# CHAPTER 12
# INTERMOLECULAR FORCES: LIQUIDS AND SOLIDS

## PRACTICE EXAMPLES

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**1A** The substance with the highest boiling point will have the strongest intermolecular forces. The weakest of van der Waals forces are London forces, which depend on molar mass (and surface area): $C_3H_8$ is 44 g/mol, $CO_2$ is 44 g/mol, and $CH_3CN$ is 41 g/mol. Thus, the London forces are approximately equal for these three compounds. Next to consider are dipole–dipole forces. $C_3H_8$ is essentially nonpolar; its bonds are not polarized to an appreciable extent. $CO_2$ is nonpolar; its two bond moments cancel each other. $CH_3CN$ is polar and thus has the strongest intermolecular forces and should have the highest boiling point. The actual boiling points are -78.44° C for $CO_2$, -42.1° C for $C_3H_8$, and 81.6° C for $CH_3CN$.

**1B** Dispersion forces, which depend on the number of electrons (molar mass) and structure, are one of the determinants of boiling point. The molar masses are: $C_8H_{18}$ (114.2 g/mol), $CH_3CH_2CH_2CH_3$ (58.1 g/mol), $(CH_3)_3CH$ (58.1 g/mol), $C_6H_5CHO$ (106.1 g/mol), and $SO_3$ (80.1 g/mol). We would expect $(CH_3)_3CH$ to have the lowest boiling point because it has the lowest molar mass and the most compact (ball-like) shape, whereas $CH_3CH_2CH_2CH_3$, which has the same mass but is longer and hence has more surface area (more chances for intermolecular interactions), should have the second highest boiling point. We would expect $SO_3$ to be next in line as it is also non-polar, but more massive than $C_4H_{10}$. $C_6H_5CHO$ should have a boiling point higher than the more massive $C_8H_{18}$ because benzaldehyde is polar while octane is not. Actual boiling points are given in parentheses in the following ranking. $(CH_3)_3CH$ (-11.6 °C) < $CH_3CH_2CH_2CH_3$ (-0.5°C) < $SO_3$ (44.8°C) $C_8H_{18}$ (125.7 °C) < $C_6H_5CHO$ (178°C)

**2A** Values of $\Delta H_{vap}$ are in kJ/mol so we first determine the amount in moles of diethyl ether.

$$\text{Heat} = 2.35\text{ g }(C_2H_5)_2O \times \frac{1\text{ mol }(C_2H_5)_2O}{74.12\text{ g }(C_2H_5)_2O} \times \frac{29.1\text{ kJ}}{1\text{ mol }(C_2H_5)_2O} = 0.923\text{ kJ}$$

**2B**

$$\Delta H_{overall} = \Delta H_{cond} + \Delta H_{cooling}$$

$$\Delta H_{cond} = 0.0245\text{ mol} \times (-40.7\text{ kJ mol}^{-1}) = -0.997\text{ kJ} = -997\text{ J}$$

$$\Delta H_{cooling} = 0.0245\text{ mol} \times (4.21\text{ J g}^{-1}\ {}^{\circ}\text{C}^{-1})(85.0\ {}^{\circ}\text{C} - 100.0\ {}^{\circ}\text{C})(18.0153\text{ g mol}^{-1}) = -27.9\text{ J}$$

$$\Delta H_{overall} = -997\text{ J} + -27.9\text{ J} = -1025\text{ J or } -1.025\text{ kJ}$$

**3A** d = 0.701 g/L at 25 °C for $C_6H_{14}$ (molar mass = 86.177 g $mol^{-1}$)
Consider a 1.00 L sample. This contains 0.701 g $C_6H_{14}$.

$$\text{moles } C_6H_{14} \text{ in 1.00 L sample} = 0.701\text{ g } C_6H_{14} \times \frac{1\text{ mol } C_6H_{14}}{86.177\text{ g } C_6H_{14}} = 8.13 \times 10^{-3}\text{ mol } C_6H_{14}$$

Find pressure using the ideal gas law: $P=\dfrac{nRT}{V}=\dfrac{(8.31\times 10^{-3}\text{ mol})(\dfrac{0.08206\text{ L atm}}{\text{K mol}})(298\text{K})}{1.00\text{ L}}$

$$P = 0.199\text{ atm or }151\text{ Torr}$$

**3B** From Figure 12-9, the vapor pressure is ≈ 420 mmHg or $420\text{ mmHg}\times\dfrac{1\text{ atm}}{760\text{ Torr}}=0.553\text{ atm}$

molar mass = 74.123 g mol$^{-1}$. $P=\dfrac{nRT}{V}=\dfrac{\left(\dfrac{\text{mass}}{\text{molar mass}}\right)\text{RT}}{V}=\dfrac{(\text{density})\text{RT}}{\text{molar mass}}$

or $\text{d}=\dfrac{(\text{molar mass})\text{P}}{\text{RT}}=\dfrac{\left(74.123\dfrac{\text{g}}{\text{mol}}\right)(0.553\text{ atm})}{\left(0.08206\dfrac{\text{L atm}}{\text{Kmol}}\right)(293\text{ K})}=1.70\text{ g L}^{-1}\approx 1.7\text{ g/L}$

**4A** We first calculate pressure created by the water at 80.0 °C, assuming all 0.132 g $H_2O$ vaporizes.

$$P_2=\frac{nRT}{V}=\frac{\left(0.132\text{ g H}_2\text{O}\times\dfrac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}}\right)\times 0.08206\dfrac{\text{L atm}}{\text{mol K}}\times 353.2\text{ K}}{0.525\text{ L}}\times\frac{760\text{ mmHg}}{1\text{ atm}}=307\text{ mmHg}$$

At 80.0 °C, the vapor pressure of water is 355.1 mmHg, thus, all the water exists as vapor.

**4B** The result of Example 12-3 is that 0.132 g $H_2O$ would exert a pressure of 281 mmHg if it all existed as a vapor. Since that 281 mmHg is greater than the vapor pressure of water at this temperature, some of the water must exist as liquid. The calculation of the example is based on the equation $P=nRT/V$, which means that the pressure of water is proportional to its mass. Thus, the mass of water needed to produce a pressure of 92.5 mmHg under this situation is

$$\text{mass of water vapor}=92.5\text{ mmHg}\times\frac{0.132\text{ g H}_2\text{O}}{281\text{ mmHg}}=0.0435\text{ g H}_2\text{O}$$

$$\text{mass of liquid water}=0.132\text{ g H}_2\text{O total}-0.0435\text{ g H}_2\text{O vapor}=0.089\text{ g liquid water}$$

**5A** From Table 12-1 we know that $\Delta H_{vap}=38.0\text{ kJ/mol}$ for methyl alcohol. We now can use the Clausius-Clapeyron equation to determine the vapor pressure at $25.0^\circ\text{C}=298.2\text{ K}$.

$$\ln\frac{P}{100\text{ mmHg}}=\frac{38.0\times 10^3\text{ J mol}^{-1}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{(273.2+21.2)\text{K}}-\frac{1}{298.2\text{K}}\right)=+0.198$$

$$\frac{P}{100\text{ mmHg}}=\text{e}^{+0.198}=1.22\qquad P=1.22\times 100\text{ mmHg}=121\text{ mmHg}$$

**5B** The vapor pressure at the normal boiling point $\left(99.2^\circ\text{C} = 372.4\text{ K}\right)$ is 760 mmHg precisely. We can use the Clausius-Clapeyron equation to determine the vapor pressure at $25^\circ\text{C} = 298\text{ K}$.

$$\ln\frac{P}{760\text{ mmHg}} = \frac{35.76\times 10^3\text{ J mol}^{-1}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{372.4\text{ K}} - \frac{1}{298.2\text{ K}}\right) = -2.874$$

$$\frac{P}{760\text{ mmHg}} = e^{-2.874} = 0.0565 \qquad P = 0.0565\times 760\text{ mmHg} = 42.9\text{ mmHg}$$

**6A** We first look to molar masses: Ne (20.2 g/mol), He (4.0 g/mol), $Cl_2$(70.9 g/mol), $(CH_3)_2CO$ (58.1 g/mol), $O_2$(32.0 g/mol), and $O_3$ (48.0 g/mol). Both $(CH_3)_2CO$ and $O_3$ are polar, $O_3$ weakly so (because of its uneven distribution of electrons). We expect $(CH_3)_2CO$ to have the highest boiling point, followed by $Cl_2$, $O_3$, $O_2$, Ne, and He. In the following ranking, actual boiling points are given in parentheses. He (-268.9 °C), Ne (-245.9 °C), $O_2$ (-183.0 °C), $O_3$ (-111.9 °C), $Cl_2$ (-34.6 °C), and $(CH_3)_2CO$ (56.2 °C).

**6B** The magnitude of the enthalpy of vaporization is strongly related to the strength of intermolecular forces: the stronger these forces, the more endothermic the vaporization process. The first three substances all are nonpolar and, therefore, their only intermolecular forces are London forces, whose strength primarily depends on molar mass. The substances are arranged in order of increasing molar mass: $H_2 = 2.0\text{ g/mol}$, $CH_4 = 16.0\text{ g/mol}$, $C_6H_6 = 78.1\text{ g/mol}$, and also in order of increasing heat of vaporization. The last substance has a molar mass of 61.0 g/mol, which would produce intermolecular forces smaller than those of $C_6H_6$ if $CH_3NO_2$ were nonpolar. But the molecule is definitely polar. Thus, the strong dipole–dipole forces developed between $CH_3NO_2$ molecules make the enthalpy of vaporization for $CH_3NO_2$ larger than that for $C_6H_6$, which is, of course, essentially non-polar.

**7A** Moving from point R to P we begin with $H_2O$(g) at high temperature (>100°C). When the temperature reaches the point on the vaporization curve, OC, water condenses at constant temperature (100°C). Once all of the water is in the liquid state, the temperature drops. When the temperature reaches the point on the fusion curve, OD, ice begins to form at constant temperature (0°C). Once all of the water has been converted to $H_2O$(s), the temperature of the sample decreases slightly until point P is reached.

Since solids are not very compressible, very little change occurs until the pressure reaches the point on the fusion curve OD. Here, melting begins. A significant decrease in the volume occurs (≈10%) as ice is converted to liquid water. After melting, additional pressure produces very little change in volume because liquids are not very compressible.

**7B**

1.00 mol $H_2O$. At point R, T = 374.1 °C or 647.3 K

$$V_{\text{point R}} = \frac{nRT}{P} = \frac{(1.00\,\text{mol})\left(0.08206\,\frac{\text{L atm}}{\text{K mol}}\right)(647.3\,\text{K})}{1.00\,\text{atm}} = 53.1\text{ L}$$

1.00 mol $H_2O$ on P-R line, if 1/2 of water is vaporized, T = 100 °C(273.015 K)

$$V_{1/2\text{ vap(PR)}} = \frac{nRT}{P} = \frac{(0.500\,\text{mol})\left(0.08206\,\frac{\text{L atm}}{\text{K mol}}\right)(373.15\,\text{K})}{1.00\,\text{atm}} = 15.3\text{ L}$$

A much smaller volume results when just 1/2 of the sample is vaporized (moles of gas smaller as well, temperature is smaller). 53.1 L vs 15.3 L (about 28.8 % of the volume as that seen at point R).

