb's law (see Appendix B) to verify the conclusion concerning the relative strengths of the attractive forces in the ion pairs Na^+Cl^- and $Mg^{2+}O^{2-}$ presented in Figure 12-36.

67. The hardness of crystals is rated based on Mohs hardness values. The higher the Mohs value, the harder the material is to scratch. Which crystal will have the highest Mohs value: NaF, NaCl, or KCl?

68. Will the mineral villaumite (NaF) or periclase (MgO) have a higher Mohs hardness value (see Exercise 67)?

Crystal Structures

69. Explain why there are *two* arrangements for the closest packing of spheres rather than a single one.

70. Argon, copper, sodium chloride, and carbon dioxide all crystallize in the fcc structure. How can this be when their physical properties are so different?

71. Consider the two-dimensional lattice shown here.
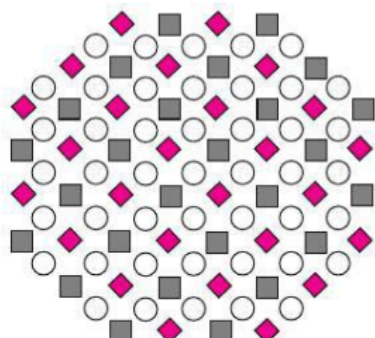
(a) Identify a unit cell.
(b) How many of each of the following elements are in the unit cell: ◆, ■, and ○ ?
(c) Indicate some simpler units than the unit cell, and explain why they cannot function as a unit cell.

72. As we saw in Section 12-6, stacking spheres always leaves open space. Consider the corresponding situation in two dimensions: Squares can be arranged to cover all the area, but circles cannot. For the arrangement of circles pictured here, what percentage of the area remains uncovered?
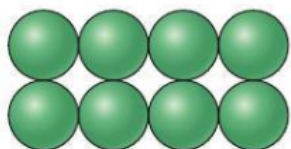

73. Tungsten has a body-centered cubic crystal structure. Using a metallic radius of 139 pm for the W atom, calculate the density of tungsten.

74. Magnesium crystallizes in the hcp arrangement shown in Figure 12-41. The dimensions of the unit cell are height, 520 pm; length on an edge, 320 pm. Calculate the density of Mg(s), and compare with the measured value of 1.738 g/cm^3.

75. Polonium (Po) is the only element known to take on the simple cubic crystal system. The distance between nearest neighbor Po atoms in this structure is 335 pm.
(a) What is the diameter of a Po atom?
(b) What is the density of Po metal?
(c) At what angle (in degrees) to the parallel faces of the Po unit cells would first order diffraction be observed when using X-rays of wavelength 1.785×10^{-10} m?

76. Germanium has a cubic unit cell with a side edge of 565 pm. The density of germanium is 5.36 g/cm^3. What is the crystal system adopted by germanium?

77. Silicon tetrafluoride molecules are arranged in a body-centered cubic unit cell. How many silicon atoms are in the unit cell?

78. Two views, a top and side view, for the unit cell for rutile (TiO_2) are shown here. (a) How many titanium atoms (blue) are in this unit cell? (b) How many oxygen atoms (red) are in this unit cell?
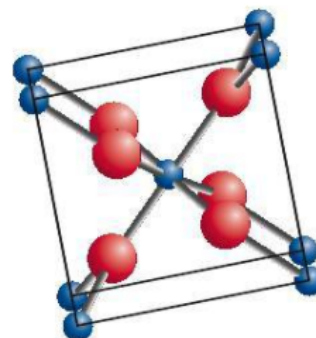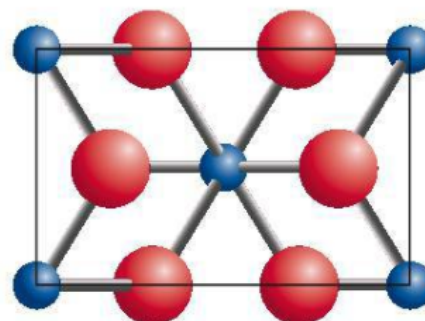
Ionic Crystal Structures

79. Show that the unit cells for CaF_2 and TiO_2 in Figure 12-50 are consistent with their formulas.
80. Using methods similar to Examples 12-10 and 12-11, calculate the density of CsCl. Use 169 pm as the radius of Cs^+.
81. The crystal structure of magnesium oxide, MgO, is of the NaCl type (Fig. 12-48). Use this fact, together with ionic radii from Figure 9-11, to establish the following.
    (a) the coordination numbers of Mg^{2+} and O^{2-};
    (b) the number of formula units in the unit cell;
    (c) the length and volume of a unit cell;
    (d) the density of MgO.

82. Potassium chloride has the same crystal structure as NaCl. Careful measurement of the internuclear distance between K^+ and Cl^- ions gave a value of 314.54 pm. The density of KCl is 1.9893 g/cm^3. Use these data to evaluate the Avogadro constant, N_A.
83. Use data from Figure 9-11 to predict the type of cubic unit cell adopted by (a) CaO; (b) CuCl; (c) LiO_2 (the radius of the O_2^- ion is 128 pm).
84. Use data from Figure 9-9 to predict the type of cubic unit cell adopted by (a) BaO; (b) CuI; (c) LiS_2. (The radii of Ba^{2+} and S_2^- ions are 135 and 198 pm, respectively.)