**51. 3 L**

**At**

**Point**

**R**

**15.3 L**
**at 100C**
**1/2 vap**

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**6B** The magnitude of the enthalpy of vaporization is strongly related to the strength of intermolecular forces: the stronger these forces are, the more endothermic the vaporization process. The first three substances all are nonpolar and, therefore, their only intermolecular forces are London forces, whose strength primarily depends on molar mass. The substances are arranged in order of increasing molar mass: $H_2 = 2.0$ g / mol, $CH_4 = 16.0$ g / mol, $C_6H_6 = 78.1$ g / mol, and also in order of increasing heat of vaporization. The last substance has a molar mass of 61.0 g/mol, which would produce intermolecular forces smaller than those of $C_6H_6$ if $CH_3NO_2$ were nonpolar. But the molecule is definitely polar. Thus, the strong dipole-dipole forces developed between $CH_3NO_2$ molecules make the enthalpy of vaporization for $CH_3NO_2$ larger than that for $C_6H_6$, which is, of course, essentially non-polar.

**8A** Strong interionic forces lead to high melting points. Strong interionic forces are created by ions with high charge and of small size. Thus, for a compound to have a lower melting point than KI it must be composed of ions of larger size, such as RbI or CsI. A compound with a melting point higher than CaO would have either smaller ions, such as MgO, or more highly charged ions, such as $Ga_2O_3$ or $Ca_3N_2$, or both, such as AlN or $Mg_3N_2$.

**8B** $Mg^{2+}$ has a higher charge and a smaller size than does $Na^+$. In addition, $Cl^-$has a smaller size than $I^-$. Thus, interionic forces should be stronger in $MgCl_2$ than in NaI. We expect $MgCl_2$ to have lower solubility and, in fact, 12.3 mol (1840 g) of NaI dissolves in a liter of water, compared to just 5.7 mol (543 g) of $MgCl_2$, confirming our prediction.

**9A** The length $(l)$ of a bcc unit cell and the radius $(r)$ of the atom involved are related by $4r = l\sqrt{3}$. For potassium, $r = 227\text{ pm}$. Then $l = 4 \times 227\text{ pm} / \sqrt{3} = 524\text{ pm}$

**9B** Consider just the face of Figure 12-46. Note that it is composed of one atom at each of the four corners and one in the center. The four corner atoms touch the atom in the center, but not each other. Thus, the atoms are in contact across the diagonal of the face. If each atomic radius is designated $r$, then the length of the diagonal is $4r(= r$ for one corner atom $+2r$ for the center atom $+r$ for the other corner atom). The diagonal also is related to the length of a side, $l$, by the Pythagorean theorem: $d^2 = l^2 + l^2 = 2l^2$ or $d = \sqrt{2}l$. We have two quantities equal to the diagonal, and thus to each other.

$$\sqrt{2}l = \text{diagonal} = 4r = 4 \times 143.1\text{ pm} = 572.4\text{ pm}$$

$$l = \frac{572.4}{\sqrt{2}} = 404.7\text{ pm}$$

The cubic unit cell volume, $V$, is equal to the cube of one side.

$$V = l^3 = (404.7\text{ pm})^3 = 6.628 \times 10^7\text{ pm}^3$$

**10A** In a bcc unit cell, there are eight corner atoms, of which $\frac{1}{8}$ of each is apportioned to the unit cell. There is also one atom in the center. The total number of atoms per unit cell is:

$= 1\text{ center} + 8\text{ corners} \times \frac{1}{8} = 2$ atoms. The density, in $\text{g/cm}^3$, for this cubic cell:

$$\text{density} = \frac{2\text{ atoms}}{(524\text{ pm})^3} \times \left(\frac{10^{12}\text{ pm}}{10^2\text{ cm}}\right)^3 \times \frac{1\text{ mol}}{6.022 \times 10^{23}\text{ atoms}} \times \frac{39.10\text{ g K}}{1\text{ mol K}} = 0.903\text{ g/cm}^3$$

The tabulated density of potassium at $20^\circ\text{C}$ is $0.86\text{ g/cm}^3$.

**10B** In a fcc unit cell the number of atoms is computed as 1/8 atom for each of the eight corner atoms (since each is shared among eight unit cells) plus 1/2 atom for each of the six face atoms (since each is shared between two unit cells). This gives the total number of atoms per unit cell as: atoms/unit cell = (1/8 corner atom × 8 corner atoms/unit cell) + (1/2 face atom × 6 face atoms/unit cell) $= 4$ atoms/ unit cell

Now we can determine the mass per Al atom, and a value for the Avogadro constant.

$$\frac{\text{mass}}{\text{Al atom}} = \frac{2.6984\text{ g Al}}{1\text{ cm}^3} \times \left(\frac{100\text{ cm}}{1\text{ m}} \times \frac{1\text{ m}}{10^{12}\text{ pm}}\right)^3 \times \frac{6.628 \times 10^7\text{ pm}^3}{1\text{ unit cell}} \times \frac{1\text{ unit cell}}{4\text{ Al atoms}}$$

$$= 4.471 \times 10^{-23}\text{ g/Al atom}$$

Therefore,

$$N_A = \frac{26.9815\text{ g Al}}{1\text{ mol Al}} \times \frac{1\text{ Al atom}}{4.471 \times 10^{-23}\text{ g Al}} = 6.035 \times 10^{23}\,\frac{\text{atoms Al}}{\text{mol Al}}$$

**11A** Across the diagonal of a CsCl unit cell are $Cs^+$ and $Cl^-$ ions, so that the body diagonal equals $2r(Cs^+)+2r(Cl^-)$. This body diagonal equals $\sqrt{3}l$, where $l$ is the length of the unit cell.

$$l=\frac{2r(Cs^+)+2r(Cl^-)}{\sqrt{3}}=\frac{2(167+181)\,\text{pm}}{\sqrt{3}}=402\,\text{pm}$$

**11B** Since NaCl is fcc, the $Na^+$ ions are in the same locations as were the Al atoms in Practice Example 12-10B, and there are 4 $Na^+$ ions per unit cell. For stoichiometric reasons, there must also be 4 $Cl^-$ ions per unit cell. These are accounted for as follows: there is one $Cl^-$ along each edge, and each of these edge $Cl^-$ ions are shared among four unit cells, and there is one $Cl^-$ precisely in the body center of the unit cell, not shared with any other unit cells. Thus, the number of $Cl^-$ ions is given by: $Cl^-$ ions/unit cell =
$\left(1/4\ Cl^-\text{ on edge}\times 12\text{ edges per unit cell}\right)+1\ Cl^-$ in body center = 4 $Cl^-$/ unit cell.
The volume of this cubic unit cell is the cube of its length. The density is:

$$\text{NaCl density}=\frac{4\text{ formula units}}{1\text{ unit cell}}\times\frac{1\text{ unit cell}}{(560\text{ pm})^3}\times\left(\frac{10^{12}\text{ pm}}{1\text{ m}}\times\frac{1\text{ m}}{100\text{ cm}}\right)^3\times\frac{1\text{ mol NaCl}}{6.022\times10^{23}\text{ f.u.}}$$
$$\times\frac{58.44\text{ g NaCl}}{1\text{ mol NaCl}}=2.21\text{ g/cm}^3$$

**12A**

| | | |
|---|---|---|
| Sublimation of Cs(g): | $Cs(s)\rightarrow Cs(g)$ | $\Delta H_{sub}=+78.2$ kJ / mol |
| Ionization of Cs(g): | $Cs(g)\rightarrow Cs^+(g)+e^-$ | $\Delta I_1=+375.7$ kJ / mol (Table 9.3) |
| $\frac{1}{2}$ Dissociation of $Cl_2$(g): | $\frac{1}{2}Cl_2(g)\rightarrow Cl(g)$ | $DE=\frac{1}{2}\times243\text{ kJ}=121.5$ kJ/mol (Table 10.3) |
| Cl(g) electron affinity: | $Cl(g)+e^-\rightarrow Cl^-(g)$ | $EA_1=-349.0$ kJ / mol (Figure 9–10) |
| Lattice energy: | $Cs^+(g)+Cl^-(g)\rightarrow CsCl(s)$ | L.E. |
| Enthalpy of formation: | $Cs(s)+\frac{1}{2}Cl_2(s)\rightarrow CsCl(s)$ | $\Delta H_f^o=-442.8$ kJ / mol |

$$-442.8\text{ kJ/mol}=+78.2\text{ kJ/mol}+375.7\text{ kJ/mol}+121.5\text{ kJ/mol}-349.0\text{ kJ/mol}+\text{ L.E.}$$
$$=+226.4\text{ kJ/mol}+\text{ L.E.}$$
$$\text{L.E.}=-442.8\text{ kJ}-226.4\text{ kJ}=-669.2\text{ kJ/mol}$$

**12B**

| | | |
|---|---|---|
| Sublimation: | $\mathrm{Ca(s) \to Ca(g)}$ | $\Delta H_{sub} = +178.2\ \mathrm{kJ/mol}$ |
| First ionization energy: | $\mathrm{Ca(g) \to Ca^+(g) + e^-}$ | $I_1 = +590\ \mathrm{kJ/mol}$ |
| Second ionization energy: | $\mathrm{Ca^+(g) \to Ca^{2+}(g) + e^-}$ | $I_2 = +1145\ \mathrm{kJ/mol}$ |
| Dissociation energy: | $\mathrm{Cl_2(g) \to 2Cl(g)}$ | $\mathrm{D.E.} = (2 \times 122)\ \mathrm{kJ/mol}$ |
| Electron Affinity: | $\mathrm{2\,Cl(g) + 2\,e^- \to 2Cl^-(g)}$ | $2\times\ \mathrm{E.A.} = 2(-349)\ \mathrm{kJ/mol}$ |
| Lattice energy: | $\mathrm{Ca^{2+}(g) + 2\,Cl^-(g) \to CaCl_2(s)}$ | $\mathrm{L.E.} = -2223\ \mathrm{kJ/mol}$ |
| Enthalpy of formation: | $\mathrm{Ca(s) + Cl_2(s) \to CaCl_2(s)}$ | $\Delta H_f^o = ?$ |

$$\Delta H_f^o = \Delta H_{sub} + I_1 + I_2 + \text{D.E.} + (2\times\ \text{E.A.}) + \text{L.E.}$$

$$= 178.2\ \text{kJ/mol} + 590\ \text{kJ/mol} + 1145\ \text{kJ/mol} + 244\ \text{kJ/mol} - 698\ \text{kJ/mol} - 2223\ \text{kJ/mol}$$
$$= -764\ \text{kJ/mol}$$

# INTEGRATIVE EXAMPLE

**A.** At 25.0 °C, the vapor pressure of water is 23.8 mmHg. We calculate the vapor pressure for isooctane with the Clausius-Clapeyron equation.

$$\ln\frac{P}{760\ \text{mmHg}} = \frac{35.76\ \times 10^3\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{(99.2+273.2)\ \text{K}} - \frac{1}{298.2\ \text{K}}\right) = -2.87$$

$P = e^{-2.87} \times 760\ \text{mmHg} = 43.1\ \text{mmHg}$ which is higher than $H_2O$'s vapor pressure.

**B.** **(a)** and **(b)** We will work both parts simultaneously.

| | | |
|---|---|---|
| Sublimation of Mg(s): | $\mathrm{Mg(s) \longrightarrow Mg(g)}$ | $\Delta H_{\mathrm{sub}} = +146\ \mathrm{kJ}$ |
| First ionization of Mg(g): | $\mathrm{Mg(g) \longrightarrow Mg^+(g) + e^-}$ | $I_1 = +737.7\ \mathrm{kJ}$ |
| Second ionization of Mg(g): | $\mathrm{Mg^+(g) \longrightarrow Mg^{2+}(g) + e^-}$ | $I_2 = +1451\ \mathrm{kJ}$ |
| $\frac{1}{2}$ Dissociation of $O_2$(g): | $\mathrm{\frac{1}{2}\,O_2(g) \longrightarrow O(g)}$ | $\Delta H_{\mathrm{dis}} = +249\ \mathrm{kJ}$ |
| First electron affinity: | $\mathrm{O(g) + e^- \longrightarrow O^-(g)}$ | $\mathrm{EA_1} = -141.0\ \mathrm{kJ}$ |
| Second electron affinity: | $\mathrm{O^-(g) + e^- \to O^{2-}(g)}$ | $\mathrm{EA_2}$ |
| Lattice energy: | $\mathrm{Mg^{2+}(g) + O^{2-}(g) \longrightarrow MgO(s)}$ | $\mathrm{L.E.} = -3925\ \mathrm{kJ}$ |
| Enthalpy of formation: | $\mathrm{Mg(s) + \frac{1}{2}\,O_2(g) \longrightarrow MgO(s)}$ | $\Delta H_f^\circ = -601.7\ \mathrm{kJ}$ |

$$-601.7\ \text{kJ} = +146\ \text{kJ} + 737.7\ \text{kJ} + 1451\ \text{kJ} + 249\ \text{kJ} - 141.0\ \text{kJ} + \text{EA}_2 - 3925\ \text{kJ}$$

$$\text{EA}_2 = +881\ \text{kJ}$$

# EXERCISES

## Intermolecular Forces

**1.** **(a)** HCl is not a very heavy diatomic molecule. Thus, the London forces between HCl molecules are expected to be relatively weak. Hydrogen bonding is weak in the case of H—Cl bonds; Cl is not one of the three atoms (F, O, N) that form strong hydrogen bonds. Finally, because Cl is an electronegative atom, and H is only moderately electronegative, dipole–dipole interactions should be relatively strong.

**(b)** In $Br_2$ neither hydrogen bonds nor dipole–dipole attractions can occur (there are no H atoms in the molecule, and homonuclear molecules are nonpolar). London forces are more important in $Br_2$ than in HCl since $Br_2$ has more electrons (heavier).

**(c)** In ICl there are no hydrogen bonds since there are no H atoms in the molecule. The London forces are as strong as in $Br_2$ since the two molecules have the same number of electrons. However, dipole–dipole interactions are important in ICl, due to the polarity of the I—Cl bond.

**(d)** In HF London forces are not very important; the molecule has only 10 electrons and thus is quite small. Hydrogen bonding is obviously the most important interaction developed between HF molecules.

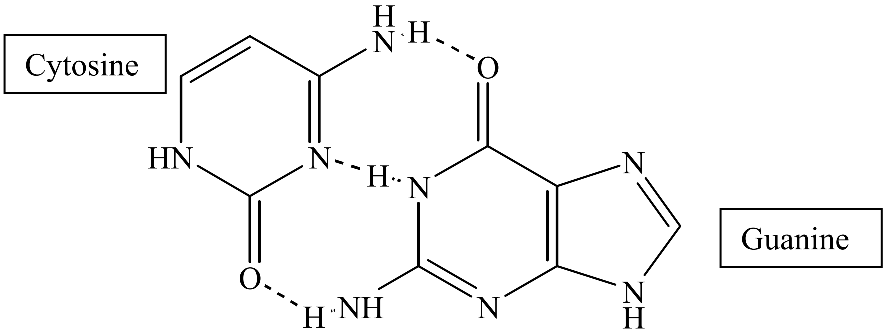
**(e)** In $CH_4$, H bonds are not important (the H atoms are not bonded to F, O, or N). In addition the molecule is not polar, so there are no dipole-dipole interactions. Finally, London forces are quite weak since the molecule contains only 10 electrons. For these reasons $CH_4$ has a very low critical temperature.

**3.** (c) < (b) < (d) < (a)
(ethane thiol) (ethanol) (butanol) (acetic acid)
Viscosity will depend on the intermolecular forces. The stronger the intermolecular bonding, the more viscous the substance.

**5.** We expect $CH_3OH$ to be a liquid from among the four substances listed. Of these four molecules, $C_3H_8$ has the most electrons and should have the strongest London forces. However, only $CH_3OH$ satisfies the conditions for hydrogen bonding (H bonded to and attracted to N, O, or F) and thus its intermolecular attractions should be much stronger than those of the other substances.

**7.** Three water molecules: the two lone pairs on the oxygen will interact with two hydrogens on two different water molecules, and one will interact with the hydrogen attached to O itself.

**9.** There are three H-bonds:



## Surface Tension and Viscosity

**11.** Since both the silicone oil and the cloth or leather are composed of relatively nonpolar molecules, they attract each other. The oil thus adheres well to the material. Water, on the other hand is polar and adheres very poorly to the silicone oil (actually, the water is repelled by the oil), much more poorly, in fact, than it adheres to the cloth or leather. This is because the oil is more nonpolar than is the cloth or the leather. Thus, water is repelled from the silicone-treated cloth or leather.

**13.** Molasses, like honey, is a very viscous liquid (high resistance to flow). The coldest temperatures are generally in January (in the northern hemisphere). Viscosity generally increases as the temperature decreases. Hence, molasses at low temperature is a very slow flowing liquid. Thus there is indeed a scientific basis for the expression “slower than molasses in January.”

**15.** $CCl_4 < CH_3CH_2OCH_2CH_3 < CH_3OH$. The trend follows the increasing strength of intermolecular forces, going from weak (London dispersion) to moderate (dipole–dipole) to strong (H-bond).

**17.** The intermolecular interactions in butanol are dominated by H-bonding, which is much stronger than the London dispersion forces dominant in pentane.

## Vaporization

**19.** The process of evaporation is endothermic, meaning it requires energy. If evaporation occurs from an uninsulated container, this energy is obtained from the surroundings, through the walls of the container. However, if the evaporation occurs from an insulated container, the only source of the needed energy is the liquid that is evaporating. Therefore, the temperature of the liquid will decrease as the liquid evaporates.

**21.** We use the quantity of heat to determine the number of moles of benzene that vaporize.

$$V = \frac{nRT}{P} = \frac{\left(1.54\,\text{kJ} \times \dfrac{1\,\text{mol}}{33.9\,\text{kJ}}\right) \times 0.08206\dfrac{\text{L atm}}{\text{mol K}} \times 298\,\text{K}}{95.1\,\text{mmHg} \times \dfrac{1\,\text{atm}}{760\,\text{mmHg}}} = 8.88\,\text{L}\,C_6H_6(\text{l})$$

**23.** 25.00 mL of $N_2H_4$ (25 °C) density (25°C) = 1.0036 g $mL^{-1}$ (molar mass = 32.0452 g $mol^{-1}$)

mass of $N_2H_4$ = (volume) × (density) = (25.00 mL) × (1.0036 g $mL^{-1}$) = 25.09 g $N_2H_4$

$$n_{N2H4} = 25.09\text{ g }N_2H_4 \times \frac{1\,\text{mol}\,N_2H_4}{32.0452\,\text{g}\,N_2H_4} = 0.7830\text{ mol}$$

Energy required to increase temperature from 25.0 °C to 113.5 °C ($\Delta t$ =88.5 °C)

$$q_{heating} = (n)(C)(\Delta t) = (0.7829\underline{5}\text{ mol }N_2H_4)\left(\frac{98.84\,\text{J}}{1\text{ mol}\,N_2H_4\ {}^{\circ}\text{C}}\right)(88.\ 5\ {}^{\circ}\text{C}) = 6848.7\text{ J or }6.85\text{ kJ}$$

$$q_{vap} = (n_{N_2H_4})(\Delta H_{vap}) = (0.7829\underline{5}\text{ mol }N_2H_4)\left(\frac{43.0\,\text{kJ}}{1\text{ mol}\,N_2H_4}\right) = 33.7\text{ kJ}$$

$$q_{overall} = q_{heating} + q_{vap} = 6.85\text{ kJ} + 33.7\text{ kJ} = 40.5\text{ kJ}$$

**25.** $$\text{heat needed} = 3.78\text{ L H}_2\text{O}\times\frac{1000\text{ cm}^3}{1\text{ L}}\times\frac{0.958\text{ g H}_2\text{O}}{1\text{ cm}^3}\times\frac{1\text{ mol H}_2\text{O}}{18.02\text{ g H}_2\text{O}}\times\frac{40.7\text{ kJ}}{1\text{ mol H}_2\text{O}} = 8.18\times10^3\text{ kJ}$$

$$\text{amount CH}_4\text{ needed} = 8.18\times10^3\text{ kJ}\times\frac{1\text{ mol CH}_4}{890\text{ kJ}} = 9.19\text{ mol CH}_4$$

$$V = \frac{nRT}{P} = \frac{9.19\,\text{mol}\times0.08206\,\text{L atm mol}^{-1}\text{K}^{-1}\times296.6\,\text{K}}{768\,\text{mmHg}\times\dfrac{1\,\text{atm}}{760\,\text{mmHg}}} = 221\text{ L methane}$$

## Vapor Pressure and Boiling Point

**27.** **(a)** We read up the $100^{\circ}\text{C}$ line until we arrive at $C_6H_7N$ curve (e). This occurs at about 45 mmHg.

**(b)** We read across the 760 mmHg line until we arrive at the $C_7H_8$ curve (d). This occurs at about $110^{\circ}\text{C}$.