Lattice Energy

85. *Without doing calculations*, indicate how you would expect the lattice energies of LiCl(s), KCl(s), RbCl(s), and CsCl(s) to compare with the value of -787 kJ mol^{-1} determined for NaCl(s) on page 563. [*Hint:* Assume that the enthalpies of sublimation of the alkali metals are comparable in value. What atomic properties from Chapter 9 should you compare?]
86. Determine the lattice energy of KF(s) from the following data: $\Delta_f H°[KF(s)] = -567.3$ kJ mol^{-1}; enthalpy of sublimation of K(s), 89.24 kJ mol^{-1}; enthalpy of dissociation of $F_2(g)$, 159 kJ mol^{-1} F_2; E_i for K(g), 418.9 kJ mol^{-1}; E_{ea} for F(g), -328kJ mol^{-1}.
87. Refer to Example 12-12. Together with data given there, use the data here to calculate $\Delta_f H°$ for 1 mol

$MgCl_2(s)$. Explain why you would expect $MgCl_2$ to be a much more stable compound than MgCl. (The second ionization energy of Mg is 1451 kJ mol^{-1}; the lattice energy of $MgCl_2(s)$ is -2526 kJ mol^{-1} $MgCl_2$.)
88. In ionic compounds with certain metals, hydrogen exists as the hydride ion, H^-. Determine the electron affinity of hydrogen; that is, $\Delta_r H$ for the process $H(g) + e^- \rightarrow H^-(g)$. To do so, use data from Section 12-7; the bond energy of $H_2(g)$ from Table 10.3; -812 kJ mol^{-1} for the lattice energy of NaH(s); and -57 kJ mol^{-1} NaH for the enthalpy of formation of NaH(s).

Integrative and Advanced Exercises

89. When a wax candle is burned, the fuel consists of *gaseous* hydrocarbons appearing at the end of the candle wick. Describe the phase changes and processes by which the solid wax is ultimately consumed.
90. The normal boiling point of water is 100.00 °C and the enthalpy of vaporization at this temperature is $\Delta_{vap}H = 40.657$ kJ mol^{-1}. What would be the boiling point of water if it were based on a pressure of 1 bar instead of the standard atm?
91. A supplier of cylinder gases warns customers to determine how much gas remains in a cylinder by weighing the cylinder and comparing this mass to the original mass of the full cylinder. In particular, the customer is told not to try to estimate the mass of gas available from the measured gas pressure. Explain the basis of this warning. Are there cases where a measurement of the gas pressure *can* be used as a measure of the remaining available gas? If so, what are they?
92. Use the following data and data from Appendix D to determine the quantity of heat needed to convert 15.0 g of solid mercury at -50.0 °C to mercury vapor at 25 °C. Specific heats: Hg(s), 24.3 J mol^{-1} K^{-1}; Hg(l), 28.0 J mol^{-1} K^{-1}. Melting point of Hg(s), -38.87 °C. Heat of fusion, 2.33 kJ mol^{-1}.
93. To vaporize 1.000 g water at 20 °C requires 2447 J of heat. At 100 °C, 10.00 kJ of heat will convert 4.430 g $H_2O(l)$ to $H_2O(g)$. Do these observations conform to your expectations? Explain.

94. Estimate how much heat is absorbed when 1.00 g of Instant Car Kooler vaporizes. Comment on the effectiveness of this spray in cooling the interior of a car. Assume the spray is 10% $C_2H_5OH(aq)$ by mass, the temperature is 55 °C, the heat capacity of air is 29 J mol^{-1} K^{-1}, and use $\Delta_{vap}H$ data from Table 12.4.
95. Because solid *p*-dichlorobenzene, $C_6H_4Cl_2$, sublimes rather easily, it has been used as a moth repellent. From the data given, estimate the sublimation pressure of $C_6H_4Cl_2(s)$ at 25 °C. For $C_6H_4Cl_2$; mp = 53.1 °C; vapor pressure of $C_6H_4Cl_2(l)$ at 54.8 °C is 10.0 mmHg; $\Delta_{fus}H = 17.88$ kJ mol^{-1}; $\Delta_{vap}H = 72.22$ kJ mol^{-1}.
96. A 1.05 mol sample of $H_2O(g)$ is compressed into a 2.61 L flask at 30.0 °C. Describe the point(s) in Figure 12-30 representing the final condition.
97. One handbook lists the sublimation pressure of *solid* benzene as a function of *Kelvin* temperature, T, as log P (mmHg) = 9.846 − 2309/T. Another handbook lists the vapor pressure of *liquid* benzene as a function of *Celsius* temperature, t, as log P (mmHg) = 6.90565 − 1211.033/(220.790 + t). Use these equations to estimate the normal melting point of benzene, and compare your result with the listed value of 5.5 °C.
98. By the method used to graph Figure 12-20, plot ln P versus 1/T for liquid white phosphorus, and estimate

(a) its normal boiling point and (b) its enthalpy of vaporization, $\Delta_{vap}H$, in kJ mol^{-1}. Vapor pressure data: 76.6 °C, 1 mmHg; 128.0 °C, 10 mmHg; 166.7 °C, 40 mmHg; 197.3 °C, 100 mmHg; 251.0 °C, 400 mmHg.

99. Assume that a skater has a mass of 80 kg and that his skates make contact with 2.5 cm^2 of ice. (a) Calculate the pressure in atm exerted by the skates on the ice. (b) If the melting point of ice decreases by 1.0 °C for every 125 atm of pressure, what would be the melting point of the ice under the skates?

100. Estimate the boiling point of water in Leadville, Colorado, elevation 3170 m. To do this, use the barometric formula relating pressure and altitude: $P = P_0 \times 10^{-Mgh/2.303\,RT}$ (where P = pressure in atm; $P_0 = 1$ atm; acceleration due to gravity, $g = 9.81$ m s^{-2}; molar mass of air, $M = 0.02896$ kg mol^{-1}; $R = 8.3145$ J mol^{-1}K^{-1}; and T is the Kelvin temperature). Assume the air temperature is 10.0 °C and that $\Delta_{vap}H = 41$ kJ mol^{-1} H$_2$O.

101. Inspection of the straight-line graphs in Figure 12-20 suggests that the graphs for benzene and water intersect at a point that falls off the page. At this point, the two liquids have the same vapor pressure. Estimate the temperature and the vapor pressure at this point by a calculation based on data obtainable from the graphs.

102. A cylinder containing 151 lb Cl$_2$ has an inside diameter of 10 in. and a height of 45 in. The gas pressure is 100 psi (1 atm = 14.7 psi) at 20 °C. Cl$_2$ melts at −103 °C, boils at −35 °C, and has its critical point at 144 °C and 76 atm. In what state(s) of matter does the Cl$_2$ exist in the cylinder?

103. In acetic acid vapor, some molecules exist as monomers and some as dimers (see Figure 12-9). If the density of the vapor at 350 K and 1 atm is 3.23 g/L, what percentage of the molecules must exist as dimers? Would you expect this percent to increase or decrease with temperature?

104. A 685 mL sample of Hg(l) at 20 °C is added to a large quantity of liquid N$_2$ kept at its boiling point in a thermally insulated container. What mass of N$_2$(l) is vaporized as the Hg is brought to the temperature of the liquid N$_2$? For the specific heat of Hg(l) from 20 to −39 °C use 0.138 J g^{-1}°C^{-1}, and for Hg(s) from −39 to −196 °C, 0.126 J g^{-1}°C^{-1}. The density of Hg(l) is 13.6 g/mL, its melting point is −39 °C, and its enthalpy of fusion is 2.30 kJ mol^{-1}. The boiling point of N$_2$(l) is −196 °C, and its $\Delta_{vap}H$ is 5.58 kJ mol^{-1}.

105. Sketched here are two hypothetical phase diagrams for a substance, but neither of these diagrams is possible. Indicate what is wrong with each of them.
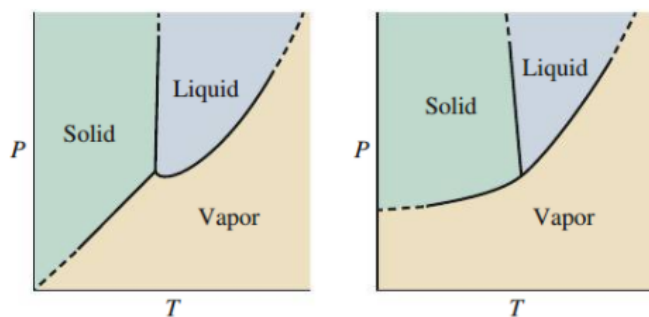
106. A chemistry handbook lists the following equation for the vapor pressure of NH$_3$(l) as a function of temperature. What is the normal boiling point of NH$_3$(l)?

$$\log_{10} P(\text{mmHg}) = 9.95028 - 0.003863T - \frac{1473.17}{T}$$

107. The triple point temperature of bismuth is 544.5 K and the normal boiling point is 1832 K. Imagine that a 1.00 mol sample of bismuth is heated at a constant rate of 1.00 kJ min^{-1} in an apparatus in which the sample is maintained under a constant pressure of 1 atm. In the manner shown in Figure 12-24 and as much to scale as possible, that is in terms of times and temperatures, sketch the heating curve that would be obtained in heating the sample from 300 K to 2000 K. Use the following data. $\Delta_{fus}H = 10.9$ kJ mol^{-1} for Bi(s); $\Delta_{vap}H = 151.5$ kJ mol^{-1} for Bi(l); average molar heat capacities, in J mol^{-1}K^{-1}, 28 for Bi(s), 31 for Bi(l), and 21 for Bi(g). [Hint: Under the conditions described, no vapor appears until the normal boiling point is reached.]