**29.** Use the ideal gas equation, $n = \text{moles Br}_2 = 0.486\text{ g Br}_2\times\frac{1\text{ mol Br}_2}{159.8\text{ g Br}_2} = 3.04\times10^{-3}\text{ mol Br}_2$.

$$P = \frac{nRT}{V} = \frac{3.04\times10^{-3}\text{ mol Br}_2\times0.08206\text{ L atm mol}^{-1}\text{ K}^{-1}\times298.2\text{ K}}{0.2500\text{ L}}\times\frac{760\text{ mmHg}}{1\text{ atm}} = 226\text{ mmHg}$$

**31.** **(a)** In order to vaporize water in the outer container, heat must be applied (i.e., vaporization is an endothermic process). When this vapor (steam) condenses on the outside walls of the inner container, that same heat is liberated. Thus condensation is an exothermic process.

**(b)** Liquid water, condensed on the outside wall, is in equilibrium with the water vapor that fills the space between the two containers. This equilibrium exists at the boiling point of water. We assume that the pressure is 1.000 atm, and thus, the temperature of the equilibrium must be 373.15 K or $100.00^\circ$ C. This is the maximum temperature that can be realized without pressurizing the apparatus.

**33.** Use the Clausius-Clapeyron equation, and the vapor pressure of water at $100.0^\circ\text{C}$ (373.2 K) and $120.0^\circ\text{C}$ (393.2 K) to determine $\Delta H_{vap}$ of water near its boiling point. We then use the equation again, to determine the temperature at which water's vapor pressure is 2.00 atm.

$$\ln\frac{1489.1\text{ mmHg}}{760.0\text{ mmHg}}=\frac{\Delta H_{vap}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{373.2\text{ K}}-\frac{1}{393.2\text{ K}}\right)=0.6726=1.639\times10^{-5}\,\Delta H_{vap}$$

$$\Delta H_{vap}=4.104\times10^{4}\text{ J/mol}=41.04\text{ kJ/mol}$$

$$\ln\frac{2.00\text{ atm}}{1.00\text{ atm}}=0.6931=\frac{41.04\times10^{3}\text{ J mol}}{8.3145\text{ J mol}^{-1}\text{ K}^{-1}}\left(\frac{1}{373.2\text{ K}}-\frac{1}{T}\right)$$

$$\left(\frac{1}{373.2\text{ K}}-\frac{1}{T_{bp}}\right)=0.6931\times\frac{8.1345\text{ K}^{-1}}{41.03\times10^{3}}=1.404\times10^{-4}\text{ K}^{-1}$$

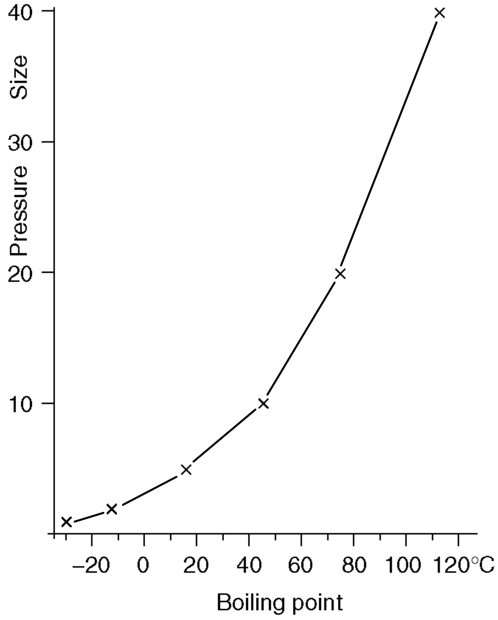
$$\frac{1}{T_{bp}}=\frac{1}{373.2\text{ K}}-1.404\times10^{-4}\text{ K}^{-1}=2.539\times10^{-3}\text{ K}^{-1}\quad T_{bp}=393.9\text{ K}=120.7^\circ\text{ C}$$

**35.** The 25.0 L of He becomes saturated with aniline vapor, at a pressure equal to the vapor pressure of aniline.

$$n_{aniline}=(6.220\text{ g}-6.108\text{ g})\times\frac{1\text{ mol aniline}}{93.13\text{ g aniline}}=0.00120\text{ mol aniline}$$

$$P=\frac{nRT}{V}=\frac{0.00120\text{ mol}\times0.08206\text{ L atm mol}^{-1}\text{ K}^{-1}\times303.2\text{ K}}{25.0\text{ L}}=0.00119\text{ atm}=0.907\text{ mmHg}$$

**37.**



The graph of pressure vs. boiling point for Freon-12 is shown.

At a temperature of $25^\circ$ C the vapor pressure is approximately 6.5 atm for Freon-12. Thus the compressor must be capable of producing a pressure greater than 6.5 atm.

## The Clausius-Clapeyron Equation

**39.** We use the Clausius-Clapeyron equation (12.2) to answer this question.

$T_1 = (56.0+273.2)\ \text{K} = 329.2\ \text{K} \qquad T_2 = (103.7+273.2)\ \text{K} = 376.9\ \text{K}$

$$\ln\frac{10.0\ \text{mmHg}}{100.0\ \text{mmHg}} = \frac{\Delta H_{vap}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{376.9\ \text{K}} - \frac{1}{329.2\ \text{K}}\right) = -2.30 = -4.624\times10^{-5}\,\Delta H_{vap}$$

$\Delta H_{vap} = 4.97\times10^{4}\ \text{J/mol} = 49.7\ \text{kJ/mol}$

**41.** Once again, we will employ the Clausius-Clapeyron equation.

$T = 56.2^{\circ}\ \text{C is } T = 329.4\ \text{K}$

$$\ln\frac{760\ \text{mmHg}}{375\ \text{mmHg}} = \frac{25.5\times10^{3}\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{T} - \frac{1}{329.4\ \text{K}}\right) = 0.706$$

$$\left(\frac{1}{T} - \frac{1}{329.4\ \text{K}}\right) = \frac{0.706\times8.3145}{25.5\times10^{3}}\ \text{K}^{-1} = 2.30\times10^{-4}\ \text{K}^{-1} = 1/T - 3.03_6\times10^{-3}\ \text{K}^{-1}$$

$1/T = (3.03_6 + 0.230)\times10^{-3}\ \text{K}^{-1} = 3.266\times10^{-3}\ \text{K}^{-1} \qquad T = 306\ \text{K} = 33^{\circ}\ \text{C}$

**43.** Normal boiling point = 179 °C and critical point = 422 °C and 45.9 atm

$$\ln\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{vap}}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad \ln\left(\frac{45.9}{1}\right) = \frac{\Delta H_{vap}}{8.3145\ \text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{452.2\,\text{K}} - \frac{1}{695.2\,\text{K}}\right)$$

$\Delta H_{vap} = 41.2\ \text{kJ mol}^{-1}$

$$\ln\left(\frac{1}{P}\right) = \frac{41{,}200\,\text{J mol}^{-1}}{8.3145\,\text{J K}^{-1}\text{mol}^{-1}}\left(\frac{1}{373.2} - \frac{1}{452.2\,\text{K}}\right) \quad P = 0.0981\ \text{atm or } 74.6\ \text{Torr}$$

## Critical Point

**45.** Substances that can exist as a liquid at room temperature (about $20^{\circ}$ C) have critical temperature above $20^{\circ}$ C, 293 K. Of the substances listed in Table 12.5, $CO_2(T_c = 304.2\ \text{K})$, $HCl(T_c = 324.6\ \text{K})$, $NH_3(T_c = 405.7\ \text{K})$, $SO_2(T_c = 431.0\ \text{K})$, and $H_2O(T_c = 647.3\ \text{K})$ can exist in liquid form at 20 °C. In fact, $CO_2$ exists as a liquid in $CO_2$ fire extinguishers.

## Melting and Freezing

**47.** **(a)** $\text{heat evolved} = 3.78 \text{ kg Cu} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{13.05 \text{ kJ}}{1 \text{ mol Cu}} = 776 \text{ kJ evolved or}$

$\Delta H$ = -776 kJ

**(b)** $\text{heat absorbed} = (75 \text{ cm} \times 15 \text{ cm} \times 12 \text{ cm}) \times \frac{8.92 \text{ g}}{1 \text{ cm}^3} \times \frac{1 \text{ mol Cu}}{63.55 \text{ g Cu}} \times \frac{13.05 \text{ kJ}}{1 \text{ mol Cu}} = 2.5 \times 10^4 \text{ kJ}$

## States of Matter and Phase Diagrams

**49.** Let us use the ideal gas law to determine the final pressure in the container, assuming that all of the dry ice vaporizes. We then locate this pressure, at a temperature of $25^\circ$ C, on the phase diagram of Figure 12-28.

$$P = \frac{nRT}{V} = \frac{\left(80.0 \text{ g CO}_2 \times \frac{1 \text{ mol CO}_2}{44.0 \text{ g CO}_2}\right) \times 0.08206 \frac{\text{L atm}}{\text{mol K}} \times 298 \text{ K}}{0.500 \text{ L}} = 88.9 \text{ atm}$$

Although this point ($25^\circ$ C and 88.9 atm) is most likely in the region labeled “liquid” in Figure 12–28, we computed its pressure assuming the $CO_2$ is a gas. Some of this gas should condense to a liquid. Thus, both liquid and gas are present in the container. Solid would not be present unless the temperature is below -50 °C at ~ 88.9 atm.

**51.** **(a)** The upper-right region of the phase diagram is the liquid region, while the lower-right region is the region of gas.

**(b)** Melting involves converting the solid into a liquid. As the phase diagram shows, the lowest pressure at which liquid exists is at the triple point pressure, namely, 43 atm. 1.00 atm is far below 43 atm. Thus, liquid cannot exist at this pressure, and solid sublimes to gas instead.

**(c)** As we move from point $A$ to point $B$ by lowering the pressure, initially nothing happens. At a certain pressure, the solid liquefies. The pressure continues to drop, with the entire sample being liquid while it does, until another, lower pressure is reached. At this lower pressure the entire sample vaporizes. The pressure then continues to drop, with the gas becoming less dense as the pressure falls, until point $B$ is reached.

**53.** 0.240 g of $H_2O$ corresponds to 0.0133 mol $H_2O$. If the water does not vaporize completely, the pressure of the vapor in the flask equals the vapor pressure of water at the indicated temperature. However, if the water vaporizes completely, the pressure of the vapor is determined by the ideal gas law.

**(a)** $30.0^\circ$ C, vapor pressure of $H_2O$ = 31.8 mmHg = 0.0418 atm

$$n = \frac{PV}{RT} = \frac{0.0418 \text{ atm} \times 3.20 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 303.2 \text{ K}}$$

$n$ = 0.00538 mol $H_2O$ vapor, which is less than 0.0133 mol $H_2O$;

This represents a non-eqilibrium condition, since not all the $H_2O$ vaporizes.