108. The crystal structure of lithium sulfide (Li$_2$S), is pictured here. The length of the unit cell is 5.88 × 10^2 pm. For this structure, determine
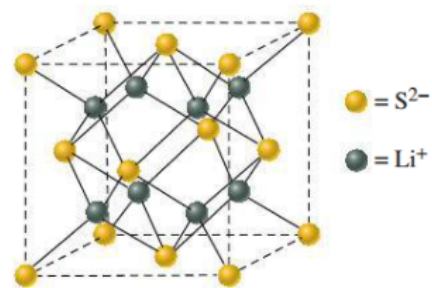
(a) the coordination numbers of Li$^+$ and S^{2-};
(b) the number of formula units in the unit cell;
(c) the density of Li$_2$S.

109. Refer to Figure 12-44 and Figure 12-48. Suppose that the two planes of ions pictured in Figure 12-44 correspond to the top and middle planes of ions in the NaCl unit cell in Figure 12-48. If the X-rays used have a wavelength of 154.1 pm, at what angle θ would the diffracted beam have its greatest intensity? [Hint: Use $n = 1$ in equation (12.5).]

110. Use the analyses of a bcc structure on page 555 and the fcc structure in Exercise 146 to determine the percent voids in the packing-of-spheres arrangement found in the fcc crystal structure.

111. One way to describe ionic crystal structures is in terms of cations filling voids among closely packed anions. Show that in order for cations to fill the tetrahedral voids in a close packed arrangement of anions, the radius ratio of cation, r_c, to anion, r_a, must fall between the following limits $0.225 < r_c/r_a < 0.414$.

112. Use the unit cell of diamond in Figure 12-32(b) and a carbon-to-carbon bond length of 154.45 pm, together with other relevant data from the text, to calculate the density of diamond.

113. The enthalpy of formation of NaI(s) is −288 kJ mol^{-1}. Use this value, together with other data in the text, to

calculate the lattice energy of NaI(s). [*Hint:* Use data from Appendix D also.]

114. Show that the formation of $NaCl_2(s)$ is very unfavorable; that is, $\Delta_f H°[NaCl_2(s)]$ is a large *positive* quantity. To do this, use data from Section 12-7 and assume that the lattice energy for $NaCl_2$ would be about the same as that of $MgCl_2$, -2.5×10^3 kJ mol^{-1}.

115. A crystalline solid contains three types of ions, Na^+, O^{2-}, and Cl^-. The solid is made up of cubic unit cells that have O^{2-} ions at each corner, Na^+ ions at the center of each face, and Cl^- ions at the center of the cells. What is the chemical formula of the compound? What are the coordination numbers for the O^{2-} and Cl^- ions? If the length of one edge of the unit cell is a, what is the shortest distance from the center of a Na^+ ion to the center of an O^{2-} ion? Similarly, what is the shortest distance from the center of a Cl^- ion to the center of an O^{2-} ion?

116. A certain mineral has a cubic unit cell with calcium at each corner, oxygen at the center of each face, and titanium at its body center. What is the formula of the mineral? An alternate way of drawing the unit cell has calcium at the center of each cubic unit cell. What are the positions of titanium and oxygen in such a representation of the unit cell? How many oxygen atoms surround a particular titanium atom in either representation?

117. Calculate the radius ratio (r_+/r_-) for CaF_2. Suggest an alternative structure to that shown in Figure 12-50(b) that better conforms to the radius ratio you compute.

118. In some barbecue grills the electric lighter consists of a small hammer-like device striking a small crystal, which generates voltage and causes a spark between wires that are attached to opposite surfaces of the crystal. The phenomenon of causing an electric potential through mechanical stress is known as the piezoelectric effect. One type of crystal that exhibits the piezoelectric effect is lead zirconate titanate. In this perovskite crystal structure, a titanium(IV) ion sits in

the middle of a tetragonal unit cell with dimensions of 0.403 nm × 0.398 nm × 0.398 nm. At each corner is a lead(II) ion, and at the center of each face is an oxygen anion. Some of the Ti(IV) are replaced by Zr(IV). This substitution, along with Pb(II), results in the piezoelectic behavior.
 (a) How many oxygen ions are in the unit cell?
 (b) How many lead(II) ions are in the unit cell?
 (c) How many titanium(IV) ions are in the unit cell?
 (d) What is the density of the unit cell?

119. Ionic liquids (ILs) are salts that are in the liquid state. At a given temperature, ILs have lower vapor pressures than molecular compounds in the liquid state because the forces of attraction between oppositely charged ions are much stronger than intermolecular forces. Thus, ILs tend to be much less volatile and less flammable than many other liquids. ILs are of interest because of their potential role as "safer" and "greener" solvents. Two examples of ionic liquids are 1-butyl-3-methylimidazolium tetrafluoroborate, [Bmim][BF$_4$], and 1-allyl-3-methylimidazolium chloride, [Amim]Cl, both of which consist of a relatively large organic cation and an inorganic anion.
 (a) Look up and then draw the structures of the ions making up these two ILs.
 (b) Find the melting points for these two ILs and for NaCl.
 (c) Explain why the melting points of these two ILs are much lower than that of NaCl.

120. In a 1999 study of cobalt nanocrystals, D. P. Dinega and M. G. Bawendi discovered that cobalt forms an interesting cubic structure unlike any of the cubic structures described in this chapter. They called this new form ε-cobalt to distinguish it from the more commonly encountered hcp and fcc forms of cobalt. For ε-cobalt, the unit cell has an edge length of 609.7 pm and contains 20 atoms. The density of ε-cobalt is $\rho = 8.635$ g cm^{-3}. Use these data to estimate the number of cobalt atoms in a spherical nanocrystal of ε-cobalt if the diameter of the nanocrystal is 2 nm.

Feature Problems

121. Intermolecular forces play vital and varied roles in nature. For example, these forces enable gecko lizards to climb walls and hang upside down from ceilings, seemingly defying gravity. Intermolecular forces—more specifically, hydrogen bonds—are the reason that DNA molecules, carriers of the genetic code for most living organisms, exist as a double helix. The helical structure of proteins, the molecules that catalyze biochemical reactions occurring in our bodies and regulate metabolic processes, is also the result of hydrogen bonding. In Section 12-1, we learned about the physical basis of different types of intermolecular forces, such as dipole–dipole, dipole–induced dipole, and instantaneous dipole–induced dipole (dispersion) interactions. We also discussed the relative strengths of these different types of interactions and the percent contributions they make to the attraction between molecules. This problem focuses on doing calculations to verify the claims made in Section 12-1.

For two *identical* molecules separated from each other by a distance much greater than their own dimensions, the average potential energy of interaction, E, is approximately

$$E = -\frac{1}{r^6}\left[\frac{2\mu^4}{3k_BT}\cdot\frac{1}{(4\pi\epsilon_0)^2} + 2\mu^2\alpha\cdot\frac{1}{(4\pi\epsilon_0)} + \frac{3}{4}\alpha^2 E_i\right]$$

In the equation above, μ is the molecular dipole moment in C m, α is the molecular polarizability in m^3, E_i is the first ionization energy of the molecule in J, and r is the center of mass separation in m between the two molecules. In addition, $\epsilon_0 = 8.854 \times 10^{-12}$ C^{2}J^{-1}m^{-1} is the permittivity of vacuum, $k_B = 1.3807 \times 10^{-23}$ J K^{-1} is the Boltzmann constant, and T is the temperature in K. The first term in the equation above represents the dipole–dipole interaction, the second term represents the dipole–induced dipole interaction, and the third term represents the dispersion interaction.

Use the equation above and data from the table that follows to answer the questions below. Assume the center of mass separation, r, between molecules is exactly 400 pm and the temperature is 298 K.

(a) For each substance in the table, calculate E, as well as the contributions to E from dipole–dipole, dipole–induced dipole, and dispersion interactions. Express E and the various contributions to E in kJ mol^{-1}.

(b) Use your results from (a) to calculate, for each substance, the percent contribution made by each type of interaction.

(c) What is the range of values of E calculated in (a)? Briefly comment on how these values compare in magnitude with the (covalent) bond energies, D, given in Table 10.3.

(d) Use your results from (a) to prepare three separate graphs of $\Delta_{vap}H$ versus $-E$, one graph for *each* class of compounds shown in the table (halides, alcohols, and hydrocarbons). What do these graphs illustrate?

(e) The formula for E indicates that the contribution from dipole–dipole interactions decreases as temperature increases. Explain.

| Substance[a]	μ, D	α, 10^{-25} cm^3	E_i, kJ mol^{-1}	$\Delta_{vap}H$,[b] kJ mol^{-1}
Halides				
HF	1.826	8.0	1548	7.49[c]
HCl	1.1086	26.3	1230	16.15
HBr	0.8272	36.1	1125	17.61[d]
HI	0.448	54.4	1002	19.76
Water and Alcohols				
H_2O	1.8546	14.5	1218	40.65
CH_3OH	1.70	32.9	1047	35.21
CH_3CH_2OH	1.69	54.1	1006	38.56
$CH_3(CH_2)_2OH$	1.55	67.4	982	41.44
$CH_3(CH_2)_3OH$	1.66	88.8	964	43.29
Hydrocarbons				
CH_4	0.0	25.93	1217	8.19
CH_3CH_3	0.0	44.7	1115	14.69
$CH_3CH_2CH_3$	0.0	62.9	1057	19.04
$(CH_3)_3CH$	0.132	81.4	1020	21.30
$CH_3(CH_2)_2CH_3$	0.0	82.0	1016	22.44
$CH_3(CH_2)_3CH_3$	0.0	99.9	992	25.70

[a]All values in this table are from the *CRC Handbook*, 95th edition, except where noted.
[b]The $\Delta_{vap}H$ values are measured at the substance's normal boiling point.
[c]This value is from the *Handbook of Inorganic Compounds*, 2nd edition, by Dale L. Perry.
[d]This value is from the *Air Liquide Gas Encyclopedia*, http://encyclopedia.airliquide.com.