The pressure in the flask is 0.0418 atm. (from tables)

**(b)** $50.0^\circ$ C, vapor pressure of $H_2O$ = 92.5 mmHg = 0.122 atm

$$n = \frac{PV}{RT} = \frac{0.122 \text{ atm} \times 3.20 \text{ L}}{0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 323.2 \text{ K}}$$

= 0.0147 mol $H_2O$ vapor > 0.0133 mol $H_2O$; all the $H_2O$ vaporizes. Thus,

$$P = \frac{nRT}{V} = \frac{0.0133 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 323.2 \text{ K}}{3.20 \text{ L}} = 0.110 \text{ atm} = 83.8 \text{ mmHg}$$

**(c)** $70.0^\circ$ C All the $H_2O$ must vaporize, as this temperature is higher than that of part (b). Thus,

$$P = \frac{nRT}{V} = \frac{0.0133 \text{ mol} \times 0.08206 \text{ L atm mol}^{-1} \text{ K}^{-1} \times 343.2 \text{ K}}{3.20 \text{ L}} = 0.117 \text{ atm} = 89.0 \text{ mmHg}$$

**<u>55.</u>** **(a)** According to Figure 12-28, $CO_2(s)$ exists at temperatures below $-78.5°$C when the pressure is 1 atm or less. We do not expect to find temperatures this low and partial pressures of $CO_2(g)$ of 1 atm on the surface of Earth.

**(b)** According to Table 12.5, the critical temperature of $CH_4$, the maximum temperature at which $CH_4(l)$ can exist, is 191.1 K = -82.1 °C. We do not expect to find temperatures this low on the surface of Earth.

**(c)** Since, according to Table 12.5, the critical temperature of $SO_2$ is 431.0 K = 157.8 °C, $SO_2(g)$ can be found on the surface of Earth.

**(d)** According to Figure 12–27, $I_2(l)$ can exist at pressures less than 1.00 atm between the temperatures of 114 °C and 184 °C. There are very few places on Earth that reach temperatures this far above the boiling point of water at pressures below 1 atm. One example of such a place would be the mouth of a volcano high above sea level. Essentially, $I_2(l)$ is not found on the surface of Earth.

**(e)** According to Table 12.5, the critical temperature — the maximum temperature at which $O_2(l)$ exists — is 154.8 K = $-118.4$ °C. Temperatures this low do not exist on the surface of Earth.

**57.** **(a)** heat lost by water = $q_{\text{water}}$ = (m)(C)(Δt)

$$q_{\text{water}} = (100.0\text{ g})\left(4.18\frac{\text{J}}{\text{g }^{\circ}\text{C}}\right)(0.00\ ^{\circ}\text{C} - 20.00\ ^{\circ}\text{C})\left(\frac{1\text{kJ}}{1000\text{ J}}\right) = -8.36\text{ kJ}$$

Using $\Delta H_{\text{cond}} = -\Delta H_{\text{vap}}$ and heat lost by system = heat loss of condensation + cooling

$$q_{\text{steam}} = (175\text{ g H}_2\text{O})\left(4.18\frac{\text{J}}{\text{g }^{\circ}\text{C}}\right)(0.0\ ^{\circ}\text{C} - 100.0\ ^{\circ}\text{C})\left(\frac{1\text{kJ}}{1000\text{ J}}\right)$$

$$+(175\text{ g H}_2\text{O})\left(\frac{1\text{mol H}_2\text{O}}{18.015\text{g H}_2\text{O}}\right)\left(\frac{-40.7\text{kJ}}{1\text{mol H}_2\text{O}}\right)$$

$q_{\text{steam}}$ = -395.4 kJ + -73.2 kJ = -468.6 kJ or ~ -469 kJ

total energy to melt the ice = $q_{\text{water}} + q_{\text{steam}}$ = -8.37 kJ + −469 kJ = −477 kJ

$$\text{moles of ice melted} = (477\text{ kJ})\left(\frac{1\text{mol ice}}{6.01\text{kJ}}\right) = 79.4\text{ mol ice melted}$$

$$\text{mass of ice melted} = (79.4\text{ mol H}_2\text{O})\left(\frac{18.015\text{g H}_2\text{O}}{1\text{mol H}_2\text{O}}\right)\left(\frac{1\text{kg H}_2\text{O}}{1000\text{g H}_2\text{O}}\right) = 1.43\text{ kg}$$

mass of unmelted ice = 1.65 kg − 1.43 kg = 0.22 kg

**(b)** mass of unmelted ice = 0.22 kg (from above)
heat required to melt ice = $n\cdot\Delta H_{\text{fusion}}$

$$\text{heat required} = (0.22\text{ kg ice})\left(\frac{1000\text{g H}_2\text{O}}{1\text{kg H}_2\text{O}}\right)\left(\frac{1\text{mol H}_2\text{O}}{18.015\text{g H}_2\text{O}}\right)\left(\frac{6.01\text{kJ}}{1\text{mol H}_2\text{O}}\right) = 73.\underline{4}\text{ kJ}$$

Next we need to determine heat produced when 1 mole of steam (18.015 g) condenses and cools from 100.°C to 0.0 °C.

Heat evolved can be calculated as shown below:

$$= (1\text{ mol H}_2\text{O})\left(\frac{-40.7\text{kJ}}{1\text{mol H}_2\text{O}}\right) + (18.015\text{ g})\left(4.18\frac{\text{J}}{\text{g }^{\circ}\text{C}}\right)(0.0\ ^{\circ}\text{C} - 100.\ ^{\circ}\text{C})\left(\frac{1\text{kJ}}{1000\text{ J}}\right)$$

= -40.7 kJ + -7.53 kJ = -48.2 kJ per mole of $H_2O(g)$ or per 18.015 g $H_2O(g)$

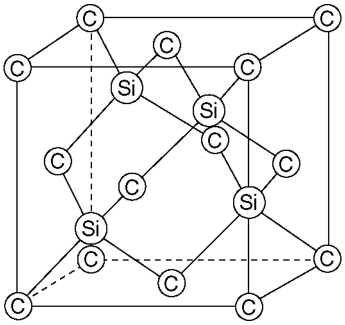
$$\text{mass of steam required} = (73.\underline{4}\text{ kJ})\left(\frac{1\text{mol H}_2\text{O(g)}}{48.2\text{kJ}}\right)\left(\frac{18.015\text{g H}_2\text{O}}{1\text{mol H}_2\text{O}}\right) = 27\text{ g steam}$$

**59.** The liquid in the can is supercooled. When the can is opened, gas bubbles released from the carbonated beverage serve as sites for the formation of ice crystals. The condition of supercooling is destroyed and the liquid reverts to the solid phase. An alternative explanation follows. The process of the gas coming out of solution is endothermic (heat is required). (We know this to be true because the reaction solution of gas in water → gas + liquid water proceeds to the right as the temperature is raised, a characteristic direction of an endothermic reaction.) The required heat is taken from the cooled liquid, causing it to freeze.

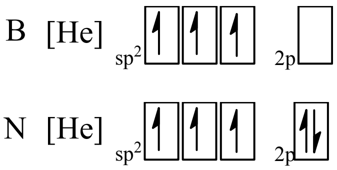
## Network Covalent Solids

**61.** One would expect diamond to have a greater density than graphite. Although the bond distance in graphite, "one-and-a-half" bonds, would be expected to be shorter than the single bonds in diamond, the large spacing between the layers of C atoms in graphite makes its crystals much less dense than those of diamond.

**63.** **(a)** We expect Si and C atoms to alternate in the structure, as shown at the right. The C atoms are on the corners ($8 \times 1/8 = 1$ C atom) and on the faces ($6 \times 1/2 = 3$ C atoms), a total of four C atoms/unit cell. The Si atoms are each totally within the cell, a total of four Si atoms/unit cell.



**(b)** To have a graphite structure, we expect $sp^2$ hybridization for each atom. The hybridization schemes for B and N atoms are shown to the right. The half-filled $sp^2$ hybrid orbitals of the boron and nitrogen atoms overlap to form the $\sigma$ bonding structure, and a hexagonal array of atoms. The $2p_z$ orbitals then overlap to form the $\pi$ bonding orbitals. Thus, there will be as many $\pi$ electrons in a sample of BN as there are in a sample of graphite, assuming both samples have the same number of atoms.



## Ionic Bonding and Properties

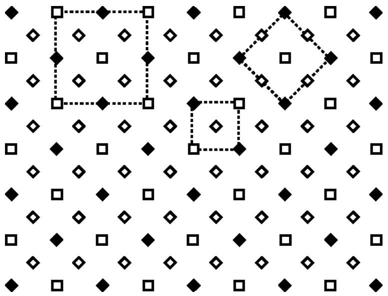
**65.** We expect forces in ionic compounds to increase as the sizes of ions become smaller and as ionic charges become greater. As the forces between ions become stronger, a higher temperature is required to melt the crystal. In the series of compounds NaF, NaCl, NaBr, and NaI, the anions are progressively larger, and thus the ionic forces become weaker. We expect the melting points to decrease in this series from NaF to NaI. This is precisely what is observed.

**67.** NaF will give the highest Mohs value, because hardness is a function of stronger bonds, which are also shorter, and are affected by charge and size of the anions and cations. NaF has the smallest anion, and is tied with NaCl for the smallest cation.

## Crystal Structures

**69.** In each layer of a closest packing arrangement of spheres, there are six spheres surrounding and touching any given sphere. A second similar layer then is placed on top of this first layer so that its spheres fit into the indentations in the layer below. The two different closest packing arrangements arise from two different ways of placing the third layer on top of these two, with its spheres fitting into the indentations of the layer below. In one case, one can look down into these indentations and see a sphere of the bottom (first) layer. If these indentations are used, the closest packing arrangement *abab* results (hexagonal closest packing). In the other case, no first layer sphere is visible through the indentation; the closest packing arrangement *abcabc* results (cubic closest packing).

**71.** **(a)** We naturally tend to look at crystal structures in right-left, up-down terms. If we do that here, we might be tempted to assign a unit cell as a square, with its corners at the centers of the light-colored squares. But the crystal does not "know" right and left or top and bottom. If we look at this crystal from the lower right corner, we see a unit cell that has its corners at the centers of dark-colored diamonds. These two types of unit cells are outlined at the top of the diagram below.



**(b)** The unit cell has one light-colored square fully inside it. It has four light-colored "circles" (which the computer doesn't draw as very round) on the edges, each shared with one other unit cell. So there are a total of $4 \times 1/2 = 2$ circles per unit cell. Also, the unit cell has four dark-colored diamonds, one at each corner, and each diamond is shared with four other unit cells, for a total of $4 \times 1/4 = 1$ diamond per unit cell.

**(c)** One example of an erroneous unit cell is the small square outlined near the center of the figure drawn in part (a). Notice that simply repeatedly translating this unit cell toward the right, so that its left edge sits where its right edge is now, will not generate the lattice.