122. In a capillary rise experiment, the height (h) to which a liquid rises depends on the density (d) and surface tension (γ) of the liquid and the radius of the capillary (r). The equation relating these quantities and the acceleration due to gravity (g) is $h = 2\gamma/dgr$. The sketch provides data obtained with ethanol. What is the surface tension of ethanol?

$\rightarrow| |\leftarrow r = 0.50$ mm

$h = 1.1$ cm

$d = 0.789$ g/mL
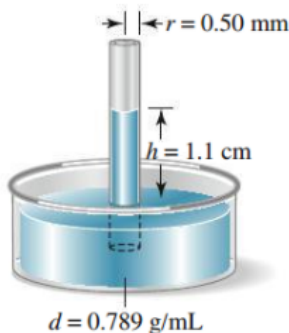
123. We have learned that the enthalpy of vaporization of a liquid is generally a function of temperature. If we wish to take this temperature variation into account, we cannot use the Clausius–Clapeyron equation in the form given in the text (that is, equation 12.2). Instead, we must go back to the differential equation upon which the Clausius–Clapeyron equation is based and reintegrate it into a new expression. Our starting point is the following equation describing the rate of change of vapor pressure with temperature in terms of the enthalpy of vaporization, the difference in molar volumes of the vapor (V_g), and liquid (V_l), and the temperature.

$$\frac{dP}{dT} = \frac{\Delta_{vap}H}{T(V_g - V_l)}$$

Because in most cases the volume of one mole of vapor greatly exceeds the molar volume of liquid,

we can treat the V_1 term as if it were zero. Also, unless the vapor pressure is unusually high, we can treat the vapor as if it were an ideal gas; that is, for one mole of vapor, $PV = RT$. Make appropriate substitutions into the above expression, and separate the P and dP terms from the T and dT terms. The appropriate substitution for $\Delta_{vap}H$ means expressing it as a function of temperature. Finally, integrate the two sides of the equation between the limits P_1 and P_2 on one side and T_1 and T_2 on the other.

(a) Derive an equation for the vapor pressure of $C_2H_4(l)$ as a function of temperature, if $\Delta_{vap}H = 15{,}971 + 14.55\,T - 0.160\,T^2$ (in J mol^{-1}).

(b) Use the equation derived in (a), together with the fact that the vapor pressure of $C_2H_4(l)$ at 120 K is 10.16 Torr, to determine the normal boiling point of ethylene.

124. All solids contain defects or imperfections of structure or composition. Defects are important because they influence properties, such as mechanical strength. Two common types of defects are a missing ion in an otherwise perfect lattice, and the slipping of an ion from its normal site to a hole in the lattice. The holes discussed in this chapter are often called *interstitial sites*, since the holes are in fact interstices in the array of spheres. The two types of defects described here are called *point defects* because they occur within specific sites. In the 1930s, two solid-state physicists, W. Schottky and J. Fraenkel, studied the two types of point defects: A Schottky defect corresponds to a missing ion in a lattice, while a Fraenkel defect corresponds to an ion that is displaced into an interstitial site.

(a) An example of a Schottky defect is the absence of a Na^+ ion in the NaCl structure. The absence of a Na^+ ion means that a Cl^- ion must also be absent to preserve electrical neutrality. If one NaCl unit is missing per unit cell, does the overall stoichiometry change, and what is the change in density?

(b) An example of a Fraenkel defect is the movement of a Ag^+ ion to a tetrahedral interstitial site from its normal octahedral site in AgCl, which has a structure like NaCl. Does the overall stoichiometry of the compound change, and do you expect the density to change?

(c) Titanium monoxide (TiO) has a sodium chloride-like structure. X-ray diffraction data show that the edge length of the unit cell is 418 pm. The density of the crystal is 4.92 g/cm^3. Do the data indicate the presence of vacancies? If so, what type of vacancies?

125. In an ionic crystal lattice each cation will be attracted by anions next to it and repulsed by cations near it. Consequently the coulomb potential leading to the lattice energy depends on the type of crystal. To get the total lattice energy you must sum all of the electrostatic interactions on a given ion. The general form of the electrostatic potential is

$$V = \frac{Q_1 Q_2 e^2}{d_{12}}$$

where Q_1 and Q_2 are the charges on ions 1 and 2, d_{12} is the distance between them in the crystal lattice. and e is the charge on the electron.

(a) Consider the linear "crystal" shown below.