**73.** In Figure 12–45 we see that the body diagonal of a cube has a length of $\sqrt{3}l$, where $l$ is the length of one edge of the cube. The length of this body diagonal also equals $4r$, where $r$ is the radius of the atom in the structure. Hence $4r = \sqrt{3}l$ or $l = 4r \div \sqrt{3}$. Recall that the volume of a cube is $l^3$, and $\sqrt{3} = 1.732$.

$$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{\dfrac{2\ \text{W atoms}}{1\,\text{unit cell}} \times \dfrac{1\ \text{mol W}}{6.022\times 10^{23}\,\text{W atoms}} \times \dfrac{183.85\,\text{g W}}{1\,\text{mol W}}}{\left(\dfrac{4\times 139\,\text{pm}}{1.732} \times \dfrac{1\,\text{m}}{10^{12}\,\text{pm}} \times \dfrac{100\,\text{cm}}{1\,\text{m}}\right)^3} = 18.5\ \text{g}/\text{cm}^3$$

This compares well with a tabulated density of $19.25\ \text{g}/\text{cm}^3$.

**75.** **(a)** 335 pm = 2 radii or 1 diameter. Hence Po diameter = 335 pm

**(b)** 1 Po unit cell = $(335\ \text{pm})^3 = 3.76 \times 10^7\ \text{pm}^3$ ($3.76 \times 10^{-23}\ \text{cm}^3$) per unit cell.

$$\text{density} = \frac{m}{V} = \frac{3.47\times 10^{-22}\,\text{g}}{3.76\times 10^{-23}\ \text{cm}^3} = 9.23\ \text{g cm}^{-3}$$

**(c)** $n = 1$, d = 335 pm and $\lambda = 1.785 \times 10^{-10}$ or 178.5 pm Solve for $\sin\theta$, then determine $\theta$.

$$\sin\theta = \frac{n\lambda}{2d} = \frac{(1)(1.785\ \text{x}\ 10^{-10})}{2(335\times 10^{-12})} = 0.266\underline{4} \text{ or } \theta = 15.4\underline{5}^\circ$$

**77.** There are 8 $SiF_4$ molecules with the Si atoms at each corner of the cube, and one molecule in the center. Therefore, there are 8×1/8 + 1 = 2 Si atoms per unit cell.

## Ionic Crystal Structures

**79.** $CaF_2$**:** There are eight $Ca^{2+}$ ions on the corners, each shared among eight unit cells, for a total of one $(8\times 1/8)$ corner ion per unit cell. There are six $Ca^{2+}$ ions on the faces, each shared between two unit cells, for a total of three $(6\times 1/2)$ face ions per unit cell. This gives a total of four $Ca^{2+}$ ions per unit cell. There are eight $F^-$ ions, each wholly contained within the unit cell. The ratio of $Ca^{2+}$ ions to $F^-$ ions is 4 $Ca^{2+}$ ions per 8 $F^-$ ions: $Ca_4F_8$ or $CaF_2$. $TiO_2$. There are eight $Ti^{4+}$ ions on the corners, each shared among eight unit cells, for a total of one $Ti^{4+}$ corner ion $(8\times 1/8)$ per unit cell. There is one $Ti^{4+}$ ion in the center, wholly contained within the unit cell. Thus, there are a total of two $Ti^{4+}$ ions per unit cell. There are four $O^{2-}$ ions on the faces of the unit cell, each shared between two unit cells, for a total of two $(4\times 1/2)$ face atoms per unit cells. There are two $O^{2-}$ ions totally contained within the unit cell. This gives a total of four $O^{2-}$ ions per unit cell. The ratio of $Ti^{4+}$ ions to $O^{2-}$ ions is 2 $Ti^{4+}$ ions per 4 $O^{2-}$ ion: $Ti_2O_4$ or $TiO_2$.

**81.** **(a)** In a sodium chloride type of lattice, there are six cations around each anion and six anions around each cation. These oppositely charged ions are arranged as follows: one above, one below, one in front, one in back, one to the right, and one to the left. Thus the coordination number of $Mg^{2+}$ is 6 and that of $O^{2-}$ is 6 also.

**(b)** In the unit cell, there is an oxide ion at each of the eight corners; each of these is shared between eight unit cells. There also is an oxide ion at the center of each of the six faces;

each of these oxide ions is shared between two unit cells. Thus, the total number of oxide ions is computed as follows.

$$\text{total \# of oxide ions} = 8 \text{ corners} \times \frac{1 \text{ oxide ion}}{8 \text{ unit cells}} + 6 \text{ faces} \times \frac{1 \text{ oxide ion}}{2 \text{ unit cells}} = 4\ O^{2-} \text{ ions}$$

There is a magnesium ion on each of the twelve edges; each of these is shared between four unit cells. There also is a magnesium ion in the center which is not shared with another unit cell.

$$\text{total \# of } Mg^{2+} \text{ ions} = 12 \text{ adjoining cells} \times \frac{1 \text{ magnesium ion}}{4 \text{ unit cells}} + 1 \text{ central } Mg^{2+} \text{ ion}$$

$$= 4\ Mg^{2+} \text{ ions (Thus, there are four formula units per unit cell of MgO.)}$$

**(c)** Along the edge of the unit cell, $Mg^{2+}$ and $O^{2-}$ ions are in contact. The length of the edge is equal to the radius of one $O^{2-}$, plus the diameter of $Mg^{2+}$, plus the radius of another $O^{2-}$.

$$\text{edge length} = 2\times O^{2-} \text{ radius} + 2\times Mg^{2+} \text{ radius} = 2\times140 \text{ pm} + 2\times72 \text{ pm} = 424 \text{ pm}$$

The unit cell is a cube; its volume is the cube of its length.

$$\text{volume} = (424 \text{ pm})^3 = 7.62\times10^7 \text{ pm}\left(\frac{1 \text{ m}}{10^{12} \text{ pm}} \times \frac{100 \text{ cm}}{1 \text{ m}}\right)^3 = 7.62\times10^{-23} \text{ cm}^3$$

**(d)** $$\text{density} = \frac{\text{mass}}{\text{volume}} = \frac{4 \text{ MgO f.}u}{7.62\times10^{-23} \text{ cm}^3} \times \frac{1 \text{ mol MgO}}{6.022\times10^{23} \text{ f.}u.} \times \frac{40.30 \text{ g MgO}}{1 \text{ mol MgO}} = 3.51 \text{ g/cm}^3$$

Thus, there are four formula units per unit cell of MgO.

**83.** **(a)** CaO → radius ratio = $\frac{r_{Ca^{2+}}}{r_{O^{2-}}} = \frac{100 \text{pm}}{140 \text{pm}} = 0.714$

Cations occupy octahedral holes of a face centered cubic array of anions.

**(b)** CuCl → radius ratio = $\frac{r_{Cu^{+}}}{r_{Cl^{-}}} = \frac{96 \text{pm}}{181 \text{pm}} = 0.530$

Cations occupy octahedral holes of a face centered cubic array of anions.

**(c)** $LiO_2$ → radius ratio = $\frac{r_{Li^{+}}}{r_{O_2^{-}}} = \frac{59 \text{pm}}{128 \text{pm}} = 0.461$

Cations occupy octahedral holes of a face centered cubic array of anions.

## Lattice Energy

**85.** Lattice energies of a series such as LiCl(s), NaCl(s), KCl(s), RbCl(s), and CsCl(s) will vary approximately with the size of the cation. A smaller cation will produce a more exothermic lattice energy. Thus, the lattice energy for LiCl(s) should be the most exothermic and CsCl(s) the least in this series, with NaCl(s) falling in the middle of the series.

**87.**

| | | |
|---|---|---|
| Second ionization energy: | $Mg^{+}(g) \rightarrow Mg^{2+}(g) + e^{-}$ | $I_2 = 1451$ kJ/mol |
| Lattice energy: | $Mg^{2+}(g) + 2\ Cl^{-}(g) \rightarrow MgCl_2(s)$ | L.E. = −2526 kJ / mol |
| Sublimation: | $Mg(s) \rightarrow Mg(g)$ | $\Delta H_{sub} = 146$ kJ/mol |
| First ionization energy | $Mg(g) \rightarrow Mg^{+}(\ g) + e^{-}$ | $I_1 = 738$ kJ/mol |
| Dissociation energy: | $Cl_2(g) \rightarrow 2\ Cl(g)$ | D.E. = $(2 \times 122)$kJ/mol |
| Electron affinity: | $2\ Cl(g) + 2\ e^{-} \rightarrow 2\ Cl^{-}(g)$ | $2\times$ E.A. = $2(-349)$ kJ/mol |

$$\Delta H_f^{\,o} = \Delta H_{sub} + I_1 + I_2 + \text{ D.E.} + \left(2\times \text{ E.A.}\right) + \text{ L.E.}$$

$$= 146\ \frac{\text{kJ}}{\text{mol}} + 738\ \frac{\text{kJ}}{\text{mol}} + 1451\ \frac{\text{kJ}}{\text{mol}}1 + 244\ \frac{\text{kJ}}{\text{mol}} - 698\ \frac{\text{kJ}}{\text{mol}} - 2526\ \frac{\text{kJ}}{\text{mol}} = -645\ \frac{\text{kJ}}{\text{mol}}$$

In Example 12-12, the value of $\Delta H_f^{\,o}$ for MgCl is calculated as $-19$ kJ/mol. Therefore, $MgCl_2$ is much more stable than MgCl, since considerably more energy is released when it forms. $MgCl_2(s)$ is more stable than MgCl(s)

# INTEGRATIVE AND ADVANCED EXERCISES

**91.** In many instances, with $CO_2$ being one, the substance in the tank is not present as a gas only, but as a liquid in equilibrium with its vapor. As gas is released from the tank, the liquid will vaporize to replace it, maintaining a pressure in the tank equal to the vapor pressure of the substance at the temperature at which the cylinder is stored. This will continue until all of the liquid vaporizes, after which only gas will be present. The remaining gas will be quickly consumed, and hence the reason for the warning. However, the situation of gas in equilibrium with liquid only applies to substances that have a critical temperature above room temperature (20 °C or 293 K). Thus, substances in Table 12-5 for which gas pressure does serve as a measure of the quantity of gas in the tank are $H_2$ ($T_c$ = 33.3 K), $N_2$ ($T_c$ = 126.2 K), $O_2$ ($T_c$ = 154.8 K), and $CH_4$ ($T_c$ = 191.1 K).

**93.** For this question we need to determine the quantity of heat required to vaporize 1.000 g $H_2O$ at each temperature. At 20°C, 2447 J of heat is needed to vaporize each 1.000 g $H_2O$. At 100°C., the quantity of heat needed is

$$\frac{10.00\ \text{kJ}}{4.430\ \text{g}\ \ H_2O} \times \frac{1000\ \text{J}}{1\ \text{kJ}} = 2257\ \ \text{J/g}\ \ H_2O$$

Thus, less heat is needed to vaporize 1.000 g of $H_2O$ at the higher temperature of 100. °C. This makes sense, for at the higher temperature the molecules of the liquid already are in rapid motion. Some of this energy of motion or vibration will contribute to the energy needed to break the cohesive forces and vaporize the molecules.

**96.** If only gas were present, the final pressure would be 10 atm. This is far in excess of the vapor pressure of water at 30.0 °C (~ 0.042 atm). Most of the water vapor condenses to liquid water. (It cannot all be liquid, because the liquid volume is only about 20 mL and the system volume is 2.61 L.) The final condition is a point on the vapor pressure curve at 30.0 °C.

**99.** **(a)** $$\text{pressure} = \frac{\text{force}}{\text{area}} = \frac{80.\ \text{kg} \times 9.8067\,\text{m}\,\text{s}^{-2}}{2.5\ \text{cm}^2 \times \dfrac{1\ \text{m}^2}{10^4\ \text{cm}^2}} \times \frac{1\ \text{N}}{1\ \text{kg m s}^{-2}} \times \frac{1\ \text{atm}}{101325\ \text{N}\,\text{m}^{-2}} = 31\ \text{atm}$$

**(b)** $$\text{decrease in melting point} = 31\ \text{atm} \times \frac{1.0\ °\text{C}}{125\ \text{atm}} = 0.25\ °\text{C}$$

The ice under the skates will melt at –0.25 °C.

**100.** $P = P_0 \times 10^{-Mgh/2.303\,RT}$ Assume ambient temperature is $10.0\,°\text{C} = 283.2\,\text{K}$

$$\frac{Mgh}{2.303\ RT} = \frac{0.02896\ \text{kg/mol air} \times 9.8067\ \text{m/s}^2 \times 3170\ \text{m}}{2.303 \times 8.3145\ \text{Jmol}^{-1}\text{K}^{-1} \times 283.2\ \text{K}} = 0.166$$

$P = P_0 \times 10^{-0.166} = 1\ \text{atm} \times 0.682 = 0.682\ \text{atm} =$ atmospheric pressure in Leadville, CO.

$$\ln\frac{0.682\ \text{atm}}{1.000\ \text{atm}} = \frac{-41 \times 10^3\ \text{J/mol}}{8.3145\ \text{J mol}^{-1}\ \text{K}^{-1}}\left(\frac{1}{T} - \frac{1}{373.2\ \text{K}}\right) = -0.383$$

$$\left(\frac{1}{T} - \frac{1}{373.2\ \text{K}}\right) = -0.383 \times \frac{8.3145}{-41 \times 10^3} = +7.8 \times 10^{-5}\ \text{K}^{-1}$$

$$\frac{1}{T} = +7.77 \times 10^{-5}\ \text{K}^{-1} + 2.68 \times 10^{-3}\ \text{K}^{-1} = 2.76 \times 10^{-3}\ \text{K}^{-1} \qquad T = 360\ \text{K} = 87\ °\text{C}$$

**103.** The molar mass of acetic acid monomer is 60.05 g/mol. We first determine the volume occupied by 1 mole of molecules of the vapor, assuming that the vapor consists only of monomer molecules: $HC_2H_3O_2$.

$$\text{volume of vapor} = 60.05\ \text{g} \times \frac{1\ \text{L}}{3.23\ \text{g}} = 18.6\ \text{L}$$

Next, we can determine the actual number of moles of vapor in 18.6 L at 350 K.

$$\text{moles of vapor} = \frac{PV}{RT} = \frac{1\ \text{atm} \times 18.6\ \text{L}}{0.08206\ \text{L atm mol}^{-1}\ \text{K}^{-1} \times 350\ \text{K}} = 0.648\ \text{mol vapor}$$

Then, we can determine the number of moles of dimer and monomer, starting with 1.00 mole of monomer, and producing a final mixture of 0.648 moles total (monomer and dimer together).

| | | | |
|---|---|---|---|
| Reaction: | $2\ HC_2H_3O_2(g)$ | $\longrightarrow$ | $(HC_2H_3O_2)_2(g)$ |
| Initial: | 1.00 mol | | 0 |
| Changes: | $-2x$ mol | | $+x$ mol |
| Final: | $(1.00 - 2x)$ mol | | $x$ mol |

The line labeled “Changes” indicates that 2 moles of monomer are needed to form each mole of dimer. The line labeled “Final” results from adding the “Initial” and “Changes” lines.

$$\text{total number of moles} = 1.00 - 2x + x = 1.00 - x = 0.648 \text{ mol}$$

$$x = 0.352 \text{ mol dimer} \qquad (1.00 - 2x) = 0.296 \text{ mol monomer}$$

$$\%\text{ dimer} = \frac{0.352 \text{ mol dimer}}{0.648 \text{ mol total}} \times 100\% = 54.3\% \text{ dimer}$$

We would expect the % dimer to decrease with temperature. Higher temperatures will provide the energy (as translational energy (heat)) needed to break the relatively weak hydrogen bonds that hold the dimers together.

**104.** First we compute the mass and the amount of mercury.

$$\text{mass Hg} = 685 \text{ mL} \times \frac{13.6 \text{ g}}{1 \text{ mL}} = 9.32 \times 10^3 \text{ g} \qquad n_{\text{Hg}} = 9.32 \times 10^3 \text{ g} \times \frac{1 \text{ mol Hg}}{200.59 \text{ g}} = 46.5 \text{ mol Hg}$$

Then we calculate the heat given up by the mercury in lowering its temperature, as the sum of the following three terms.

$$\text{cool liquid} \quad = 9.32 \times 10^3 \text{ g} \times 0.138 \text{ J g}^{-1} \,^\circ\text{C}^{-1} \times (-39 \,^\circ\text{C} - 20 \,^\circ\text{C}) = -7.6 \times 10^4 \text{ J} = -76 \text{ kJ}$$

$$\text{freeze liquid} \quad = 46.5 \text{ mol Hg} \times (-2.30 \text{ kJ/mol}) = -107 \text{ kJ}$$

$$\text{cool solid} \quad = 9.32 \times 10^3 \text{ g} \times 0.126 \text{ J g}^{-1} \,^\circ\text{C}^{-1} \times (-196 + 39) \,^\circ\text{C} = -1.84 \times 10^5 \text{ J} = -184 \text{ kJ}$$

$$\text{total heat lost by Hg} = -76 \text{ kJ} - 107 \text{ kJ} - 184 \text{ kJ} = -367 \text{kJ} = -\text{heat gained by N}_2$$

$$\text{mass of N}_2\text{(l) vaporized} = 367 \text{ kJ} \times \frac{1 \text{mol N}_2}{5.58 \text{ kJ}} \times \frac{28.0 \text{g N}_2}{1 \text{ mol N}_2} = 1.84 \times 10^3 \text{ g N}_2\text{(l)} = 1.84 \text{ kg N}_2$$

**107.** We need to calculate five different times. They are shown below.

1. Heat the solid to its melting point $T_1$ =

$$1 \text{ mol Bi} \times \frac{0.028 \text{ kJ}}{\text{K mol}} \times (554.5 \text{ K} - 300 \text{ K}) \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 7.1 \text{ min}$$

2. Melt the solid $T_2 = 1 \text{ mol Bi} \times \frac{10.9 \text{ kJ}}{\text{K mol}} \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 10.9 \text{ min}$

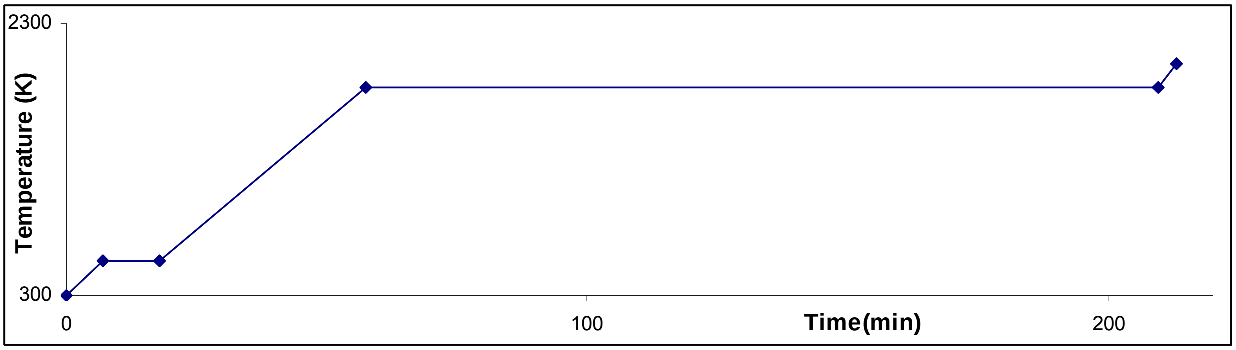
3. Heat the liquid to its boiling point $T_3$ =

$$1 \text{ mol Bi} \times \frac{0.031 \text{ kJ}}{\text{K mol}} \times (1832 \text{ K} - 554.5 \text{ K}) \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 39.6 \text{ min}$$

4. Vaporize the liquid $T_4 = 1 \text{ mol Bi} \times \frac{151.5 \text{ kJ}}{\text{K mol}} \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 151.5 \text{ min}$

5. Heat the gas to 2000 K $T_5 = 1 \text{ mol Bi} \times \frac{0.021 \text{ kJ}}{\text{K mol}} \times (2000 \text{ K} - 1832 \text{ K}) \times \frac{1 \text{ min}}{1.00 \text{ kJ}} = 3.5 \text{ min}$

A plot is shown below:



**109.** The edge length of the NaCl unit cell is 560 pm (from Example 12-11), and thus the distance between the top and the middle layers in the NaCl unit cell is 560 pm ÷ 2 = 280 pm. This is equal to the value of *d* in the Bragg equation (12.5). We first solve for sin θ and then for θ.

$$\sin\theta = \frac{n\lambda}{2d} = \frac{1\times 154.1\text{ pm}}{2\times 280\text{ pm}} = 0.275 \qquad \theta = \sin^{-1}(0.275) = 16.0°$$

## FEATURE PROBLEMS

**119.** We obtain the surface tension by substituting the experimental values into the equation for surface tension.

$$h = \frac{2\gamma}{dgr} \quad \gamma = \frac{hdgr}{2} = \frac{1.1\text{ cm}\times 0.789\text{ g cm}^{-3}\times 981\text{ cm s}^{-2}\times 0.050\text{ cm}}{2} = 21\text{ g/s}^2 = 0.021\text{ J/m}^2$$

**120.**

**(a)** $$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(V_g - V_l)} = \frac{\Delta H_{vap}}{T(V_g)} \quad Note: V_l \approx 0 \quad \text{Rearrange expression, Use } V_g = \frac{nRT}{P}$$

$$\frac{dP}{dT} = \frac{\Delta H_{vap}}{T(\frac{nRT}{P})} = \frac{\Delta H_{vap}}{\frac{nRT^2}{P}} = \frac{P\Delta H_{vap}}{nRT^2} \quad or \quad \frac{dP}{P} = \frac{\Delta H_{vap}\times dT}{nRT^2}$$