The distance between the centers of adjacent spheres is R. Assume that the blue sphere and the green spheres are cations and that the red spheres are anions. Show that the total electrostatic energy is

$$V = -\frac{Q^2 e^2}{d} \times \ln 2$$

(b) In general, the electrostatic potential in a crystal can be written as

$$V = -k_M \frac{Q^2 e^2}{R}$$

where k_M is a geometric constant, called the Madelung constant, for a particular crystal system under consideration. Now consider the NaCl crystal structure and let R be the distance between the centers of sodium and chloride ions. Show that by considering three layers of nearest neighbors to a central chloride ion, k_M is given by

$$k_M = \left(6 - \frac{12}{\sqrt{2}} + \frac{8}{\sqrt{3}} - \frac{6}{\sqrt{4}} + \cdots \right)$$

(c) Carry out the same calculation for the CsCl structure. Are the Madelung constants the same?

126. Plot the following data first as boiling point versus polarizability, and then as boiling point versus molecular mass. What conclusions can you draw from these plots?

Compound	Polarizability, 10^{-25} cm^3	Mass, u	Boiling Point, K
H_2	7.90	2.016	20.35
N_2	17.6	28.01	77.35
O_2	16.0	32.00	90.188
Cl_2	46.1	70.90	238.25
HF	24.6	20.01	292.69
HCl	26.3	36.46	188.25
HBr	36.1	80.91	206.15
HI	54.4	127.91	237.77
N_2O	30.0	44.01	184.65
CO	19.5	28.01	81.65
SO_2	37.2	64.06	263.15
H_2S	37.8	34.08	212.45
CS_2	87.4	76.13	319.45
NH_3	22.6	17.03	239.8
HCN	25.9	27.03	299.15
CH_4	26.0	16.04	109.15
C_2H_6	44.7	30.07	184.55
$CH_2{=}CH_2$	42.6	28.05	169.45
$CH{\equiv}CH$	33.3	26.04	189.15
C_3H_8	62.9	44.01	231.05
C_6H_6	103	78.11	353.25
CH_3Cl	45.6	50.49	248.95
CH_2Cl_2	64.8	84.93	313.15
$CHCl_3$	82.3	119.37	334.85
CCl_4	105	153.81	349.95
CH_3OH	32.3	32.04	338.15

127. The Born–Fajans–Haber cycle uses thermodynamic cycles to determine lattice energy. An alternative to the Born–Fajans–Haber method is one based on fundamental principles. Because the dominant interactions in an ionic crystal are Coulomb interactions, we can use the theory of electrostatics to calculate the lattice energy. Kapustinskii used these ideas and proposed the following equation:

$$U = \frac{120{,}250 \, \nu \, Z^+ Z^-}{r_0}\left(1 - \frac{34.5}{r_0}\right)(\text{kJ mol}^{-1})$$

where the number of ions per formula unit is given by ν and r_0 is equal to the sum of the ionic radii, $r_+ + r_-$ (pm). Use the equation to complete the following table:

| Compound	Lattice Energy, kJ mol^{-1}	r_-, pm	r_+, pm
NaCl		181	99
LaF$_3$		133	117
Na$_2$SO$_4$	−3389		99

Self-Assessment Exercises

128. In your own words, define or explain the following terms or symbols: **(a)** $\Delta_{vap}H$; **(b)** T_c; **(c)** instantaneous dipole; **(d)** coordination number; **(e)** unit cell.

129. Briefly describe each of the following phenomena or methods: **(a)** capillary action; **(b)** polymorphism; **(c)** sublimation; **(d)** supercooling; **(e)** determining the freezing point of a liquid from a cooling curve.

130. Explain the important distinctions between each pair of terms: **(a)** adhesive and cohesive forces; **(b)** vaporization and condensation; **(c)** triple point and critical point; **(d)** face-centered and body-centered cubic unit cell; **(e)** tetrahedral and octahedral hole.

131. Which of the following liquid properties depends on the strength of intermolecular attractions? **(a)** surface tension; **(b)** boiling point; **(c)** vapor pressure; **(d)** heat of vaporization; **(e)** all of these.

132. A liquid is in equilibrium with its vapor in a closed container. The lid of the container is removed briefly, allowing some of the vapor to escape, and then replaced. What is the immediate result of the vapor escaping? **(a)** vaporization rate decreases; **(b)** condensation rate decreases; **(c)** vaporization rate increases; **(d)** condensation rate increases; **(e)** none of these.

133. The magnitude of one of the following properties must always increase with temperature; that one is **(a)** surface tension; **(b)** density; **(c)** vapor pressure; **(d)** $\Delta_{vap}H$.

134. Of the compounds HF, CH$_4$, CH$_3$OH, N$_2$H$_4$, and CHCl$_3$, hydrogen bonding is an important intermolecular force in **(a)** none of these; **(b)** two of these; **(c)** three of these; **(d)** all but one of these; **(e)** all of these.

135. In the responses below, the vapor pressure of trichloroethene is listed for a given temperature. In which response does the given temperature correspond to the normal boiling point? **(a)** 40 Torr at 40.1 °C; **(b)** 100 Torr at 61.3 °C; **(c)** 400 Torr at 100.0 °C; **(d)** 760 Torr at 120.8 °C; **(e)** none of these.