Consider 1 mole (n = 1) and substitute in $\Delta H_{vap} = 15{,}971 + 14.55\text{ T} - 0.160\text{ T}^2$

$$\frac{dP}{P} = \frac{(15{,}971 + 14.55\,T - 0.160\,T^2)dT}{RT^2} = \frac{(15{,}971)dT}{RT^2} + \frac{(14.55\,T)dT}{RT^2} - \frac{(0.160\,T^2)dT}{RT^2}$$

Simplify and collect constants

$$\frac{dP}{P} = \frac{(15{,}971)}{R}\frac{dT}{T^2} + \frac{(14.55)}{R}\frac{dT}{T} - \frac{(0.160)}{R}dT$$ Integrate from $P_1 \rightarrow P_2$ and $T_1 \rightarrow T_2$

$$\ln\left(\frac{P_2}{P_1}\right)=\frac{(15{,}971)}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)+\frac{(14.55)}{R}\ln\left(\frac{T_2}{T_1}\right)-\frac{(0.160)}{R}(T_2-T_1)$$

**(b)** First we consider 1 mole *(n = 1)* $P_1$= 10.16 torr (0.01337 atm) and $T_1$= 120 K
Find the boiling point ($T_2$) when the pressure ($P_2$) is 1 atm.

$$\ln\left(\frac{1}{0.01337}\right)=\frac{15971}{8.3145}\left(\frac{1}{120}-\frac{1}{T_2}\right)+\frac{14.55}{8.3145}\ln\left(\frac{T_2}{120}\right)-\frac{0.160}{8.3145}(T_2-120)$$

Then we solve for $T_2$ using the method of successive approximations: $T_2$ = 169 K

## SELF-ASSESSMENT EXERCISES

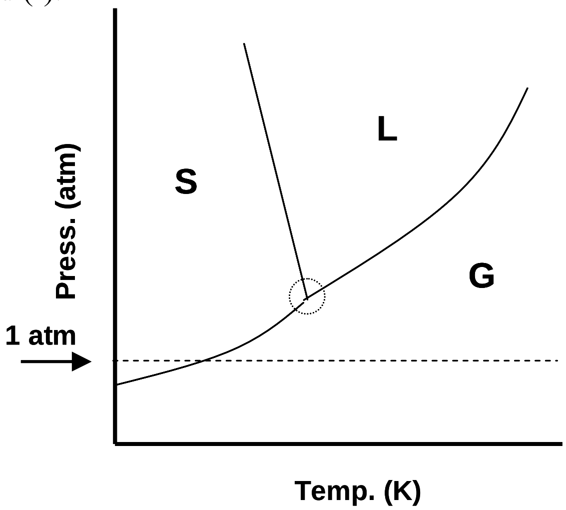
**128.** The answer is (c). As temperature increases, more molecules from a liquid get sufficient energy to escape, and thus vapor pressure increases.

**129.** The answer is (c). HF, $CH_3OH$, and $N_2H_4$ all participate in hydrogen bonding.

**130.** The answer is (b). Refer to Table 12.7.

**131.** The anwer is (a).

**132.** The answers are (d) and (f).



**133.** The species with higher boiling points are underlined.

**(a)** $C_7H_{16}$ v. $\underline{C_{10}H_{22}}$: The only interaction is London dispersion. $C_{10}H_{22}$ because it has the higher mass

**(b)** $C_3H_8$ v. $\underline{(CH_3)_2O}$: because dipole–dipole interactions are predominant, versus just London dispersion for $C_3H_8$.

**(c)** $CH_3CH_2SH$ v. $\underline{CH_3CH_2OH}$: because H-bonding dominates the inter-molecular interactions. This interaction is much weaker for $CH_3CH_2SH$.

**134.** $O_3$ is the one that is out of place. The correct order of boiling points based on molar masses is: $N_2 < F_2 < Ar < O_3 < Cl_2$. $O_3$ is the only polar molecule in the group, but this is not important enough to put it after the more massive $Cl_2$ (bp: 162 K for $O_3$ and 239 K for $Cl_2$).

**135.** The following listing reflects that organic compounds are lower melting than inorganic compounds, hydrogen bonding is an important intermolecular force for two of the compounds, and melting points of inorganic compounds are affected by ionic sizes and charges:
$Ne < C_3H_8 < CH_3CH_2OH < CH_2OHCHOHCH_2OH < KI < K_2SO_4 < MgO$

**136.** Refer to the photograph on page 518 of water boiling under a reduced pressure. If the vapor is evacuated fast enough, to supply the required $\Delta H_{vap}$, the water may cool to 0 °C and ice may begin to form.

**137.** If there is too little benzene(l) in the sealed tube in Figure 12-22 initially, the liquid will all be converted to benzene(g) before $T_c$ is reached. If too much is present initially, the liquid will expand and cause the benzene(l) to condense, and therefore only benzene(l) will be present at the time $T_c$ is reached.

**138.** **(a)** To determine whether any $CCl_4$ remains in the flask, we have to determine how many moles of $CCl_4$ are placed in the vessel, determine that how much $CCl_4$ is in the vapor phase in a vessel of 8.21 L if the vapor pressure is 110 Torr at 25 °C, and then figure out if there will be more or less $CCl_4$ in the vapor phase compared to the amount of liquid given.

$$\text{mol CCl}_4 = 3.50\text{ g CCl}_4 \times \frac{1\text{ mol CCl}_4}{153.80\text{ g CCl}_4} = 0.02276\text{ mol}$$ of liquid $CCl_4$ placed in vessel

Assuming a pressure of 110 Torr at 25 °C:

vol $CCl_4$ = 3.50 g $CCl_4$ / 1.59 $g{\cdot}mol^{-1}$ = 2.20 mL
vol inside the vessel = 8.210 L – 0.00220 L = 8.208 L
pressure = 110 Torr/760 Torr = 0.145 atm.

Moles of $CCl_4$ in the gas phase in this closed container:

$$\text{mol CCl}_4 = \frac{PV}{RT} = \frac{(0.145\text{ atm})(8.208\text{ L})}{(0.08206\text{ L}\cdot\text{atm}\cdot\text{K}^{-1})(298\text{ K})} = 0.0486\text{ mol}$$ in the vapor phase

0.0486 mol > 0.0228 mol, therefore at equilibrium, all the $CCl_4$ will be in the vapor phase.

**(b)** To determine the amount of energy required to vaporize a certain amount of $CCl_4$, we have to first determine the enthalpy of vaporization, or $\Delta H_{vap}$:

$$\ln\left(\frac{P_2}{P_1}\right)=\frac{-\Delta H_{vap}}{R}\left(\frac{1}{T_2}-\frac{1}{T_1}\right)$$

$$\ln\left(\frac{760}{110}\right)=\frac{-\Delta H_{vap}}{8.3145\ \mathrm{J\cdot mol^{-1}\cdot K}}\left(\frac{1}{350\ \mathrm{K}}-\frac{1}{298\ \mathrm{K}}\right)$$

$$\Delta H_{vap}=32.2\ \mathrm{kJ/mol}$$

The energy required to vaporize 2.00 L of $CCl_4$ is therefore determined as follows:

$$\text{energy}=2000\ \mathrm{mL}\times\frac{1.59\ \mathrm{g}}{1\ \mathrm{mL}}\times\frac{1\ \mathrm{mol\ CCl_4}}{153.80\ \mathrm{g\ CCl_4}}\times\frac{32.2\ \mathrm{kJ}}{\mathrm{mol}}=666\ \mathrm{kJ}$$

**139.** **(a)** Unit cell length: we note from the picture that the hypotenuse of the right triangle equals 4×r.

$$L^2+L^2=(4r)^2=16\cdot(128\ \mathrm{pm})^2=2.621\times10^5$$

$$L=\sqrt{2.621\times10^5/2}=362\ \mathrm{pm}$$

**(b)** volume = $(362\ \mathrm{pm})^3=4.74\times10^7\ \mathrm{pm}^3$

**(c)** 8 corners × 1/8 + 6 faces × ½ = 4 atoms/unit cell.

**(d)** Volume % is the ratio between the volume taken up by the atoms and the volume of the unit cell.

$$\frac{\text{vol of atoms}}{\text{vol of cells}}=\frac{4\times(4/3)\pi\,(128\ \mathrm{pm})^3}{4.74\times10^7\mathrm{pm}^3}\times100=74\%$$

**(e)**

$$\frac{\text{mass of Cu}}{\text{unit cell}}=\frac{4\ \text{atoms}}{\text{unit cell}}\times\frac{1\ \text{mol Cu}}{6.022\times10^{23}\ \text{atoms}}\times\frac{63.546\ \text{g Cu}}{1\ \text{mol Cu}}=4.221\times10^{-22}\,\mathrm{g}$$

**(f)** D = m/V

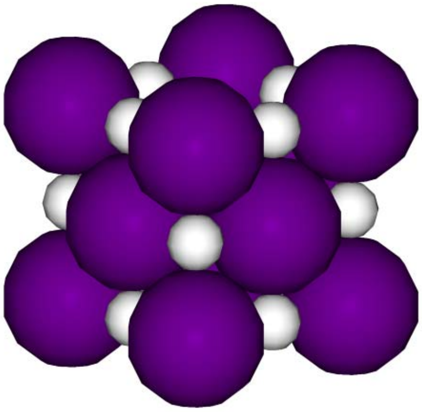
$$D=\frac{4.221\times10^{-22}\,\mathrm{g\ Cu}}{4.74\times10^7\ \mathrm{pm}^3}\times\frac{(1\times10^{-10}\mathrm{pm})^3}{(1\ \mathrm{cm})^3}=8.91\ \mathrm{g/cm^3}$$

**140.** The answer is (a). All of these liquids participate in hydrogen-bonding. Therefore, higher van der Waals interactions translate to higher surface tensions. Methanol, $CH_3OH$, is the smallest molecule, therefore has the least amount of van der Waals forces, and the lowest surface tension.

**141.** The answer is (d). All of these compounds are straight-chain hydrocarbons. Their only major intermolecular interaction is London dispersion. The lower this interaction, the lower the viscosity. N-pentane is the lightest, and therefore has the lowest viscosity.

**142.** A network covalent solid will have a higher melting point, because it takes much more energy to overcome the covalent bonds in the solid (such as, for example, diamond) than to overcome ionic interactions.

**143.** The $Li^+$ and $I^-$ have an fcc structure. Because $I^-$ is much larger, the iodide ions touch. The structure is shown below.



Since the Li-I distance is 3.02 Å, the length of the cube is 2×3.02 Å = 6.04 Å. Therefore, the face diagonal of the cube is:

$$D = \sqrt{6.04^2 + 6.04^2} = 8.54 \text{ Å}$$

Since there are 4 $I^-$ radii in the face diagonal of the cube, radius of $I^-$ is 8.54/4 = 2.13 Å

**144.** The answer is (c), because of increased pressure, the transformation that causes the greatest packing efficiency change is likely to prevail.