136. The normal boiling point of acetone is 56.2 °C, and the molar heat of vaporization is 32.0 kJ mol^{-1}. What is the boiling temperature of acetone under a pressure of 50.0 mmHg?

137. A metal that crystallizes in the body-centered cubic (bcc) structure has a crystal coordination number of **(a)** 6; **(b)** 8; **(c)** 12; **(d)** any even number between 4 and 12.

138. A unit cell of an ionic crystal **(a)** shares some ions with other unit cells; **(b)** is the same as the formula

unit; **(c)** is any portion of the crystal that has a cubic shape; **(d)** must contain the same number of cations and anions.

139. If the triple point pressure of a substance is greater than 1 atm, which two of the following conclusions are valid?
(a) The solid and liquid states of the substance cannot coexist at equilibrium.
(b) The melting point and boiling point of the substance are identical.
(c) The liquid state of the substance cannot exist.
(d) The liquid state cannot be maintained in a beaker open to air at 1 atm pressure.
(e) The melting point of the solid must be greater than 0 °C.
(f) The gaseous state at 1 atm pressure cannot be condensed to the solid at the triple point temperature.

140. In each of the following pairs, which would you expect to have the higher boiling point? **(a)** C$_7$H$_{16}$ or C$_{10}$H$_{22}$; **(b)** C$_3$H$_8$ or (CH$_3$)$_2$O; **(c)** CH$_3$CH$_2$SH or CH$_3$CH$_2$OH.

141. One of the substances is out of order in the following list based on increasing boiling point. Identify it, and put it in its proper place: N$_2$, O$_3$, F$_2$, Ar, Cl$_2$. Explain your reasoning.

142. Arrange the following substances in the expected order of increasing melting point: KI, Ne, K$_2$SO$_4$, C$_3$H$_8$, CH$_3$CH$_2$OH, MgO, CH$_2$OHCHOHCH$_2$OH.

143. Is it possible to obtain a sample of ice from liquid water without ever putting the water in a freezer or other enclosure at a temperature below 0 °C? If so, how might this be done?

144. The phenomena in Figure 12-22 will be seen at the critical temperature only if the proper amount of liquid is placed in the sealed tube initially. Why should this be the case? What would you expect to see if too little liquid was present initially? If too much liquid was present?

145. The following data are given for CCl$_4$. Normal melting point, −23 °C; normal boiling point, 77 °C; density of liquid 1.59 g/mL; $\Delta_{fus}H = 3.28$ kJ mol^{-1}; vapor pressure at 25 °C, 110 Torr.
(a) What phases—solid, liquid, and/or gas—are present if 3.50 g CCl$_4$ is placed in a closed 8.21 L container at 25 °C?

(b) How much heat is required to vaporize 2.00 L of $CCl_4(l)$ at its normal boiling point?

146. The fcc unit cell is a cube with atoms at each of the corners and in the center of each face, as shown here. Copper has the fcc crystal structure. Assume an atomic radius of 128 pm for a Cu atom.
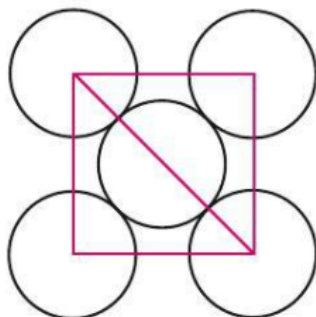
(a) What is the length of the unit cell of Cu?
(b) What is the volume of the unit cell?
(c) How many atoms belong to the unit cell?
(d) What percentage of the volume of the unit cell is occupied?
(e) What is the mass of a unit cell of copper?
(f) Calculate the density of copper.

147. Of the following liquids at 20 °C, which has the smallest surface tension? **(a)** CH_3OH; **(b)** CH_3CH_2OH; **(c)** $CH_3CH_2CH_2OH$; **(d)** $CH_3CH_2CH_2CH_2OH$.

148. Of the following liquids at 20 °C, which has the smallest viscosity? **(a)** dodecane, $C_{12}H_{26}$; **(b)** n-nonane, C_9H_{20}; **(c)** n-heptane, C_7H_{16}; **(d)** n-pentane, C_5H_{12}.

149. Would you expect an ionic solid or a network covalent solid to have the higher melting point?

150. Consider the following ions: Na^+, K^+, Ca^{2+}, Mg^{2+}, F^-, Br^-, O^{2-}, and S^{2-}. Which cation and which anion do you expect to combine to form the highest melting compound? Carefully explain your choice.

151. In the lithium iodide crystal, the Li–I distance is 3.02 Å. Calculate the iodide radius, assuming that the iodide ions are in contact.

152. Which of the following phase transitions is most likely to occur when the pressure on a metallic solid increases? **(a)** bcc to sc; **(b)** fcc to sc; **(c)** bcc to fcc; **(d)** fcc to sc.

153. Construct a concept map representing the different types of intermolecular forces and their origin.

154. Construct a concept map using the ideas of packing of spheres and the structure of metal and ionic crystals.

155. Construct a concept map showing the ideas contained in a phase diagram.